SYMPOSIUM I

Organic Thin-Film Electronics

March 28 - April 1, 2005

Chairs

A. C. Arias
Electronic Materials Laboratory
Palo Alto Research Center
3333 Coyote Hill Rd.
Palo Alto, CA 94304
650-812-4199

N. Tessler
Electrical Engineering Dept.
Technion
Haifa, 3200 Israel
972-4-829-4719

Lukas Burgi
Polymer Optoelectronics
CSEM
Badenerstrasse 569
CH-8048 Zurich, Switzerland
41-1-497-1416

J. A. Emerson
Organic Materials Dept.
Sandia National Laboratories
MS 0958
Albuquerque, NM 87185-0958
505-845-9747

Symposium Support
Ciba SC
Covion Organic Semiconductors
CSEM SA
Merck Chemicals UK
OrganicID, Inc.
Plastic Logic Ltd.
Palo Alto Research Center
Universal Display Corporation Inc.

Proceedings to be published online
(see *ONLINE PUBLICATIONS* at www.mrs.org)
as volume 871E
of the Materials Research Society
Symposium Proceedings Series.
This volume may be published in print format after the meeting.

* Invited paper

TUTORIAL

Device Physics, Charge Transport, Applications and Processing in Organic Electronics
Monday March 28, 2005
1:30 PM - 5:00 PM
Room 2001 (Moscone West)

The tutorial will be composed of two sections covering (1) the basic processes governing the operation of organic thin-film devices and (2) applications and processing approaches for these devices. The first section will describe charge injection (contact phenomena), charge transport (mobility is disordered material), charge recombination (diffusion-controlled reaction), and electron-hole pair dissociation in the context of the relevant devices, including field effect transistors, light emitting diodes, and solar cells (with an emphasis on FETs). As there is no complete agreement in the field regarding the physical models, we will describe several models and compare the underlying basic assumption and scope for each physical picture. The second portion of the tutorial will give an overview of the various applications for organic electronics, including RF labels, displays, LEDs and photovoltaics. This discussion will also include comparisons of the unique processing, performance, and materials challenges for these applications and the printing, deposition, as well as patterning technologies being developed to meet these challenges and create the targeted new functionality and low cost products.

Instructors:
Nir Tessler, Technion, Israel
Devin MacKenzie, Kovio, Inc.

SESSION I1: Materials and Organic Devices
Chair: Nir Tessler
Tuesday Morning, March 29, 2005
Room 2001 (Moscone West)

8:30 AM I1.1
Memory Elements based on Polymer Nanoparticles Blends. Luisa Dominica Bozano[1], Ryan Chiechi[3], Kenneth R. Carter[2] and J. Campbell Scott[1]; [1]IBM Almaden Research Center, San Jose, California; [2]Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts; [3]Chemistry 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). This mechanism is operative 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 (HTPA) 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 *I1.2
Progress in Organic Thin Films for Memory Storage Applications. M. Lauters, B. McCarthy, D. Sarid and G. E. Jabbour; 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 strucutures that might help shed some light on the mechanism behind the observed switching in the organic layers will be presented.

9:15 AM I1.3
Functionalized Regioregular Polyalkylthiophenes for Biosensing Applications. Simon J. Higgins[1], Fouzi Mouffouk[1], Stewart J. Brown[1], Bill Eccleston[2], Andrew Cossins[3], Daryl Williams[3], Stuart Reeman[4] and Naser Sedghi[2]; [1]Department of Chemistry, University of Liverpool, Liverpool, United Kingdom; [2]Electrical Engineering and Electronics, University of Liverpool, Liverpool, United Kingdom; [3]Biosciences, University of Liverpool, Liverpool, United Kingdom; [4]Chemical and Biological Sciences, Dstl Porton Down, Salisbury, United Kingdom.

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), localization (affinity cytochemistry, cell cytometry, and blotting technology), diagnostics (immunoassay, histopathology, and gene probes) 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 the 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 coated onto a working electrode 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.).

9:30 AM I1.4
Non-Volatile Memory Effect in Polymer Based Device for Data-Storage Applications. Yan Song[1], Qidan Ling[2], Shijin Ding[1], Chunxiang Zhu[1], Yihua Wang[3], Siu Hung Daniel Chan[1], En-Tang Kang[2] and Dim-Lee Kwong[4]; [1]Electrical and Computer Engineering, National University of Singapore, Singapore, Singapore; [2]Chemical and Biomolecular Engineering, National University of Singapore, Singapore, Singapore; [3]Institute of Microelectronics, Singapore, Singapore; [4]Electrical and Computer Engineering, The University of Texas, Austin, Austin, Texas.

Organic materials have been aggressively explored for semiconductor device applications. Very recently, organic memories have received a great attention due to their simple structure, good scalability, CMOS compatibility, and most importantly, low cost. Several kinds of organic molecular materials were found to exhibit memory effects. Polymer memory devices are potentially far less expensive to make than those based on organic molecular materials. In this paper, we report memory characteristics of MIM sandwich structure with poly(N-vinylcarbazole) (or PVK) as the active memory material. The basic device structure is a MIM structure with Indium-Tin-Oxide (ITO)/glass as the substrate, PVK as the active layer and Al as the top electrode. The toluene solution of PVK was spin-coated on the ITO, followed by solvent removal in a vacuum chamber. Finally, Al was thermally evaporated to the PVK film. The memory effect of PVK was observed in the I-V characteristics of the sandwich device. A transition from the ON state (high conductivity) to OFF state (low conductivity) occurs at a forward bias about 4 V. As for the device in the OFF state, a reverse bias about ?1.5 V changes the device from the OFF state to ON state. The main mechanism for the memory effect of the device may be caused by different traps or conformation levels occupied by electrons in the polymer. A simple model is given to explain the memory effect. The device shows a high ON/OFF current ratio of up to 1E4 and a switching time less than 5μs is observed. The effect of continuous read pulse on the ON- and OFF-states was evaluated and no resistance degradation is observed for both ON- and OFF-state after 1E6 read cycles. The retention properties of both states under ambient conditions were also characterized. A retention time of up to 13 hours was achieved. However, it is believed that the retention can be significantly improved when the device is properly encapsulated.

9:45 AM I1.5
Stability of OTFT Gas Sensors. Josephine B. Lee and Vivek Subramanian; EECS, UC Berkeley, Berkeley, California.

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 noses, ultimately enabling low-cost applications such as food packaging with integrated spoilage 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 operational lifetime study for short-term sensing applications such as disposable food spoilage detection, where continuous operation is expected to last from a few hours to a few weeks. Gas sensors 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 molecular structure, deposition technique, and 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.

10:15 AM I1.6

Modeling of Spin Injection and Spin Transport Properties in Organic and Inorganic Semiconductors. P. P. Ruden[1], J. D. Albrecht[2] and D. L. Smith[3]; [1]University of Minnesota, Minneapolis, Minnesota; [2]Air Force Research Laboratory, Wright-Patterson AFB, Ohio; [3]Los Alamos National Laboratory, Los Alamos, New Mexico.

Spin polarized charge carrier injection and transport in non-magnetic semiconductors is the key enabling mechanism for spin based electronic data processing. We present theoretical models to describe spin injection and spin transport and spin extraction in structures consisting of a ferromagnetic metal injector, a thin semiconductor layer, and a ferromagnetic metal collector. The semiconductors considered are conjugated polymers (e.g. PPV), small molecule organic molecular crystals (e.g. pentacene), and inorganic semiconductors (e.g. silicon). In thermal equilibrium the charge carriers in the semiconductor are not spin polarized. Efficient spin injection requires that the semiconductor be driven far out of local thermal equilibrium. Because the ratio of the conductivities of ferromagnetic metals and of semiconductors is very large, driving the semiconductor out of local (spin) equilibrium requires a spin-selective injection process. Tunneling, either through the depletion region near a large Schottky barrier or through a thin interfacial insulator layer, may serve as such a mechanism. Since carrier mobilities (and other relevant parameters) in polymers, organic molecular crystals, and inorganic semiconductors differ by many orders of magnitude, the conditions for achieving a state far from thermal equilibrium at the injecting contact are quite different for all of these materials. Both, organic semiconductors and inorganic semiconductors offer unique and different opportunities for the fabrication of suitable tunnel barriers. We present calculated results for spin injection and spin transport, and we derive design criteria for efficient spin injectors based on these results and on the very different fabrication and process issues relevant to the organic and inorganic semiconductor device technology.

10:30 AM *I1.7

Organic-Based Magnetic and Non-magnetic Semiconductors for Spintronics. Arthur J. Epstein[1,2], Joel S. Miller[3] and Liming Dai[4]; [1]Department of Physics, The Ohio State University, Columbus, Ohio; [2]Department of Chemistry, The Ohio State University, Columbus, Ohio; [3]Department of Chemistry, University of Utah, Salt Lake City, Utah; [4]Department of Chemical and Materials Engineering, University of Dayton, Dayton, Ohio.

Vanadium-tetracyanoethylene (V[TCNE]x, x∼2) with TC up to ∼ 100o C and room temperature resistivity ∼ $10\hat{4}$ ohm-cm is the first organic-based magnetic semiconductor. Films can be prepared on a wide variety of substrates via low-T CVD.[1] EXAFS shows V(II) ions are surrounded by six N atoms at an average distance of 2.084(5) A.[2] Angle- and T-dependent ferrimagnetic resonance (9.5 and 240 GHz) shows separate domains with magnetically ordered and glassy behaviors.[3] We achieve control of the M(H,T) and coercive field through incorporation Fe, Co, and Ni in partial replacement of V. The MR field and T dependences differ from predictions for conventional disordered semiconductors.[4] We proposed that the initial metallic half-filled pi* electronic TCNE band is split by strong Coulomb repulsion and interaction with M(II) into two oppositely spin polarized subbands forming a half-semiconductor.[5] The potential for organic-based materials in spintronic devices is explored. The spin dependent transport properties were measured in magnetic FM1/O/FM2 multilayers where FM1 and FM2 are inorganic or organic magnetic contacts with coercive fields Hc1 and Hc2 respectively, and O is an electrically active organic spacer layer. Organic layers have a low spin orbit coupling which should reduce the effects of interfacial scattering as well as allow for a much thicker spacer layer due to weak intralayer spin-flip scattering. Preliminary data collected for organic spacer layers of sexithiophene (∼500 - ∼1200 nm) with conventional and V[TCNE]x, magnetic contacts and of aligned carbon nanotubes (7 microns) show MR as large as 25% at low temperatures.[6] *Supported in part by DARPA Grant No. N00014-02-1-0593, U.S. Army Research Office Grant No. DAAD19-01-1-0562, and DOE Grant No. DE-FG02-01ER45931. [1] K.I. Pokhodnya, A.J. Epstein, and J.S. Miller, Adv. Mat. 12, 410 (2000). [2] D. Haskel, Z. Islam, J. Lang, C. Kmety, G. Srajer, K. I. Pokhodnya, A.J. Epstein, and J.S. Miller, Phys. Rev. B 70, xxx (2004). [3] V. Plachy, K.I. Pokhodnya, P.C. Taylor, J. Shi, J.S. Miller, and A.J. Epstein, Phys. Rev. B 70, 064411/1 (2004). Y. Bataiev, N.P. Raju, K.I. Pokhodnya, A.J. Epstein, and J.S. Miller, to be published. [4] K.I. Pokhodnya, V. Burtman, A.J. Epstein, J.W. Raebiger, and J.S. Miller, Adv. Mat 14, 1211 (2003). [5] V.N. Prigodin, N.P. Raju, K.I. Pokhodnya, J.S. Miller, and A.J. Epstein, Adv. Mat. 14, 1230 (2002). [6] S.J. Etzkorn, W.C. Pirkle, J.B. Yang, L.M. Dai, and A.J. Epstein, to be published.

11:00 AM I1.8

Large Magnetoresistance at Room-Temperature in Semiconducting Polymer Sandwich Devices. Govindarajan Veeraraghavan[1], Omer Mermer[2], Thomas Lee Francis[1], Yugang Sheng[2], Tho Duc Nguyen[2] and Markus Wohlgenannt[2]; [1]Department of Electrical & Computer Engineering, University of Iowa, Iowa City, Iowa; [2]Department 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, polyfluorene has emerged as a high brightness, high efficiency pi -conjugated polymer for use in OLEDs. Recently there has been a growing interest in the spin and magnetic field effects in organic semi conducting materials. We report on the discovery of a large, room temperature magnetoresistance (MR) effect in polyfluorene (poly (9,9-dioctylfluorenyl-2,7-diyl)) polymer sandwich devices in weak magnetic fields. The MR effect reaches up to 10% at fields of 10mT at room temperature. This MR effect is therefore amongst the largest of any bulk material. We characterize this effect and discuss its dependence on voltage, polymer film thickness, temperature, electrode materials, and (unintentional) impurity concentration. Negative MR is usually observed, but positive MR can also be achieved under high applied electric fields. Similar results were achieved independent of the PFO film thickness, suggesting that the observed MR effect is a bulk, rather than an electrode (interface) effect. The effect shows only weak temperature dependence and is independent of the sign and direction of the applied magnetic field. Importantly, the observed MR effect is largely independent of the top electrode (electron injector) material and occurs also in hole-only devices. This clearly indicates that the effect is related to the hole current in the devices and is not related to the electron transport or electron-hole recombination processes that also occur in OLED devices. It was verified that the observed MR effect is not related to (unintentional/ intentional) impurities such as left over catalysts from the polymerization reaction. To the best of our knowledge, the discovered MR effect is not adequately described by any of the mechanisms known to date. The polymer devices we describe can be manufactured cheaply on flexible substrates, and can be transparent. Our devices therefore hold promise for applications where large number of MR devices are required, such as magnetic random-access-memory (MRAM) and applications related to OLED display screens such as touch screens where the position of a magnetic stylus is detected (patent pending). Our devices do not require ferromagnetic electrode materials resulting in flexibility in material choice not available for other MR devices. Interested readers should further look at the preprint of our publication and a demonstration video at our website http://ostc.physics.uiowa.edu/∼wrg/. This work was supported by Carver Foundation and NSF ECS 04-23911.

11:15 AM I1.9

High-Temperature Operation of Pentacene Field-Effect Transistors with Polyimide Gate Insulators. Tsuyoshi Sekitani[1], Yusaku Kato[1], Shingo Iba[1], Takayasu Sakurai[2] and Takao Someya[2]; [1]QPEC, Univ. of Tokyo, Bunkyo-ku, Tokyo, Japan; [2]CCR, 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 cm^2/Vs when the device was heated from room temperature (RT) 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 didnft have changes after heat cycles up to 130 °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 cm^2/Vs at RT and an on/off current ratio of above 10^5 have been fabricated by a vacuum evaporation process. 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-nm-thick polyimide gate dielectric layer was prepared by spin coating and a 50-nm-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-operation apparatus, variable temperatures from 20 to 200 °C. High-precision measurements have 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 mobility was enhanced up to 0.71 cm^2/Vs when heating the device up to 160 °C compared with 0.27 cm^2/Vs at RT, which can be analyzed in terms of a transport model with carrier-hopping. Furthermore, it should be noted that no damage has been observed after the removal of many heat cycles up to 130 °C. On the other hand, annealing at the temperatures from 130 to 160 °C results in the enhancement of mobility by 26 % at RT. Excessive heating above 160 °C causes the reduction of mobility, which was ascribed to the device failure associated with the partial sublimation 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 base 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 I1.10

Organic-Inorganic Hybrid Encapsulation for P3HT Field-Effect Transistors. Noriyuki Kawashima, Kazumasa Nomoto, Masaru Wada and Jiro Kasahara; Fusion Domain Laboratory, Materials Laboratories, Sony Corporation, Ohta-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 soluble 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 N_2 atmosphere with different P3HT 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 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 just 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 I1.11

General Observation of n-Type Field-Effect Behaviour in Organic Semiconductors. Lay-Lay Chua[1,2], Peter K.-H. Ho[2,1], Jana Zaumseil[1], Jui-Fen Chang[1], Eric Ou[3], Henning Sirringhaus[1] and Richard H. Friend[1]; [1]Physics, University of Cambridge, Cambridge, United Kingdom; [2]Physics, National University of Singapore, Singapore, Singapore; [3]Institute of Materials Research and Engineering, Singapore, Singapore.

Organic semiconductors are attracting increasing attention owing their emerging applications in light-emitting displays and printable electronic circuits. One long-standing mystery of their device physics however is the strong trapping 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 conduction. We show that with the appropriate hydroxyl-free gate dielectrics, such as a 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 comparable, even for polymers that were previously believed not to be capable of supporting electron conduction. The electron mobility values we obtained, for example, for a poly(fluorene-alt-benzothiadiazole), 5x10-3 cm2/Vs; poly(fluorene-alt-bithiophene), 6x10-3 cm2/Vs; and polyfluorene, 10x10-3 cm2/Vs; 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.

SESSION I2: Materials Synthesis and Devices
Chair: Michael Chabinyc
Tuesday Afternoon, March 29, 2005
Room 2001 (Moscone West)

1:30 PM *I2.1

Functional pi-Electron Materials for Nanoelectronics. Peter Baeuerle, Department Organic Chemistry II, University of Ulm, Ulm, Germany.

Conjugated oligo- and polyheterocycles represent an important class of compounds in the field of organic materials and have successfully been used as active components in organic electronic devices, such as field effect transistors (FET) and logic circuits, light emitting diodes (LED) and full-colour displays or solar cells. In this respect, we could recently add novel structures and topologies to this field: the first fully pi-conjugated macrocyclic oligothiophenes, which combine the excellent properties of the corresponding linearly conjugated oligomers and host/guest chemistry as a completely novel perspective. On this basis, the synthesis of conjugated catenanes has been achieved. Intriguing self-assembling properties of linear conjugated oligo- and polythiophenes, as well as the macrocycles on substrates were investigated by scanning tunneling microscopy (STM) and directly allowed the determination of molecular parameters. Unprecedented superstructures of host/guest complexes on surfaces allow the formation of molecular architectures into the third dimension. By scanning tunneling spectroscopy (STS) we could demonstrate rectifying behaviour of individual complexes. Very recently, we have been able to develop novel semiconducting polymers and oligomers which contain structural elements of regioregular poly(3-hexylthiophene) and show good performances in organic solar cells.

2:00 PM I2.2

Nanowire Electrode for Organic Transistors. Shuhong Liu and Zhenan Bao; Chemical Engineering, Stanford University, Stanford, California.

Considerable efforts have been placed on searching for alternatives to conventional silicon electronics in recent years. Organic transistors are extensively studied due to lower cost and less-complex fabrication process. Present photolithographic techniques grow exponentially more expensive with decreasing feature size, and may never reach the dimensions required for new technologies. In our work, we design a new nanopatterning method that relies on self-assembly of nanowires to make organic transistors with nanoscale electrode gaps. Metal nanowires are prepared through electrochemical deposition of metal ions into porous alumina template and are derivatized by using self-assembled monolayers. Self-assembly of nanowires on metal electrodes are studied by controlling surface chemistry of the bottom electrode contacting the nanowires, surface topography of bottom electrodes, microfluidic conditions, or the combination of them. Using nanowires as source and drain electrodes, devices are made by growing organic semiconductors selectively between them. Different organic semiconductors and different growing conditions are tried. Electronic properties from transistors with different channel lengths are reported.

2:15 PM I2.3

Organic Thin Film Transistors with Contacts Printed from Metal Nanoparticles. Yiliang Wu, Yuning Li, Sandra Gardner and Beng Ong; Xerox Research Centre of Canada, Mississauga, Ontario, Canada.

Most of recent work in low-cost organic thin film transistors (OTFTs) has focused on solution processable organic semiconductors. Other OTFT materials such as printable conductor materials have not received much attention, despite their critical roles in low-cost OTFTs. We present here our design of metal nanoparticles and their low-temperature conversions to high-conductivity elements 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 nanoparticles in an organic solvent. The printed features were heated at 120-160 degree C to yield metallic electrodes with thin-film conductivities resembling those from vacuum deposition. OTFTs using these electrodes provided TFT characteristics which are essentially the same as those using vacuum deposited metal electrodes.

2:30 PM *I2.4

Structure/Property Relations in Electroactive Polymers.

Mary Galvin, [1]Materials Science and Engineering, University of Delaware, Newark, Delaware; [2]University 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 copolymer performs significantly better than the alternating or block in PLEDS 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 ?-? stack, further delocalizing the carriers. The synthetic strategy used to prepare these molecules is versatile so that the four arms in the 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.

3:30 PM I2.5

Molecular Design and Synthesis of New Electrochromic Polymers with Various Colors.

Lu Liu, Chunye Xu, Dai Ning, Calen Kaneko and Minoru Taya; Mechanic 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, the use of conducting polymers is rapidly increasing due to their ability to form durable films and because their optical properties can be tuned through molecular architecture. Recently the conducting polymers formed from 3, 4-alkylenedioxythiophene and 3, 4-alkylenedioxypyrrole and their derivatives dominate the literatures in organic electrochromism area because of their low redox potential, high stability, high contrast ratio, fast switching speed etc. Poly(3, 4-alkylenedioxythiophene) shows blue color in the reduced state and is transparent in the oxidized state. Poly(3, 4-alkylenedioxypyrrole) shows red color in the reduced state and transparent in the oxidized state. Presently one of our research goals is to achieve EC materials which show other colors, especially green, besides blue and red. In this paper we will report the study focusing on green EC materials. According to the principle of coloration, low bandgap conducting polymer is the key for green electrochromic material. A low bandgap conducting polymer can be obtained in several ways such as combination of monomer segments with different electronic structures, alternation of strong electron donating and electron withdrawing moieties, etc. We applied these strategies in our study and obtained a series of new EC materials containing thiophene and 3, 4-alkylenedioxythiophene segments. The coloration and other properties of these materials will be reported. We will also report other approach to green EC materials and making of EC devices.

3:45 PM I2.6

High Contrast Ratio and Long Lifetime Polymer Electrochromic Devices (ECDs).

Chunye Xu, Dai Ning, Lu Liu, Calen Kaneko, Fengyu Su and Minoru Taya; University of Washington, Seattle, Washington.

Electrochromic windows (ECDs) have attracted much of the recent interest of electrochromism. ECDs that exhibit high contrast ratios (Δ%T) between their bleached and colored states are of special fascinating for use in dialed-tint windows, large area displays and automatic dimming mirrors. Such windows promise actively controlled, continuously tunable light transmittance. In this field, utilizing conjugated polymers as electroactive layers have received increased attention owing to their ease of color tuning properties, fast switching times, and high contrast ratios. Our laboratory has developed several new electrochromic coloring EC films and EC windows. In this study, a preparing and characterization of ECD which was based a cathodic EC polymer film, Poly[3,3-dimethyle-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine] (PProDOT-(CH3)2) is reported. The device was constructed by sandwiching a gel electrolyte between PProDOT-(CH3)2 EC film deposited on an Indium Tin oxide (ITO) glass and counter electrode which is an ITO glass coated by Vanadium oxide thin film. Device contrast ratios, measured as Δ%T, ranged from 2% to 62%. A lifetime of over 100,000 cycles of 1 inch by 1 inch device between the fully oxidized and fully reduced states has been achieved. The switching speed could be reached 1 second between the bleached state and colored state. The device also has a long open circuit memory. It could keep colored and transparent states without electric charge for 30 days, and transmittance was lost less than 6% and 2% respectively. This property is huge benefit to window application and economizing on energy. Their devices (windows) were increased in area from 0.028 inch x 0.04 inch, to 1 inch x 1 inch, 3 inch x 3 inch, 6 inch x 6 inch and larger. This study also focused on optimizing characteristics of PProDOT-(CH3)2 EC film, gel electrolyte and device assembly.

4:00 PM *I2.7

Recent Work of the Organic Materials for Electronics Consortium of the EPSRC, UK.

Michael Lewis Turner[1], Martin Grell[2], Philip Hodge[1], J. Emyr Macdonald[3] and Stephen G. Yeates[4]; [1]School of Chemistry, University of Manchester, Manchester, United Kingdom; [2]Department of Physics, University of Sheffield, Sheffield, United Kingdom; [3]Department of Physics, University of Cardiff, Cardiff, United Kingdom; [4]Avecia Ltd, Manchester, 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 anodised gate insulators in OFETs (iii) The fabrication of OFETs with organic ferroelectric gate insulators (iv) The use of phase image electrochemical force microscopy in organic electronics.

4:30 PM I2.8

Highly Efficient Multifunctional Phosphorescent Dendrimers Consisting of an Iridium-Complex Core and Charge-Transporting Dendrons for Organic Light-Emitting Devices.

Toshimitsu Tsuzuki[1], Nobuhiko Shirasawa[2], Toshiyasu Suzuki[2] and Shizuo Tokito[1]; [1]Scicence and Technical Research Laboratories, Japan Broadcasting Corporation (NHK), Setagaya-ku, Tokyo, Japan; [2]Research Center for Molecular-scale Nanoscience, Institute for Molecular Science, Okazaki, Aichi, Japan.

We report on novel emitting materials, multifunctional phosphorescent dendrimers, for highly efficient and solution processable organic light-emitting devices (OLEDs). These dendrimers have a phosphorescent core and dendrons based on charge-transporting building blocks. In the OLEDs using these dendrimers, charge carriers are transported by the dendrons and phosphorescence is generated from the phosphorescent core. The bulky dendrons in the dendrimer increase the quantum yield of photoluminescence by isolating the phosphorescent core from the neighboring phosphorescent cores. By using non-conjugated alkyl chains to link the charge-transporting building blocks, the dendrimers would be more soluble and lowering of the dendron's triplet energy would be prevented. The dendrons and the phosphorescent core were also linked by non-conjugated alkyl chains to avoid an electronic interaction between the phosphorescent core and the dendrons. We have synthesized the multifunctional phosphorescent dendrimers that consist of *fac*-tris(2-phenylpyridine)iridium [$\mathrm{Ir(ppy)_3}$] or iridium(III)bis(2-phenylpyridinato-N,$\mathrm{C^{2'}}$)acetylacetonate [$\mathrm{(ppy)_2Ir(acac)}$] as a phosphorescent core and charge-transporting dendrons based on building blocks of hole-transporting *N*-phenylcarbazole or electron transporting 3,4,5-triphenyl-1,2,4-triazole. The photoluminescence (PL) spectra for the phosphorescent dendrimers in a dilute solution were similar to the PL spectrum of $\mathrm{Ir(ppy)_3}$ or $\mathrm{(ppy)_2Ir(acac)}$ in the dilute solution. Good-quality films of the phosphorescent dendrimers were obtained by spin-coating from solutions. The OLEDs using the dendrimers were fabricated in combination with a 10-nm-Ca/100-nm-Al cathode and a 35-nm-thick hole-injecting layer of 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-dicholoroethane 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/m^2 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 I2.9

Substituted Indolo[3,2-b]Carbazoles: A New Class of Stable, High Mobility Organic Semiconductors for Thin Film Transistors. Yuning Li, Yiliang 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 (TFTs). Both 5,11-disubstituted and peripherally substituted indolo[3,2-b]carbazoles with proper substituents self-organized into highly crystalline terrace-layered structures under suitable processing conditions. Organic TFTs using channel semiconductors of this nature exhibited excellent field-effect transistor properties, with mobility up to 0.15 cm2 V-1 s-1 and current on/off ratio to 107. By virtue of their relatively low HOMO levels and large band gaps, this class of semiconductors displayed excellent environmental stability under ambient conditions, an appealing characteristic for organic TFT applications.

SESSION I3: Poster Session: Organic Based Materials and Devices

Chairs: Ana Claudia Arias, Lukas Burgi, John Emerson
and Nir Tessler
Tuesday Evening, March 29, 2005
8:00 PM
Salons 8-15 (Marriott)

I3.1

Ambipolar Charge Transport in Poly(3-hexylthiophene) (P3HT) Field-Effect Transistors. Jana Zaumseil[1], Lay-Lay Chua[1,2], Peter K. H. Ho[2,1], Richard H. Friend[1] and Henning Sirringhaus[1]; [1]Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom; [2]Department 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. F8BT, F8) and polyphenylenevinylenes (e.g. MEH-PPV, OC1C10-PPV) 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 electrons and show efficient n-type 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.

I3.2

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 dielectrics 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.

I3.3

Control of Thin Film Transistor Operations with Polar Self-Assembled Monolayers. Yoshi Iwasa[1], Takao Nishikawa[2], Shin-ichiro Kobayashi[1], Taishi Takenobu[1], Tatsuya Shimoda[2], Tadaoki Mitani[2], Hisao Ishii[3] and Michio Niwano[3]; [1]Institute for Materials Reserch, Tohoku University, Sendai, Japan; [2]School of Materilas Science, JAIST, Ishikawa, Japan; [3]Research Institute for Electrical Communication, Tohoku University, Sendai, Japan.

Organic thin film transistors (TFT) 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 view point of both basic sciences and practical applications, 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 SiO$_2$ 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 SiO$_2$ gate insulators. The effectiveness of SAMs has been also shown on organic single crystal field effect transistors. In this work we concentrated on SAMs with perfluoroalkylsilane (CF$_3$)(CF$_2$)$_7$(CH$_2$)$_2$Si(OC$_2$H$_5$)$_3$ as a source molecule, which is abbreviated as FAS in the following. This molecule was shown to have an ability of accumulating holes and depleting electrons in conduction channels of p-type pentacene and n-type C$_{60}$ TFTs, respectively. Here we report an ambipolar operation in field effect transistors of C$_{60}$ by modification of semiconductor/metal electrode interface with FAS molecules. Kelvin probe experiments revealed that the work function of the gold surface modified with FAS molecules increased by 0.55 eV as compared to the untreated gold. Hole injection into fullerenes is qualitatively understood in terms of this work function change induced by polar FAS molecules. The present results indicate that the charge injection from electrodes to organic semiconductors can be controlled simply by modification of semiconductor/metal interface without changing materials themselves, demonstrating usefulness of the interface modification technique in organic TFTs. [1] S. Kobayashi et al., Nature Mater. 3, 317 (2004).

I3.4

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

The performance of polymer based electronic devices has shown great improvements over the past years. Polymer light emitting diodes (LEDs) show high luminescence 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 encapsulated 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 insulator material segregates to the top surface encapsulating the underlying semiconductor. 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.

I3.5

Photo-Induced Effects in Organic Field-Effect Transistors. Vitaly Podzorov[1], Vladimir Pudalov[2] and Michael Gershenson[1]; [1]Physics Department, Rutgers University, Piscataway, New Jersey; [2]Lebedev Physical Institute, Moscow, Russian Federation.

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 the optical properties of these materials. The talk 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 ARO MURI (DAAD 19-99-1-0252). [1] V. Podzorov et al., Appl. Phys. Lett. 82, 1739 (2003); ibid. 83, 3504 (2003). [2] V. Podzorov et al., Phys. Rev. Lett. 93, 086602 (2004). [3] V. Podzorov et al., cond-mat/0406738

I3.6

Organic Thin Film Phototransistors: Materials and Mechanism. Dong-Yu Kim[1], Yong-Young Noh[1] and Kiyoshi Yase[2]; [1]Dept. of Materials Science and Engineering, Gwangju Institute of Science and Technology (K-JIST), Gwangju, South Korea; [2]Photonic 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 photoconducting layer. Among these, 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 avalanche photodiodes. In this presentation, we will discuss on OPTs having a high reponsivity 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.

I3.7

Orientation of Organic Semiconductor Films on Photoreactive Polyimide Films and its Influence on Field-Effect Transistor Characteristics. Hiroshi Kikuchi[1], Yuichiro Uchida[2], Yoshihide Fujisaki[1], Hiroto Sato[1], Taiichiro Kurita[1], Kuniharu Takizawa[2] and Fumio Sato[1]; [1]NHK Science & Technical Research Laboratories, Tokyo, Japan; [2]Seikei 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 cyclobutane tetracarboxylic dianhydride (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 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 was increased from 0-75 J/cm^2. 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 cm^2/Vs for the SiO2 gate-insulator and from 0.5 to 1.9 cm^2/Vs for the Ta2O5 gate-insulator under air-environment conditions. The current on/off ratio was over 10^6. Most of the characteristic parameters of the FETs, such as carrier mobility and on/off current ratio, 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.

I3.8

A Novel Concept of Vertical Organic Transistor with Low Working Voltage and High Output Current. Liping 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 an organic transistor with a unique device structure and device operation principle, i.e. by modulating the charge injection. Our transistor consists of an active cell such as 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, hence, the I-V characteristics of the top active cell is modified. 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 mechanism will be provided. The demonstrated transistor with its enhanced operating characteristics creates new directions for organic transistors and their applications.

I3.9

Low Voltage All-Polymer Transistor Utilizing a Hygroscopic Insulator. Tomas G. Backlund[1], Henrik G. O. Sandberg[1,2], Ronald Osterbacka[1] and Henrik Stubb[1]; [1]Physics, Abo Akademi, Turku, Finland; [2]VTT Information Technology, Espoo, Finland.

Thin-film transistors (TFTs) based on solution-processable 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 polymer materials is a demanding task. We report on two properties that can be used to improve the performance of TFTs. By using a hygroscopic insulator, polyvinylphenol (PVP), in the TFTs we have fabricated high performance all-polymer transistors operating on voltages below two volts with distinct linear and saturated regimes.[1] The transistors can be fabricated and operated in ambient air, but when operating the devices in controlled surroundings 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 movement at the active layer interface is presented.[2] There is also an interest of orienting the active layer in TFTs as it has been shown that orienting 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.[3] 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 PVP 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 orientating 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)

I3.10

Design and Synthesis of Functionalized Pentacene for Organic Field-Effect Transistors. Abhijit Basu Mallik, Mang-mang Ling and Zhenan 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 V-1 s-1 on polymer gate dielectrics) (1). However most of the efforts in improving the performance of pentacene-based OFETs have so far relied 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 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 final goal 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, L6.5.1-L6.5.11. 2) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. J. Am. Chem. Soc. 2001, 123, 9482-9483. 3) Meng, H.; Bendikov, M.; Mitchell, G.; Helgeson, R.; Wudl, F.; Bao, Z.; Siegrist, T.; Kloc, C.; Chen, C.-H. Adv. Mater. 2003, 15, 1090-1093.

I3.11

Fullerene Based n-type Organic Thin-Film Transistors. Joshua N. Haddock, Benoit Domercq and Bernard Kippelen; 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 fullerenes molecules, C_{60} and C_{70}. Transistors were fabricated on heavily doped silicon wafers with thermally grown SiO_2 as the gate oxide with Ti/Au bottom contact source and drain electrodes. Previous work with these materials in similar geometries has shown field effect mobilities as high as 0.5 cm^2/Vs for C_{60} [1] and 0.002 cm^2/Vs for C_{70} [2], both reported for devices with organic films deposited and tested under ultra-high vacuum conditions. Here, we report mobilities for C_{60} ranging from 0.02 cm^2/Vs up to 0.5 cm^2/Vs (depending on channel dimensions), and mobilities from 0.003 cm^2/Vs up to 0.04 cm^2/Vs for C_{70}. 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. [1] S. Kobayashi et. al., Fabrication and characterization of C_{60} thin-film transistors with high field effect mobility. Appl. Phys. Lett., 82(25), 4581-4583, 2003. [2] Haddon, R.C., C_{70} Thin Film Transistors. J. Am. Chem. Soc., 188, 3041-3042, 1996.

I3.12

High Performance Organic Thin Film Transistors Based on Cyclohexyl-Substituted Organic Semiconductors. Jason Locklin[1], Zhenan Bao[2] and Rigoberto Advincula[1]; [1]Chemistry, University of Houston, Houston, Texas; [2]Chemical Engineering, Stanford University, Stanford, California.

Various cyclohexyl end-capped oligomeric semiconductors based on oligothiophene, oligothiophene-fluorene, and perylene dimide 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 made with these oligomers has been investigated using TEM, AFM, and X-ray Diffraction. Field effect mobility as high as 0.17 cm^2/V.s was observed in fluorene-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.

I3.13

Impact of Polymer Nanostructure on Performance of Regioregular Poly(3-hexylthiophene) Thin Film Transistor. Shijun Jia[1,2], Troy D. Hammond[1], Shawn P. Williams[1], Richard D. McCullough[2] and Tomasz Kowalewski[2]; [1]Plextronics, Inc., Pittsburgh, Pennsylvania; [2]Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania.

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 morphologies of thin films prepared from regioregular head-to-tail poly(3-hexylthiophene) (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 polystyrene) can 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 crystallization and long range aggregation in - π 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 nanostructures ("nanograins"). Experiments with FET in which 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.

I3.14

Charge Carrier Transport in Field Effect Transistors Based on Tricyanovinyl-capped Oligothiophenes. Xiuyu Cai[1], Michael Burand[2], Christopher Newman[1], Kent Mann[2] and C. Daniel Frisbie[1]; [1]Department of Chemical Engineering and Materials Science, University of Minnesota, Twin Cities, Minneapolis, Minnesota; [2]Department 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 0.035 cm^2/Vs and 10^6 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 1.1×10^{-4} cm^2/Vs.

I3.15

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 the device stability test of novel organic semiconductors for OTFTs. The mobility as high as 0.5 cm2/Vs and the on/off ratio over 10$\hat{7}$ 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 10$\hat{6}$ 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.

I3.16

Surface and Interfacial Study of Organic Semiconductor Field Effect Transistor for Label-less DNA Biosensor. Melissa Stickle[1], Sandrine Rivillon[2], Yves J. Chabal[1], Refik Kortan[5], Zhenan Bao[3], Vitaly Podzorov[2], Michael Gershenson[2] and Howard Katz[4]; [1]Biomedical Engineering, Rutgers University, Piscataway, New Jersey; [2]Physics and Astronomy, Rutgers University, Piscataway, New Jersey; [3]Chemical Engineering, Stanford University, Stanford, California; [4]Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland; [5]Rutgers 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 by comparing 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 modes, absent both on the original substrate and in the molecule itself. Complementary 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 diffraction. 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 performed to assess the unit cell organization in relationship to substrate temperature. A herringbone packing model is proposed for the more rigid molecule, while the organic semiconductor with flexible terminal groups shows agreement with a smectic E phase modeling. Preliminary electrical data indicates that field-effect behavior can be achieved with mobility larger than 0.01 cm^2/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.

I3.17

Single Molecular Layer Thin Film Transistors. Veit 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 achieving this high degree of order, equally important tasks are 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-dihexylquarterthiophene (DH4T) and α,ω-dihexylsexithiophene (DH6T) as active materials. Devices are prepared on oxidised highly doped silicon wafers. The silicon acts as common gate electrode and the SiO_2 as gate insulator. Gold/titanium electrodes in bottom contact geometry are patterned lithographically and act 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 by vacuum sublimation the SiO_2 surface is terminated either by hexamethyldisilazane (HMDS) or by 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 *insitu* electrical characterization under ultra-high vacuum conditions. The maximum of the drain current was found after growth of only one or two molecular layers depending on the growth conditions. This result underlines the crucial importance of the insulator surface preparation and the careful control of the initial stages of the organic layer growth. Secondly this *insitu* technique is applied to manufacture systematically organic field effect transistors with a single molecular layer. These devices show rather high mobility values of about 0.03 cm^2/Vs for DH4T 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 on transistors after the growth process reveals 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.

I3.18

Effective Dopant Analysis for the High Performance Poly(3-Hexylthiophene) Field-Effect Transistors.
Shinichi Kawamura[1,2], Manabu Yoshida[3], Satoshi Hoshino[3] and Toshihide Kamata[3]; [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 is one of the key technology for flexible and printable electronics, thus many research effort has been devoted to the development of high performance polymer FETs. Regioregular poly(3-hexylthiophene) (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 is mainly originated in the 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, recently. Some papers reported that the high mobility could be obtained by the unintentional doping effects which was quite unclear reason. 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 the Rieke method. 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 the field effect mobility also. In order to isolate the effect of each impurity species, we have prepared several samples with different purities by using several purification techniques. In the study for the relationship between the FET performance and impurity species, we have found that free halogens were the main origin and other constituents were not so effective to increase the mobility. Doped halogens in the P3HT film should act as an acceptor which increase the intrinsic carrier density. Furthermore, we have found that such p-dopant also assists to form highly stacked structures. The quinoid configulation of P3HT was induced by the dopant in the solution. As it has a planar configuration, it seems to be helpful to form the stacking structure between the adjacent polymer molecules. These factors seem to be origins for the increase of the 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 brought about improvement of the sub-threshold region, namely reduction of off-current and threshold voltage without decrease of the on-current. It resulted in keeping high mobility and large on/off ratios at the accumulation operation mode. We will discuss the balance of the doping and de-doping effects for the high performance of polymer FETs in this presentation.

I3.19

Programmable Polymer Thin Film and Nonvolatile Memory Device. Jianyong Ouyang, Chil-Wei Chu, 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 gold nanoparticles and 8-hydroxyquinoline sandwiched between two metal electrodes, exhibited programmable electrical bistability. This device was fabricated through 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 time, so that the device can be used as low-cost, high-density, nonvolatile memory. The mechanism for the electrical transition is attributed to an electric-field induced charge transfer between gold nanoparticle and 8-hydroxyquinoline. We anticipate that this single-layer, solution processible and programmable thin film device presents a new direction for organic electronics.

I3.20

High Mobility Pentacene Organic Field Effect Transistors Based on a Ferroelectric Polymer Gate Dielectric.
Barbara Stadlober[1], Martin Zirkl[1], Michael Beutl[1], Hannes Maresch[1], Georg Jakopic[1], Guenther Leising[1], Simona Bauer-Gogonea[2] and Siegfried Bauer[2]; [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 electret poly(vinylidene-fluoride tetrafluoroethylene hexafluoropropylene) and the polymer poly(vinyl cinnamate) as gate dielectric are reported. The electret is a high dielectric constant polymer with a dielectric constant e= 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 electret thin film may appear in several crystalline compositions ranging from ferro- to paraelectric phases spectroscopic analysis was done in order to reveal the actual phase composition which strongly determines the dielectric behaviour. The field-effect mobility was extracted from the transistor characteristics by also accounting for the parasitic series resistance from the source and drain contacts. It turned out that the device performance and the morpholgy of the semiconducting layer are closely connected and that in films having grain sizes above a critical value, intrinsic mobilities of 1cm2/Vs and more can be achieved. The use of strongly polar high dielectric constant polymer gate dielectrics seems promising for lowering the operation voltage and for an applications of organic field effect transistors in sensor systems and organic memories based on the ferro,- piezo- and pyroelectric properties of such polymers.

I3.21

Surface and Solvent Mediated Molecular Ordering of Polythiophenes and Its Effect on Field-Effect Mobility in Thin Film Transistors. Kilwon Cho, Do Hwan Kim, Yeong Don

Park and Yunseok Jang; Chemical Engineering, Pohang University of Science and Technology, Pohang, South Korea.

With the aim of enhancing the field-effect mobility by promoting surface-mediated two-dimensional molecular ordering in self-aligned regioregular poly (3-hexylthiophene), P3HT, we have controlled the intermolecular interaction at the interface between P3HT and the insulator substrate by using self-assembled monolayers (SAMs) functionalized with various groups (-NH2, -OH and -CH3). We have found that, depending on the properties of the substrate surface, the P3HT nanocrystals adopt two different orientations, parallel and perpendicular to the insulator substrate, which have field-effect mobilities that differ by more than a factor of 4, and that are as high as 0.28 cm2V-1s-1. This surprising increase in field-effect mobility arises in particular for the perpendicular orientation of the nanocrystals with respect to the insulator substrate. Further, the perpendicular orientation of P3HT nanocrystals can be explained by the following factors: the unshared electron pairs of the SAM end groups, the π-H interactions between the thienyl-backbone bearing π systems and the H (hydrogen) atoms of the SAM end groups, and interdigitation between the alkyl chains of P3HT and the alkyl chains of the SAMs. Also, one-dimensional, organic nanostructures such as nanowires and nanorods, represent the smallest dimension for efficient transport of electrons and holes, and are thus ideal building blocks for enhancing the performance of nanoscale organic field-effect transistors (OFETs). Here, we have demonstrated that one-dimensional self-assembly of regioregular poly (3-hexylthiophene) (P3HT) chains can be induced by controlling the solvent vapor pressure in the coating chamber. Nanowire lengths and length-to-width aspect ratios (L/W) are easily controlled through changes in solvent vapor pressure ($0 \sim 56.5$ kPa) during solidification. Moreover, it has been demonstrated that nanowires grow by rod-to-rod association, in which the spin coated P3HT chains appear well-oriented parallel to the insulator (SiOx) substrate. The formation of nanowires takes place by one-dimensional self-assembly, governed by π-π stacking of the regioregular P3HT units. The length of the nanowires indicates that such π-stacking extends over several micrometers. In particular, samples fabricated under high solvent vapor pressure (nanowire morphology) resulted in the occurrence of field-effect mobilities that are typically more than one order of magnitude higher than those of samples prepared under ambient conditions. The authors would like to thank the National Research Laboratory Program (Ministry of Science and Technology of Korea), the Ministry of Education of Korea for its support through its BK21 Program, and the Pohang Acceleratory Laboratory for providing the synchrotron radiation source at the 8C1, 4C2 and 3C2 beam line used in this study.

I3.22

Organic Field Effect Transistors Based on Multilayer Films via Molecular Layer Epitaxy. Yuval Ofir[1], Joseph Shappir[2] and Shlomo Yitzchaik[1]; [1]Inorganic Chemistry, Hebrew University of Jerusalem, Jerusalem, Israel; [2]Applied Physics, Hebrew University of Jerusalem, Jerusalem, Israel.

A Self-Assembly oriented technique from the vapor-phase, Molecular Layer Epitaxy (MLE), was utilized for the buildup of organic multilayers as the active channel in organic field effect transistors (OFET). Carrier gas-assisted chemical vapor deposition (CVD) of 1,4,5,8-Naphthalene tetracarboxylic dianhydride (NTCDA) and an aliphatic spacer are used in a pulsed mode for the covalent attachment of a single monolayer at a time resulting in an ordered dense multilayer film. The MLE approach uses a template layer to promote coupling between the substrate and the precursors deposited from the vapor phase. Interlayer epitaxy is governed by self-limiting vapor-phase condensation reactions while intralayer ordering is achieved via horizontal π-stacking. Resulting multilayers were characterized by means of variable angle spectroscopic Ellipsometry, AFM, Absorbance in the UV-Vis, FT-IR and Contact Angle. Multilayer structures are also built on a silicon substrate with predefined gold electrodes, using a self assembled template layer on the electrodes and on the thin gate oxide, thus allowing for the buildup of a multilayer structure covering both the electrodes and the channel area while enhancing the nature of the contact between the multilayer and the source and drain electrodes. Resulting OFET devices show n-type conductivity with a mobility of 0.031 cm^2 V^{-1} s^{-1} for a 6nm thickness MLE film, thus justifying the utilization of the technique in OFETs research and commercial uses production.

I3.23

Polymer Display with Integrated Optical Proximity and Touch Sensor. Lukas Burgi, Reto Pfeiffer, Michael Kiy, Peter Seitz, Peter Metzler and Carsten Winnewisser; CSEM, Zurich, Switzerland.

A major strength of polymer semiconductor technology is the possibility to deposit the materials by additive processes in only those areas, where their specific functionality is required, as exemplified by ink-jet printed red, green, and blue pixels in polymer displays. Here, an optical proximity and touch sensor is demonstrated that relies on the monolithic integration of a polymer LED / display and polymer photodiodes.[1] In its current form, the polymer light source and the polymer photodiode pixel array are integrated on the same side of standard glass or flexible polymer substrates. The polymer LEDs are based on a blend of polyfluorenes with peak emission close to 550 nm, and a blend of a C60-derivative and poly(3-hexylthiophene) is used for the bulk heterojunction photodiodes. The sensor can be operated either in proximity mode or as a touch sensor. For the former, light emitted by the polymer LED is reflected from nearby objects and falls back onto the photodiode pixels, leading to a signal enhancement. In the case of the touch sensor, we exploit the fact that the slightest touch of the sensor leads to a change of the effective refractive index, which in turn influences the angle of total reflection and therefore the guided modes in the substrate. This results in a change (generally a decrease) of the photodiode signals. Signal detection and background subtraction is achieved by modulation of the polymer LED and a corresponding pixel-wise lock-in demodulation of the signal of the photodiodes. As examples we will demonstrate a position sensitive touch sensor and a simple on-off touch switch based on a light-emitting logo (display) fabricated with LogoLED^{TM} technology.[2] [1] European Patent 1467224, 2004 [2] www.logoled.com

I3.24

Electroluminescence Spectral Imaging in Polymer Blend Light Emitting Diodes. Noriyuki Takada, Kiyohiko Tsutsumi and Toshihide Kamata; Photonics Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba, Ibaraki, Japan.

The spectral imaging for electroluminescence (EL) characterization in the light emitting diode (LED) based on blends of poly[2,7-(9,9-di-n-octylfluorene)] (PFO) and poly[2,7-(9,9-di-n-octylfluorene)-alt-(1,4-phenylene-((4-sec-butylphenyl)amino)-1,4-phenylene)] (TFB) was performed using the imaging micro-spectroscopy system, which has functions both micro-spectroscopy measurement and imaging analysis. EL spectra of whole units (the observed area was composed of ensemble of $1.25\times1.04\mu$m unit) were classified into several spectra according to the difference of spectral properties, such as the emission peak wavelength, the spectral linewidth, the ratio between intensities of emission peaks (in case that an EL spectrum has two or more emission peaks). These classified spectra were stored in a spectral library and arbitrary colors were assigned to them. Using this imaging technique, it is possible to elucidate what and where emission species are located within an emission surface. We compared between analyzed EL spectral images and macroscopic EL performance and found that EL spectral images are intimately related with EL efficiency. Furthermore, from the analysis of EL spectral images around a black spot, the morphology control of PFO may be important to improve EL efficiency.

I3.25

Efficient Red, Green, and Blue OLEDs using Heteroleptic Iridium Tris-Cyclometalates. Arnold Tamayo[1], Biwu Ma[2], Peter Djurovich[1] and Mark E. Thompson[1,2]; [1]Chemistry, University of Southern California, Los Angeles, California; [2]Material Science, University of Southern California, Los Angeles, California.

We have fabricated monochromatic organic light emitting diodes (OLEDs) using novel heavy metal complexes as phosphorescence emitters. These OLEDs can be fabricated in any color, ranging from blue to red. The key advance in our work is to efficiently utilize all of the excitons created in the electroluminescent process, giving OLEDs with efficiencies close to the theoretical limit of 100%. The high level of spin orbit coupling in heavy metal complexes gives efficient intersystem crossing, leading to strongly emissive triplet excited states. This paper will described the syntheses, and photophysics of novel heteroleptic iridium tris cyclometalates and their use as emissive materials. Device fabricated with these materials have turn on voltages of < 5 volts, have quantum efficiencies ranging from 3-9% and brightness 7000-40000 cd/m2 at 10V.

I3.26

Abstract Withdrawn

I3.27

Influence of Cavity Q-factor on Near-Infrared Emitting Microcavity Organic Light Emitting Diodes. Chi Hang Cheung[1], Aleksandra B. Djurisic[1], Chung Yin Kwong[2], Hoi Lam Tam[4], Kok Wai Cheah[4], Zheng Tong Liu[1], Wai Kin Chan[3] and Po Ching Chui[2]; [1]Department of Physics, The University of Hong Kong, Hong Kong, Hong Kong; [2]Department of Electrical and Electronic Engineering, The University of Hong Kong, Hong Kong, Hong Kong; [3]Department of Chemistry, The University of Hong Kong, Hong Kong, Hong Kong; [4]Department of Physics, Hong Kong Baptist University, Hong Kong, Hong Kong.

Microcavity organic light emitting diodes (MOLEDs) are of great interests 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 N, N' - di(naphthalene-1-yl) - N,N' - diphenylbenzidine (NPB), while Alq was the emissive and electron transporting layer. The bilayer structure was sandwiched between two silver mirrors. In order to investigate the influence of cavity Q-factor to the emission spectra, 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.

I3.28

One and Two-Color Tandem Organic Photovoltaic Cells.

Leonidas C. Palilis[1,2], Gary K. Kushto[1], Woohong Kim[1,2] and Zakya H. Kafafi[1,2]; [1]Naval Research Laboratory, Washington, District of Columbia; [2]SFA Inc., Largo, Maryland.

One and two-color tandem organic photovoltaics (OPVs) based on p/n (electron donor/electror 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 triarylamine N,N'- diphenyl-N,N'-(2-napthyl)-(1,1'-phenyl) -4,4'-diamine (NPD) and copper phtalocyanine (CuPc), and electron acceptors such as C60 and 3,4,9,10-perylenetetracarboxylic bis-benzimidazole (PTCBI) were used at the p/n junction. One-color NPD/C60/Agx/NPD/C60 and two color NPD/C60/Agx/CuPc/C60 OPVs exhibited relatively high fill factors of 0.4-0.45 and open circuit voltages of 1.30 and 1.65 V, almost equal to the sum of the open circuit voltages of the top and bottom cells. The paper will discuss the performance of these tandem cells based on the absorption and charge separation/collection of the cells in the UV-Vis spectral range, the photoaction spectra (incident-photon-to-current efficiency in the UV-Vis) and the illumination intensity dependence of the photovoltaic parameters. The influence of the series and shunt resistance on the cell performance was examined by fitting the dark and illuminated current-voltage characteristics to the Shockley equation. Finally, preliminary results on flexible tandem OPVs using the conducting polymer (3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) as the anode will be reported.

I3.29

Improving the Interface in Organic-Inorganic Hybrid Photovoltaic Cells.

Yuxiang Liu[1], Shawn Scully[1], Natalya Dallas[1], Michael McGehee[1], Carine Edder[2], Jinsong Liu[3], Jean Frechet[3] and Sean Shaheen[4]; [1]Stanford University, Stanford, California; [2]Molecular Foundry, Berkeley, California; [3]UC Berkeley, Berkeley, California; [4]NREL, 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 components, or it can slow 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 the interface modifier is slightly less than that of the light absorbing material, Forster 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 these opportunities to improve 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 surface, 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 when the energy levels of the two conjugated polymers are chosen correctly most of the excitons formed within 15 nm of the interface are harvested due to efficient Forster energy transfer. We have been able to double the power conversion efficiency of flat fluorine-doped tin oxide/titania/polymer/silver PV cells using this method. Cyclic voltammetry 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. PV cell IV curves and Kelvin probe measurements show that the open circuit voltage is reduced by 0.2 V if every monomer in the polymer has a carboxylic acid moiety covalently bound to the titania because of the dipole that is introduced at the interface. If only 10 % of the monomers have a carboxylic acid moiety, then the reduction in open circuit voltage is almost eliminated. A full characterization of these polymers and PV cells will be presented.

I3.30

Hybrid Solar Cells based on Nanoporous TiO2 and a New Spirofluorene-Thiophene Copolymer with Oxidative Stability.

Jang Jo, Doojin Vak, 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 reported in a polymer thin film consisting of fluorene-based polymers such as poly 9,9-dioctylfluorene-co-bithiophene (F8T2). Therefore, F8T2 has emerged as a hole transporting material in high efficiency hybrid solar cells consisting of interpenetrating networks of TiO2 and polymer semiconductors due to its high hole mobility known in field effect transistors. However, most of devices fabricated from polyfluorene-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 nanopores 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 spiroanthracenefluorene 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.

I3.31

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 polymer 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 on the basis of a charge transfer process. This absorption quenching 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 evidenced by FTIR 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 interaction between the p-type donor polymer and the n-type acceptor was studied and optimum weight ratio of the two components was achieved to give high power conversion efficiencies.

I3.32

Advantages of a Novel Method for Direct-Write Fabrication of Polymer Devices.

Paul Rugheimer, 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 display technology, high-speed communication and electronics. 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 through a pulled-glass micropipette*. In addition to control of the deposition speed and thus the shear rate that the polymer is subjected to, we can ultrasonically agitate the polymer solution immediately prior to deposition. It is expected that the application of this shear force and ultrasonics during deposition might provide extra control over properties of the resulting film not available through spin-coating. Also, because our method is a direct-write technology capable of writing over large areas, it holds potential for rapid prototyping of polymer devices. Since pulled-glass micropipettes have openings ranging from 100microns to as small as 100nm, the size of the devices which can be made using this process are compatible with the range of sizes available for conventional silicon electronics. We have fabricated ridge-waveguide structures using this instrument. To achieve the desired feature sizes and low roughness required for waveguide structures requires knowledge and control of the wetting characteristics of the substrate. We discuss the effect of substrate wetting-angle on the resulting waveguide edge-roughness as well as the effect of various polymer-solvent combinations on the resulting waveguide structures. Some constraints as well as many advantages to such direct-write technology will be discussed. Supported by NSF. * - B.J. Larson, S.D. Gillmor, and M.G. Lagally, Rev. Sci. Instr., 75(4), 832-836, 2004.

I3.33

Carrier-Injection and Transport Mechanism of in-situ Polymerized Polyaniline Films. Rodrigo Fernando Bianchi[1,2], Silmar Antonio Travain[1] and Jose Alberto Giacometti[3]; [1]Departmento de Fisica e Ciencia dos Materiais, Universidade de Sao Paulo, Sao Carlos, Sao Paulo, Brazil; [2]Departamento de Sistemas Eletronicos, Escola Politecnica da Universidade de Sao Paulo, Sao Paulo, Sao Paulo, Brazil; [3]Faculdade de Ciencia e Tecnologia, Unesp, Presidente Prudente, Sao Paulo, Brazil.

We present a study of the electric carrier-injection and transport mechanism in thin polyaniline (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 arrays as interdigitated 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 the thin PAni-electrodes systems that encompass: (i) the variable range hopping in a positional random and energetically disordered system of localized states, (ii) the charge injection from the polymer-metal contact, and (iii) the influence of space charge-limited current through the polymer bulk. Fittings of dc and ac electrical characteristics are in good agreement with experimental data. The dependence of the zero-field contact barrier (PAni-Al 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.

I3.34

A Combined Optical Approach to Structural Determination of Semi-Conducting Polymer Thin Films. Marc Gurau[1], Dean DeLongchamp[2] and Lee Richter[1]; [1]Surface and Microanalysis Science Division, National Institute of Standards and Technology, Gaithersburg, Maryland; [2]Polymers 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 metrologies used to characterize the various components of such devices. Previous work on thin films of prototypical semi-conducting polymers 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 absorptions of the different molecular weight polymers upon annealing 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 indicates that the hexyl 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 structures of these systems through further analysis of the spectroscopic data is presented.

I3.35

Time Dependent Parallel Resistance in an Organic Schottky Contact. Arash Takshi and John D. Madden; Electrical and Computer Engineering, University of British Columbia (UBC), Vancouver, British Columbia, Canada.

The lifetime of organic electronic devices is still a big barrier to their wide spread use. Although a lot of research has been done on dark spots in OLEDs, few papers discuss degradation of nonemissive organic diodes. We have studied the electrical characteristics of Schottky contacts between regioregular Poly (3-hexylthiophene) and aluminum. The devices are fabricated by spin coating of the polymer on gold electrodes as anodes in air and are left in vacuum for four days to remove oxygen and moisture from the surface of the polymer film. The Schottky contact fabrication and encapsulation of the devices are done by depositing a thick layer of aluminum as the cathode and protective layer. The current-voltage measurement of the junction in the reverse direction shows a resistive path in parallel to the Schottky contact which is a sign of ohmic contact between semiconductor and cathode in some regions. Reduction of this parallel resistance by a factor of five and a shift in turn on voltage of about 0.5V are observed over the duration of a few weeks of testing. In addition the degradation process is studied by comparing the characteristics of this device to another that was not used for a month after fabrication. The differences in the current-voltage curves show a rapid degradation in the forward bias current in the used device, while the reverse current is not much different. Accumulation of undesired ions or the diffusion of the aluminum atoms to the semiconductor are possible reasons of producing high carrier concentration regions in the semiconductor. This results in a strong tunneling current, which appears as an ohmic characteristic under reverse bias. On the basis of this data, an electrical circuit model which includes time dependent parameters is proposed for the Schottky contact that fits the experimental results well.

I3.36

Improving the Charge Carrier Mobility of Conjugated Polymers by Chain Alignment in Nanopores. Bhavani Srinivasan[1], Kevin M. Coakley[1], Chia Goh[1], Yuxiang Liu[2] and Michael D. McGehee[1]; [1]Department of Materials Science Engineering, Stanford University, Stanford, California; [2]Department of Chemistry, Stanford University, Stanford, California.

We have formed films of anodic alumina with arrays of straight nanopores on indium tin oxide (ITO) electrodes. We filled the pores 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, which is known to have anisotropic transport characteristics, we see a substantial (> 50x) 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. Including this correction, we obtained a mobility of greater than 0.006 cm^2/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 cm^2/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 enhancement in mobility in the anodic 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 annealing conditions to further optimize the mobility. 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 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.

I3.37

Ambipolar Charge Transport in a Methanofullerene.

Sachetan M. Tuladhar[1], James Kirkpatrick[1], Stelios A. Choulis[2], Dmitry Poplavskyy[2], Donal D. C. Bradley[1] and Jenny Nelson[1]; [1]Department of Physics, Imperial College London, London, United Kingdom; [2]OSRAM, Opto Semiconductors, Inc., San Jose, California.

Blends of conjugated polymer with methanofullerenes such as [6,6]-phenyl C 61 -butyric 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 fullerenes 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 of polymer:PCBM solar 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, and 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 the PCBM phase is likely to be responsible for the increase in hole mobility in MDMO-PPV:PCBM blends when PCBM is added to the blend. [1] e.g. F. Paginger et al, Adv.Funct.Mater. 13, 85 (2003) S.M. Tuladhar et al. Adv. Funct.Mater. (in press). [2] J. van Duren et al, Adv. Funct. Mater., 14, 425-434 (2004). [3] R. Pacios et al, Synth. Met. 137, 1469-70 (2003); S.A.Choulis et al, Appl.Phys.Lett. 83, 3812 (2003).

I3.38

Charge Mobilities in pi-Stacked Architectures.

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 decaflurodiphenyl (FDP) show a herringbone packing of the aromatic ring systems similar to that observed in pentacene films. However, molecular complexes consisting of a 1:1 DP to FDP ratio pack with a face-to-face stacking of the aromatic rings due to electrostatic interactions between the electron-rich rings of DP and the electron-deficient rings of FDP. These structures provide different packing arrays of aromatic rings with similar electronic structures. Films of DP, FDP, and DP:FDP can be grown by blade casting or chemical vapor deposition. Charge mobilities through these structures were measured in organic thin-film transistors. Results for DP, FDP, and the 1:1 molecular complex will be presented as well as those for related systems.

I3.39

Control of Ferroelectric Poly (Vinylidene Fluoride-Co-Trifluoroethylene)/Metal Electrode Interfaces using Self Assembled Monolayers.

Cheolmin Park and Youn Jung Park; Materials Science and Engineering, Yonsei University, Seoul, South Korea.

As polymeric materials, poly vinylidene fluroride (PVDF) and its copolymers with trifluoroethylene (TrFE) are of particular interest for their ferroelectric properties and the nonvolatile memory device applications. Ferroelectric polymer storage device includes a ferroelectric polymer thin film sandwiched between arrays of 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 crystal orientation in the film. When thin films (50nm to 200nm) 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 crystallite orientation in thin films on stiff metal electrode. In order to control ferroelectric polymer/metal interfaces, a variety of self-assembled monolayers (SAMs) of alkanethiolates including hexadecanethiol (HDT), mercaptohexadecanoic acid (MHA) were formed as an interlayer between either Au or Pt bottom electrode and copolymer film. The remanent polarization of copolymer thin film significantly increased approximately 200% on the modified bottom electrode by SAMs, which is highly desirable for bistable memory devices. The formation of SAMs with different ligands such as CH3 and COOH on the metal surfaces gave rise to variation of polarization levels. In addition, we investigated the effect of polarization switching behavior on bottom metal electrodes: Au and Pt. The evolution of ferroelectric and P(VDF-TrFE) crystalline microdomains as a function of film thickness with the presence of interlayer was characterized by atomic force microscope (AFM) and transmission electron microscope (TEM). Enhancement of ferroelectric behavior by SAMs was interpreted by both preferred crystalline microstructure and controlled surface energy of metal electrode.

I3.40

The Role of Symmetry and Charge Delocalization in Two-Dimensional Conjugated Molecules for Optoelectronic Applications.

Hermona Christian[1], Zukhra I. Niazimbetova[2] and Mary E. Galvin[1]; [1]Materials Science and Engineering, University of Delaware, Newark, Delaware; [2]Rohm 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 facile 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 phenylenevinylene (PPV) based molecule containing oxadiazole moieties in a para- position with respect to each other, p-OXA-X. The introduction of the electron deficient oxadiazole unit into the hole transporting PPV backbone serves to better balance charge injection and transport. The present work focuses on the synthesis and characterization of 2-D PPV based molecules that have the oxadiazole moieties in an ortho- and meta- position relative to each other - termed o-OXA-X and m-OXA-X, respectively. Comparing these molecules we plan to explore the role of symmetry and charge delocalization in this class of compounds. Despite having different linear segments, o-OXA-X and m-OXA-X have nearly identical photophysical properties as p-OXA-X suggesting a similar charge delocalization mechanism. However, in LEDs with hole and electron injecting layers, the performance of these molecules varies, with o-OXA-X performing the best and exhibiting external quantum, luminance and power efficiencies of 0.46 %, 1.5 cd/A, and 1.1 lm/W, respectively. These results are compared with m-OXA-X and p-OXA-X.

I3.41

Layer-by-Layer J-Aggregate Thin Films with Absorption Constant of 10^6 cm^{-1} in Optoelectronic Applications.

M. Scott Bradley, Jonathan R. Tischler 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 exciton-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 development of previously unachievable unique optoelectronic devices, such as the recently demonstrated exciton-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-[3-[5,6-dichloro-1-ethyl-3-(3-sulfopropyl)-2(3H)-

benzimidazolidene]-1-propenyl]-1-ethyl-3-(3-sulfopropyl) benzimidazolium hydroxide, inner salt, sodium salt (TDBC) J-aggregates, alternately adsorbed with Poly(diallyldimethylammonium chloride) (PDAC) on glass substrates. Atomic force microscopy (AFM) shows that the first few bi-layers form layered structures, which give way to Stransky-Krastanov-type growth in subsequent bi-layer deposition. We combine thickness measurements from AFM and spectroscopic data to determine the optical constants of the films, and find that at the peak absorption wavelength 594 nm, the films possess an absorption coefficient of $\alpha = 1.05 \pm 0.1 * 10^6$ cm^{-1}, among the highest ever measured for a neat thin film. The optical constants were calculated by fitting spectroscopic data for films in the layered growth regime to a model based on propagation and matching matrices. We also report that variation of the adsorption step times in the LBL process affects the morphological and optical properties of the films and thereby alter the angular-dependent strong-coupling behavior of these films when incorporated in a microcavity. The presented method is a general approach to generating thin films with very large absorption constant and promises to be an enabling step to the fabrication of novel devices that utilize strong coupling of light and matter.

I3.42

Indium-Tin Oxide Surface Modification via Solution Etching, Small Molecules and Polymers: Enhancement of Electron Transfer Rates to Probe Molecules. Fathima Saneeha Marikkar, Rolnald Wysocki, Michael Brumbach, Chet Carter, Adam G. Simmonds and Neal R. Armstrong; Chemistry, University of Arizona, Tucson, Arizona.

Charge injection at the interface between transparent conducting oxides (TCO), such as indium-tin oxide (ITO) and various organic hole transport materials, is a critical determinant in the optimization of efficiencies of both organic light emitting diodes (OLEDs) and organic photovoltaics (OPVs). We have recently shown that i) electronic heterogeneity ii) effective work function; iii) wettability by non-polar organic materials; and iv) 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 appropriate chemisorption protocols. This talk will focus on the use of electrochemical reactions, using solution probe molecules, to measure rates of heterogeneous electron transfer, where changes in these rates, as surface modification proceeds, can be correlated to changes in both OLED and OPV device performance. TCO surfaces, such as ITO, generally possess large areas which are electroinactive, regardless of conventional cleaning and plasma or ozone pretreatment steps.One of our current studies involves a strong etching procedure, which smoothes and reduces the electronic heterogeneity of the ITO surface. In addition Conducting polymer chemisorption (layer-by-layer growth), and small molecule chemisorption, can enhance rates of charge transfer by up to a factor of 10-50x. These changes are correlated by a doubling of OLED efficiency, and nearly the same level of improvement in vacuum-deposited OPVs. Recent research will be presented on various modification strategies using conducting polymers like poly-(aniline) and various forms of poly-thiophenes to evaluate the possibility of further enhancing the heterogeneous electron transfer rate at TCO surfaces.

I3.43

Advanced Surface Modification of Indium Tin Oxide for Improved Charge Injection in Organic Devices. Eric L. Hanson[3,1], Norbert Koch[2,3], Jeffrey Schwartz[1] and Steven L. Bernasek[1]; [1]Department of Chemistry, Princeton University, Princeton, New Jersey; [2]Institut fuer Physik, Humboldt-Universitaet zu Berlin, Berlin, Germany; [3]CRG Chemical, San Diego, California.

A new method is described for surface modification of ITO with an electroactive self-assembled organic monolayer (SAM) to enhance hole injection in an electronic device. This procedure involves sequential formation of a self-assembled monolayer of a π-conjugated organic semiconductor on the ITO surface followed by doping with a strong electron acceptor. The semiconductor SAM is covalently bound to the ITO to ensure strong adhesion and interface stability, and reduction of the hole injection barrier in these devices is accomplished by formation of a charge transfer complex by doping within the SAM. This gives rise to very high current densities in simple hole-only and organic light emitting devices compared to untreated ITO devices.

I3.44

Exploring Charge Transfer and Transport in Conjugated Polymer Films with Scanning Probe Microscopy. David Coffey[1] and David Ginger[2]; [1]Physics, University of Washington, Seattle, Washington; [2]Chemistry, University of Washington, Seattle, Washington.

Bulk device measurements can average over important and interesting local variations in the nanoscale optical and electronic properties present in conjugated polymer films. In this poster we present the results of our recent investigations of locally mapped photoconductivity, electroluminescence, and photoinduced charging in thin films of organic semiconductors. We discuss the correlations between these effects and the various length scales present in unpatterned films, as well as in polymer films that have been patterned using surface templates generated with Dip-Pen Nanolithography.

I3.45

Patterning Nanoscale Phase Separation in Conjugated Polymer Blends with Dip-Pen Nanolithography. David Coffey[1] and David Ginger[2]; [1]Physics, University of Washington, Seattle, Washington; [2]Chemistry, University of Washington, Seattle, Washington.

The nanoscale morphology of phase-separated conjugated polymer blends is known to impact the performance of polymer light-emitting and photovoltaic devices. To probe this issue in more detail we have used the scanning-probe lithographic technique of Dip-Pen Nanolithography (DPN) to generate nanoscale surface templates with which we can control the local film morphology. We present the range of micro- and nanoscale features we are able to achieve with the DPN templating approach and the application of this technique to the study of the local optoelectronic properties of phase-separated polymer blends. We discuss the application of this method to studies of the correlation between local morphology and properties such as energy and charge transfer in controlled geometries. Samples are characterized on the micro- and nanoscale using combinations of optical spectroscopy, conventional AFM, conductive probe AFM, and electrostatic force microscopy.

I3.46

The Effect of Oxygen Exposure on Pentacene Electronic Structure. Antje Vollmer[1], Oana D. Jurchescu[2], Imad Arfaoui[2], Thomas T. M. Palstra[2], Petra Rudolf[2], Jens Niemax[3], Jens Pflaum[3], Ingo Salzmann[4], Juergen P. Rabe[4] and Norbert Koch[4]; [1]BESSY GmbH, Berlin, Germany; [2]Materials Science Center, Rijksuniversiteit Groningen, Groningen, Netherlands; [3]3. Physikalisches Institut, Stuttgart University, Stuttgart, Germany; [4]Institut f. Physik, Humboldt University Berlin, Berlin, Germany.

The reliable determination of charge 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 environmental conditions for mobility measurements. Another issue is long term stability of devices made from organic materials, as oxidation is believed to be a major reason for early device failure. We use ultraviolet photoelectron spectroscopy (UPS) to investigate the effect of oxygen and air exposure on the electronic structure of pentacene single crystals and thin films. It is found that O_2 and water do not react noticeably with pentacene, whereas ozone readily oxidizes the organic compound. In extensive tests we have observed no reaction of pentacene with molecular oxygen and water (on the time scale of several hours), even if pentacene is optically excited. More importantly, it is found that oxygen diffusion through pentacene thin films (and single crystal surfaces) is reversible, and does not leave behind (after re-evacuation) electrically active electronic states that would lead to p-type doping of the organic bulk material. This is evidenced by a lack of energy shifts in UPS spectra of pentacene before and after exposure to O_2 and to air. However, oxygen exposure lowers the hole injection barrier at the interface between Au and pentacene by 0.25 eV, presumably due to a modification of the Au surface properties. Finally, it is demonstrated that rapid oxidation of pentacene occurs in air only in the presence of ultraviolet light, due to the formation of highly reactive ozone.

I3.47

Study and Comparison of Conducting Polymer Hole Injection Layers in Light Emitting Devices. Carl Tengstedt[1], Che-H. Hsu[2], Chi Zhang[3], Ian D. Parker[3], William R. Salaneck[4] and Mats Fahlman[1]; [1]Department of Science and Technology, Linkopings University, Norrkopig, Sweden; [2]Experimental Station, Dupont Displays, Wilmington, Delaware; [3]Dupont Displays, Santa Barbara, California; [4]Department of Physics, Linkopings University, Linkoping, Sweden.

A set of polyaniline- and poly(3.4-ethylene dioxythiophene)-based materials were studied as hole injection layers in polymer light emitting devices. The studies included photoelectron spectroscopy, optical absorption, atomic force microscopy, conductivity measurements and device characterization. The choice of polymeric counterion was found to influence both work function and film morphology. The work function of the polymer films spanned the range of well over 1 eV and the surface region of the films were found to be low in conducting polymer content compared to the bulk. The different chemical, physical and electronic properties of the hole injection layers affected device performance in terms of turn on voltage, efficiency and life time. The variations in device performance are explained using the materials properties of the hole injection layers and by describing the interdependence between the hole injection layer and the anode contact, and the hole injection layer and the electroluminescent polymer.

I3.48

Rational Design of N-Type Semiconductor Materials for Organic Electronics. Colin C. Reese, Nels C. Hansen, Mang-Mang Ling, Mark Roberts, Abhijit Mallik and Zhenan Bao; Chemical Engineering, Stanford University, Stanford, California.

Organic materials are of great interest for incorporation into electronics 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 amorphous inorganics 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 in general been poor compared their p-type counterparts. In addition to the challenges common to both types of materials, such as synthetic requirements, a poor understanding of both film growth mechanisms and energy level requirements, specific problems need be addressed for n-type semiconductor design. In particular, a limited number of building blocks exist for their construction, which are often fluorinated and difficult to process. In addition, the anionic forms of organics – present during operation of n-channel devices – are often easily oxidized, yielding issues with air stability. 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 imide 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.

I3.49

Abstract Withdrawn

SESSION I4: Charge Transport and Device Physics

Chair: Timothy Von Werne
Wednesday Morning, March 30, 2005
Room 2001 (Moscone West)

8:30 AM *I4.1

Charge Transport and Electrical Stability in Poly(thiophene) Thin-Film-Transistors. Alberto Salleo[1], Armin Voelkel[1], Tze Wee Chen[2], Michael Chabinyc[1], John Northrup[1] and Robert Street[1]; [1]PARC, Palo Alto, California; [2]Electrical Engineering Dept., Stanford University, Palo Alto, California.

The performance of polymer TFTs has increased steadily in the last years. Studying charge transport and electrical stability is extremely important for the practical application of these devices. We used a regio-regular poly(thiophene) (PQT-12) to fabricate polymer TFTs. Different polymer processing conditions led to varying degrees of order in the film and room-temperature mobilities varying between 0.1 cm^2/V.s and 0.004 cm^2/V.s. Moreover, differences of more than two orders of magnitude in carrier mobility were obtained by treating the dielectric interface with different chlorosilane coupling agents. The polycrystalline microstructure of the films suggests a band-like transport mechanism with trapping at band tails. In an effort to determine the trap-free (band-like) mobility of PQT-12, we correlated the gate dependence of the mobility with its temperature dependence in all our films. It was found that the field-effect mobility is thermally activated in all films at $T<200$ K and that the activation energy depends on the charge density. The experimental data agrees well with a *multipletrappingandrelease* model. The differences in room-temperature mobility are essentially due to different widths of the shallow donor distribution at the edge of the valence band caused by structural disorder in the film. The intrinsic mobility of the mobile states in the ordered regions of the film is the same in all the films and is estimated to be between 1 and 10 cm^2/V.s. The performance of polymer TFTs is further limited by a slow decay of the output current during operation (bias stress). This decay is due to charge trapping in the channel. We measured current in decays in DC and pulsed gate mode as a function of pulse duration and duty cycle. We distinguish two different trap populations: fast and slow traps. Only fast traps are reversible at room temperature and they equilibrate after a few hundred to 1500 s. depending on gate voltage. The decay rate and the equilibrium population of the fast traps are consistent with the formation of self-trapped bipolarons. In order to improve understanding of the mechanism of hole capture, and the reverse dissociation of the bipolarons, the kinetics and its temperature dependence were measured. Finally, decay data are used to infer the bias-stress-limited lifetime of devices operated at low duty-cycles, such as the transistors used in display backplanes.

9:00 AM I4.2

Combined Electrochemical Kinetic and Electronic Transport Model of the Doping of a Thin Conjugated Polymer Film. Nathaniel D. Robinson and Magnus Berggren; ITN - Organic Electronics, Linkoping University, Norrkoping, Sweden.

Electrochemical doping and dedoping of conjugated polymers has created a new sort of electronic devices including electrochromic displays, light-emitting chemical cells, sensors and general electronic components that can be used for transistor-to-transistor logic on flexible paper and plastic substrates. Our understanding of the electrochemical switching of these materials begins from classical electrochemistry, just as our initial description of the semi-conducting nature of conjugated polymers was based on our experience with crystalline semiconductors. However, as with the models based on silicon, traditional electrochemical models fall short of describing the kinetics of electrochemical switching in conjugated polymers, especially when it comes to the conformational rearrangements (both physical and electronic) that occur within the polymer chains upon the creation or destruction of charge carriers. The first steps of improving simple descriptions of the electrochemical doping/dedoping of conjugated polymers will be presented, using experimental observations of the so-called "moving front" in a thin film polymer electrode as the basis for the discussion. A model including electron and ion transport and electrochemical kinetics has been solved using a finite-element time-stepping scheme and compared directly with experimental data. Although based in electrochemistry, the work is motivated by a desire to explain the functionality of electronic devices such as the electrochemical transistor, as these devices are maturing into technology appropriate for reel-to-reel manufacturing.

9:15 AM I4.3

Semi-Analytical Models of the Carrier Concentration Dependence of the Mobility in Organic Materials with Gaussian Disorder. R. Coehoorn, Philips Research Laboratories, Eindhoven, Netherlands.

Recent experimental work has revealed that for organic semiconductors the higher charge carrier mobility in field effect transistors (FETs) compared to the mobility in light emitting devices (LEDs) is due to the much higher carrier concentration in a FET. The carrier concentration dependence has important consequences for the device modelling, and requires one to reconsider, e.g., the dependence of the mobility on the field in a LED [2]. The observation that the concentration dependence is weak in the LED regime cannot be explained from the Vissenberg and Matters (VM) percolation model [3], which has been used successfully to analyse the FET mobility. The VM model assumes hopping in an exponential density of states (DOS). Several authors have found, however, that the observed concentration dependence can be understood qualitatively if a Gaussian DOS is assumed [4, 5]. In this contribution we compare results of calculations of the mobility using four semi-analytical models with exact numerical results [6]. All models assumed Miller-Abrahams hopping rates. We have for the first time applied the VM model and a recently proposed hopping model by Martens et al. [7] to the case of a Gaussian DOS. We include in our study the already existing models by Arkhipov et al. [4] and Roichman and Tessler (Mean Medium Approximation, MMA) [5]. All calculations were carried out as a function of the temperature and of the density of hopping sites, in the low-field limit. In spite of the widely different approaches used, the concentration dependence of the mobility is quite similar for all models. The temperature dependences of the mobilities, on the other hand, are significantly different, in particular those obtained from the MMA. We explain this in terms of the underlying physics. The semi-analytical models suggest a useful analytical expression for the mobility, leading to an accurate compact mobility model. We demonstrate the importance of including the concentration dependence of the mobility for a single layer LED that is based on a commonly used polymer such as PPV. Finally, we make a critical comparison between the experimental mobility, from [1], and the concentration dependence as obtained from assuming a Gaussian DOS. [1]. C. Tanase et al., Phys. Rev. Lett. 91, 216601 (2003). [2]. P.W.M. Blom, C. Tanase, D.M. de Leeuw and R. Coehoorn (unpublished). [3]. M.C.J.M. Vissenberg and M. Matters, Phys. Rev. B. 57, 12964 (1998). [4]. V.I. Arkhipov et al., J. Phys. Cond. Matt. 14, 9899 (2002). [5]. Y. Roichman and N. Tessler, Synth. Metals 135-136, 443 (2003). [6]. W.F. Pasveer et al., Proceedings of the ICSM (2004). [7]. H.C.F. Martens et al., Phys. Rev. B 67, 121203 (2003).

9:30 AM I4.4

Intrinsic Charge Transport in Organic Field-Effect Transistors. Vitaly Podzorov[1], Etienne Menard[2], Valery Kiryukhin[1], John Rogers[2] and Michael Gershenson[1]; [1]Physics Department, Rutgers University, Piscataway, New Jersey; [2]Dept. of Materials Science and Engineering, University of Illinois at Urbana Champaign, Urbana, Illinois.

Organic field-effect transistors (OFETs) are essential components of modern electronics. Despite the rapid progress of organic electronics, understanding of fundamental aspects of the charge transport in organic devices is still lacking. Recently, the OFETs based on pure and highly ordered organic molecular crystals have been fabricated with innovative techniques that preserve the high quality of single-crystal organic surfaces. This technological progress facilitated the study of transport mechanisms in organic semiconductors [1-4]. It has been demonstrated that the intrinsic polaronic transport, not dominated by disorder, with a remarkably high mobility of "holes" mu ~ 20 cm2/Vs can be achieved in these devices at room temperature [4]. The signatures of the intrinsic polaronic transport are the anisotropy of the carrier mobility and an increase of mu with cooling. These and other aspects of the charge transport in organic single-crystal field-effect transistors will be discussed. Supported by the NSF (DMR 0405208, ECE 0437932) and ARO MURI (DAAD 19-99-1-0252). [1] V. Podzorov et al., Appl. Phys. Lett. 82, 1739 (2003); ibid. 83, 3504 (2003). [2] V. C. Sundar et al., Science 303, 1644 (2004). [3] R. W. I. de Boer et al., Phys. Stat. Sol. (a) 201, 1302 (2004). [4] V. Podzorov et al., Phys. Rev. Lett. 93, 086602 (2004

9:45 AM I4.5

Nanoscale Measurements of Transport and Injection in Undoped/Doped Organic Thin Film Transistors. Oren Tal[1], Calvin K. Chan[2], Yohai Roichman[3], Nir Tessler[3], Antoine Kahn[2] and Yossi Rosenwaks[1]; [1]Electrical Engineering - Physical Electronics, Tel Aviv University, Tel Aviv, Israel; [2]Electrical Engineering, Princeton University, Princeton, New Jersey; [3]Electrical Engineering, Technion, Israel Institute of Technology, Haifa, Israel.

The charge carrier injection and transport properties of organic semiconductors are still poorly understood. This offers an excellent opportunity for exploring a field that combines basic research with important technological applications. We have measured the dependence of carrier transport and injection on the local charge concentration and electric field in undoped and intentionally-doped organic thin films. The measurements were conducted on organic thin film transistors based on spin coated polymer (MEHPPV) films and evaporated organic molecular film (alpha-NPD, pure and doped with F4-TCNQ). Organic thin film transistors were scanned by Kelvin probe force microscopy (KPFM), simultaneously with I-V measurements in order to extract the current and nanometer scale distribution of potential, electric field and charge concentration across the device under different operation modes. We report on several transport and injection phenomena that are unique to organic thin layer systems. For example: (a) at low carrier concentrations their mobility decreases with increasing electric field however increasing the concentration inverts this tendency; (b) the dependence of the mobility on carrier concentration under low electric field saturates at high carrier concentrations; (c) the mobility decreases and the hole injection barrier is lowered as a result of doping; and (d) an increase of the effective charge injection area at the contacts as a result of increase in drain-source voltage. The results are analyzed in the context of different theoretical approaches of hopping transport in organic materials.

10:15 AM *I4.6

Modelling of Charge Transport in Organic Electronic Materials. Jenny Nelson[1], Amanda Jane Chatten[1], James Kirkpatrick[1], Sachetan Man Tuladhar[1], Dmitry Poplavskyy[2] and Donal D. C. Bradley[1]; [1]Department of Physics, Imperial College London, London, United Kingdom; [2]OLED Research and Development, Osram Opto Semiconductors Inc, San Jose, CA 95134, California.

Understanding the mechanism of charge transport in organic electronic materials is critical to the development of improved organic solar cells, LEDs and other opto- electronic 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 Disorder Model and its variants [1,2]. Although useful for comparative studies, these models are unhelpful for identifying the microscopic transport mechanism or for relating the charge transport properties to the chemical or physical structure of the materials. We will report on recent progress in the development 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 polyfluorene polymers [3] and amorphous films of spirofluorene-arylamine small molecules [4]. Our results demonstrate the following: (i) the importance of polaronic effects and intermolecular interactions in charge transfer; (ii) the importance of simulating the relevant experimental technique, particularly in the case of dispersive transport, and (iii) how the influence of variations in film morphology (introduced e.g. through annealing) and variations in chemical structure may be incorporated into models of the charge mobility. [1] H.Baessler, Phys. Status Solidi (b) 175, 15 (1993). [2] S. V. Novikov et al., Phys. Rev. Lett. 81, 4472 (1998); Z.G.Yu et al., Phys. Rev. Lett. 84, 721 (2000). [3] D. Poplavskyy, T. Kreouzis, A. J. Campbell, J. Nelson, and D. D. C. Bradley, Mater. Res. Soc. Symp. Proc. 725, P.1.4.1 (2002). [4] D. Poplavskyy and J. Nelson, J. Appl.Phys. 93, 341 (2003); J.Kirkpatrick and J. Nelson, (submitted 2004)

10:45 AM I4.7

Turn-on and Charge Build-up Dynamics in Polymer Field Effect Transistors. Yohai Roichman and Nir Tessler; Electrical Engineering, Technion, Haifa, Israel.

We present detailed experimental and theoretical study of the current switch on and charge build-up dynamics in polymer field effect transistors. We use close-loop contact configuration that eliminates extrinsic capacitance charging and allows measuring the transistor characteristics only. By measuring the currents transient at both drain and source contacts we can identify the channel charging effects and the role of both contacts. We find that the charging current follows a power-law decay which is, naturally, dependent on the channel length. To better understand the fine features found in the experiment we have devised a simple, transmission-line like, model that reproduces the dynamics of the system. Using this model we can use the transient curves to unambiguously determine the threshold voltage and the mobility. This model is simple enough that it enables to look deeper into the device physics and incorporate the details of transport (as Gaussian DOS effects [1]) into the model. Also, it is in the form that allows straight forward integration with circuit design simulators. References [1] Y. Roichman, Y. Preezant, and N. Tessler, "Analysis and modeling of organic devices," Physica Status Solidi a-Applied Research, vol. 201, pp. 1246-1262, 2004.

11:00 AM I4.8

Electron Transport in Poly (dialkoxy-p-phenylene vinylene). M. M. Mandoc, B. de Boer and P. W. M. Blom; Materials Science Centre, University of Groningen, Groningen, Netherlands.

Conjugated polymers are promising materials for application in light-emitting diodes (LEDs), 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 widely studied materials is poly (2-methoxy-5-(3′, 7′-dimethyloctyloxy)-p-phenylene vinylene) (OC_1C_{10}-PPV). It has been demonstrated that the hole current in OC_1C_{10}-PLEDs is governed by a hole mobility μ, which is strongly dependent on temperature. Typical activation energies amount to 0.4-0.5 eV, originating from hopping in a Gaussian disordered system with Gaussian site-energy distribution of width $\sigma_{DOS}\sim$0.1 eV. The electron conduction in the PPV-derivatives proved smaller than the hole conduction, which was attributed to the presence of traps [1] or lower electron mobility [2]. A lower mobility due to increased disorder or trapping by extrinsic defects is expected to increase the temperature dependence of the charge transport. However, in the limited amount of studies on electron transport presented so far a weaker temperature dependence of the electron transport has been observed as compared to holes. Consequently, the microscopic origin of the reduced electron transport in PPV derivatives and other conjugated polymers has not been resolved so far. In this work we investigate the electron conduction in poly (dialkoxy-p-phenylene vinylene) derivatives in an electron-only device configuration. In such a device the hole current needs to be strongly suppressed. However, for a Ag bottom contact, with an energy barrier for hole injection of 0.9-1 eV, we have observed that in spite of the large injection barrier the hole injection is not sufficiently suppressed. The reason is that at 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 SAM-modified 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. [1] P.W.M. Blom, M.J.M. de Jong, J.J.M. Vleggaar, Appl. Phys. Lett. 68 (1996) 3308-3310. [2] L. Bozano, S.A. Carter, J.C. Scott, G.G. Malliaras, and P.J. Brock, Appl. Phys. Lett. 74 (1999) 1132.

11:15 AM I4.9
High Electron Mobility Organic Field-Effect Transistors using Fullerene Thin Films. Birendra Thokchom Singh[1], Nenad Marjanovic[1], Gebhard Josef Matt[1], Serap Gunes[1], Niyazi Serdar Sariciftci[1], Alberto Montaigne Ramil[2], Andrei Andreev[2], Helmut Sitter[2], Reinhard Schwoediauer[3] and Siegfried Bauer[3]; [1]Linz Institute of Organic Solar Cells(LIOS), Physical Chemistry, Johannes Kepler University, Linz, Austria; [2]Institute of Semiconductor- and Solid State Physics, Johannes Kepler University, Linz, Austria; [3]Soft Matter Physics, Johannes Kepler University, Linz, Austria.

Hot wall epitaxy (HWE), working close to thermodynamical equilibrium is a well known technique for growing highly ordered organic thin films. We present n-channel organic field-effect transistors (OFETs) with HWE grown fullerene thin films. These devices exhibit high electron mobilities up to 2.5 cm^2/Vs with an on/off ratio >10^5. In addition, non-linear transport phenomena at high electric field are observed. Solution processed methanofullerene [6,6]-phenyl C$_{61}$-butyric acid methyl ester (PCBM) OFETs show lower mobilities up to 0.2 cm^2/Vs. Improvement of device performance by using novel polymeric dielectrics, optimized channel length and film growth conditions will also be outlined.

11:30 AM I4.10
Organic CMOS Technology Based on Interface Doped Pentacene. Marcus Ahles, Roland Schmechel and Heinz von Seggern; Materials Science, TU 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 semiconducting 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 n- and p- channels 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 comparable mobilities is realized and its properties will be discussed.

11:45 AM I4.11
Electric Field Dependent Transition from Dispersive to Non-Dispersive Transport in Conjugated Polymers. Lucas Fugikawa Santos[1], Gregorio Couto Faria[2,1], Antonio Rafael Andrade[2], Sergio Mergulhao[2] and Roberto Mendonca Faria[1]; [1]Instituto de Fisica de Sao Carlos, Sao Carlos, SP, Brazil; [2]Departamento de Fisica, Universidade Federal de Sao Carlos, Sao Carlos, SP, Brazil.

Time-of-flight measurements in poly(1-methoxy-4-(2-ethyl-hexyloxy) -p-phenylene vinylene (MEH-PPV) were carried out in p-GaAs/MEH-PPV/Al structures in order to evaluate the mobility of photogenerated charge carriers in the device polymeric layer. The transient photocurrent response using short excitation wavelengths (far below the absorption peak) and in a low electric field region (below 10E5 V/cm) was characteristic of dispersive charge carrier transport. On the other hand, for excitation wavelengths well-absorbed by the polymeric layer, quasi non-dispersive charge transport and practically no dependence on the external electric field was observed. In the high electric field regime (above (10E5 V/cm), the hole mobility values evaluated for all excitation wavelengths apparently converge to a definite value (about 10E-6 cm2/V.s). 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 I5: Photovoltaics
Chair: Lukas Burgi
Wednesday Afternoon, March 30, 2005
Room 2001 (Moscone West)

1:30 PM *I5.1
Development of Nano-structured Oxide Electron Conductors for Organic Photovoltaic Cells. David S. Ginley[1], Sean Shaheen[1], Matthew White[2], Calvin Curtis[1], Alex Miedaner[1], Rueben Collins[3] and Dana Olson[3]; [1]PV&EM, NREL, Golden, Colorado; [2]Physics, University of Colorado, Boulder, Colorado; [3]Physics, Colorado School of Mines, Golden, Colorado.

Organic photovoltaic (OPV) cells offer the potential for low cost, readily processible 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) either 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 nano-structures. 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 grown on substrates can be controlled to have a diameter in the desired 5-10 nm range, r and 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 I5.2
Performance of Pentacene-C$_{60}$ Heterojunction Photovoltaic Devices. Sergey Mezhenny[1], Mihaela Breban[1], Vince B. Ballaroto[1], John E. Anthony[2], Ellen D. Williams[1], Warren Herman[1] and Danilo B. Romero[1]; [1]Laboratory for Physical Sciences, University of Maryland, College Park, Maryland; [2]Department 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 (C$_{60}$) molecules. Photovoltaic devices with sandwich geometry comprising of transparent indium-tin-oxide (ITO) / [Pn/C$_{60}$]$_n$ / Al and ITO / poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) / [Pn/C$_{60}$]$_n$ / lithium fluoride (LiF) / Al with bilayer (n=1) and multilayer (n=18) have been fabricated using layer-by-layer growth of the Pn and C$_{60}$ from separate organic MBE effusion cells. Devices with Pn/C$_{60}$ bulk heterojunctions were obtained either by co-deposition of Pn and C$_{60}$ molecules or by spin-casting of blends of soluble Pn and C$_{60}$ derivatives. The multilayer devices with the PEDOT:PSS and LiF electrodes manifest an increase of the open-circuit voltage (V$_{oc}$ $\sim$ 0.25 V for the bilayer and $\sim$ 1.0 V for the multilayer) with the number of layers while the bulk heterojunction devices revealed an average value (V$_{oc}$ $\sim$ 0.45 V). Electroabsorption measurements of the built-in potentials in the corresponding devices are used to determine the internal potential drop across the devices independently. While the open-circuit voltage is lower, we observe nearly two orders of magnitude increase of the short-circuit current in the bulk heterojunction devices relative to the multilayered structures. The implications of these results for the power conversion efficiency of the pentacene/fullerene-based photovoltaic devices will be discussed. * 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 I5.3
Geminate Charge Separation in Bulk Heterojunction Photovoltaic Cells. Shanbin Zhao[1] and Peter Peumans[2]; [1]Materials Science and Engineering, Stanford University, Stanford, California; [2]Electrical 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 geminate (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 most important loss mechanism 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 carrier recombination process that takes place at the donor-acceptor immediately following exciton dissociation determines the shape of the photocurrent-voltage characteristics and contributes significantly to losses in organic donor-acceptor solar cells. We find that it is the ratio of the electron mobility of the acceptor material over the hole mobility of the donor material (or vice versa), while not the absolute carrier mobilities, determines the geminate separation probability and fill factor. These results are confirmed by intensity- and voltage-dependent photocurrent measurements on planar and bulk heterojunctions. Our studies of the effect of the bulk heterojunction geometry indicate that for fine-grained morphologies, mobility ratios approximately greater than 1000 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 I5.4

Surface Photovoltage in Polyfluorene-based Polymer Blends: Correlation between Morphology and Electronic Properties. Marco Chiesa[1], Lukas Buergi[1,2], Ji-Seon Kim[1], Rafi Shikler[1], Richard H. Friend[1] and Henning Sirringhaus[1]; [1]Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom; [2]CSEM, 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 by 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-benzothiadiazole) (F8BT) and poly-(9,9'-dioctylfluorene-co-bis-N,N'-(4-butylphenyl)-bis-N,N'-phenyl-1,4-phenylenediamine) (PFB) 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 I5.5

Exciton Migration and Quenching in Polymer Light-Emitting Diodes and Solar Cells. Denis Markov, Teunis van Woudenbergh, 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 where 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 upon injection and transport of holes and electrons. Since the electron conduction in conjugated polymers has been found to be smaller then the hole conduction, exciton formation is mainly confined in the region close to the cathode. As a result nonradiative exciton energy transfer towards the metallic cathode occurs, thereby limiting the PLED efficiency. Consequently, exciton quenching in PLEDs is a combined effect of nonradiative energy transfer to the cathode and exciton diffusion, which redistributes the exciton population. 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 spin coated poly(p-phenylene vinylene) (PPV) based derivative and evaporated C_{60} are ill-defined due to diffusion of C_{60} into the polymer, leading to an overestimation of the exciton diffusion length. This artefact is resolved by the use of a newly developed thermo-polymerizing fullerene derivative that immobilizes the electron acceptor layer. From the decay curves of polymer layers with varying thickness an exciton diffusion constant of $3\text{x}10^{-4}\text{cm}^2/\text{s}$ has been obtained. Subsequently, bilayers of metals and various poly(p-phenylene vinylene) (PPV) derivatives were 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 quenching behavior inside PLEDs is 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 polymeric electron transport top layer (ELT) is inserted between the light emitting 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 conversion efficiency is voltage independent, indicative for absence of exciton quenching as predicted by our luminescence measurements results.

3:15 PM I5.6

A Study of Exciton Diffusion and other Factors that Limit the Performance of Organic Photovoltaics. Shawn R. Scully, Yuxiang Liu, Michael Rowell 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 cells, excitons must 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 are only a few that address the dynamics of exciton diffusion. It is often assumed that the exciton diffusion length (Ld) is $\sim$ 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-P3HT, 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, quenching of excitons by surface plasmons in the metal electrode, and non unity charge collection efficiency, and show how they can be overcome. Our data suggest that materials with even modest exciton diffusion lengths can lead to high efficiency photovoltaics.

3:30 PM I5.7

Solar Cells of Low-Bandgap Polyfluorenes. Mats R. Andersson[1], Erik Perzon[1], Wendimagegn Mammo[1], Xiangjun Wang[2], Fengling Zhang[2], Frederick Oswald[3], Juan Luis Delgado[3], Pilar de la Cruz[3], Fernando Langa[3] and Olle Inganas[2]; [1]Materials and Surface Chemistry, Gothenburg, Sweden; [2]Bimolecular and Organic Electronics, Linkoping, Sweden; [3]Facultad 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 resolved. 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, something 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 prepared alternating polyfluorene copolymers has 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 mobilities similar to regioregular P3HT. 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 880 nm. Under simulated solar conditions the highest obtained power conversion efficiency for these polymers is 0.69%. The polymer synthesis, polymer properties, device structure, and device characteristics will be presented.

3:45 PM *I5.8

Device Operation of Polymer-Fullerene Bulk Heterojunction Solar Cells. Valentin D. Mihailetchi, Jan Anton Koster, J. C. (Kees) Hummelen and Paul W.M. Blom; Materials Science Centre, University of Groningen, Groningen, Netherlands.

A fundamental limitation of the photocurrent of solar cells based on a blend of poly(2-methoxy-5-(3',7'-dimethoxyloctyloxy)-p-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 limited conduction, admittance spectroscopy, 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 geminate 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 based 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 OC1C10-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 OC1C10-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.

4:15 PM I5.9

Organic/Inorganic Hybrid Thin-Film Silicon Solar Cells with Conducting Polymer p-Layer. Evan L. Williams[1], Qi Wang[2], Sean E. Shaheen[2], David S. Ginley[2], Eric A. Schiff[3] and Ghassan E. Jabbour[1]; [1]Department of Chemical and Materials Engineering & Flexible Display Center, Arizona State University, Tempe, Arizona; [2]National Renewable Energy Laboratory, Golden, Colorado; [3]Department of Physics, Syracuse University, Syracuse, New York.

We have demonstrated the feasibility of using a conductive polymer to replace the traditional a-Si:H p-layer and buffer layer, in thin-film Si based solar cells. The hybrid solar cell was fabricated on an ITO coated glass substrate and has a p-i-n stack structure. The p-layer was a spin coated film of PEDOT:PSS (poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)), the i-layer was hydrogenated amorphous silicon (a-Si:H) and the n-layer was microcrystalline silicon (μc-Si). The Si layers were grown on top of the organic film using the hot-wire chemical vapor deposition technique, with a substrate temperature of 200°C. The hybrid device exhibited an open circuit voltage (Voc) of 0.88 V with an efficiency of 2.1%. The 0.88 V value is equivalent to the typical Voc of an entirely a-Si:H cell and is better than that of such cells without a buffer layer at the p-i interface. This experimental result suggests that a conduction band offset at the polymer/i-layer interface prevents electrons from moving into the p-layer, increasing the quasi-Fermi energy splitting, thus, increasing the Voc. The physics and modeling of traditional and hybrid p-i interfaces, as well as their influence on the Voc, will be discussed.

4:30 PM I5.10

Power Dependence and Turn-on Dynamics of Polymer Photocells - Extracting Mobilities and Analyzing Morphologies. Noam Rappaport and Nir Tessler; Electrical Engineering, Technion Israel Institute of Technology, Haifa, Israel.

We present an analytic description of the loss of photocurrent efficiency at 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 quantum efficiency. 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 theoretical and experimental study to discuss the role of recombination and space charge effects in decreasing photocurrent efficiency. As a byproduct of our transient response measurements and analyses we found a new and intriguing analytic and experimental 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.

4:45 PM I5.11

Broad Photocurrent Spectral Response Window of Solar Cells with Low-Bandgap Copolyfluorene and C70-Fullerene. Xiangjun Wang[1], Erik Perzon[2], Juan Luis Delgado[3], Fernando Langa[3], Mats Andersson[2] and Olle Inganas[1]; [1]Biomolecular and organic electronics, Linkoping University, Linkoping, Sweden; [2]Materials and Surface Chemistry, Chalmers University of Technology, Goteberg, Sweden; [3]Facultad de Ciencias del Medio Ambiente, Universidad de Castilla-La Mancha, Toledo, Spain.

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 region may be another consequence when the absorption extending to the infrared wavelength [1]. 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 < l < 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-G1) and has an onset of optical absorption at l = 1000 nm . Solar cells consisting of APFO-G1 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-G1: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 wavelength of 300 < l < 1000 nm. It has a maximum of ~28% at wavelength l = 400 nm and as high as ~ 8.8% at l = 850 nm as well as 7% at l = 900 nm. A photocurrent density of 3.4 mA/cm2, open circuit voltage of 0.58 V and power conversion efficiency of 0.7% is achieved under the illumination of AM1.5 (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, P.d l Cruz, F. Zhang, F. Langa, M. Andersson, O. Inganas, Appl. Phys. Lett. 85, xxxxx, (2004). In press.

SESSION I6: Poster Session: Organic Based Materials and Devices

Chairs: Ana Claudia Arias, Lukas Burgi, John Emerson and Nir Tessler
Wednesday Evening, March 30, 2005
8:00 PM
Salons 8-15 (Marriott)

I6.1

A Structural Investigation of PF_6^- Doped Polypyrrole as a Function of Oxidation State. Mya R. Warren[1], J. D. Madden[2] and B. Bergersen[1]; [1]Physics and Astronomy, University of British Columbia, Vancouver, British Columbia, Canada; [2]Electrical 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 electrochemical switching in their operation. The behavior of 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 polypyrrole as a function of oxidation state. Polypyrrole was electrochemically deposited with the PF$_6{}^-$ counter ion at a constant current density of 0.125mA/cm^2 and a temperature of -40^{o}C. The films had a conductivity of 300S/cm and a thickness of 20μm. Films were reduced at constant current to completely remove the counter ions. X-ray photoelectron spectroscopy (XPS) confirms that the concentration of PF$_6{}^-$ in the reduced film is less than 0.01%. X-ray diffraction patterns were obtained for the polymer in the as-grown (oxidized) state and in the fully reduced state. The diffraction patterns of both show short-range order in the form of several broad crystalline peaks with d-spacings of 1.75nm, 0.65nm, and 0.34nm and one amorphous peak at 0.44nm. 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 crystal structure does not change under reduction, we suggest that the bulk of the counterions do not take up regular positions in the crystals, but are distributed in the amorphous regions of the polymer instead.

I6.2

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. This difficulty presents itself when attempting to apply a gate dielectric to conductive fiber substrates during the fabrication of fiber transistors for use in applications such as electrotextiles and optical switches. We present a dip coating process that applies a gate dielectric to metal-coated optical fibers with high uniformity and reproducibility, resulting in pentacene field-effect transistors (FETs) with excellent transistor characteristics including mobilities up to 0.4 cm2/Vs and on/off ratios up to 7000. In one case, a memory effect was demonstrated. Several gate dielectrics were successfully applied to the optical fibers, suggesting a baseline set of suitable materials for this purpose. A thorough study of the dip coating conditions is presented, including proposed explanations of the effects of different coating procedures and solution physical properties. Finally, alternative architectures that would provide much higher W/L ratios and on-currents will be described.

I6.3

Morphology, Optical Properties and Field-Effect Transistors Based on Electrospun Nanofibers of Conjugated Polymers. Amit Babel[1], Dan Li[2], Younan Xia[2] and Samson A. Jenekhe[1,2]; [1]Department of Chemical Engineering, University of Washington, Seattle, Washington; [2]Department of Chemistry, University of Washington, Seattle, Washington.

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) (PHT) or poly(9,9-dioctylfluorene) (PFO), using the 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/PHT blend nanofibers have reduced phase separation and improved efficiency for energy transfer compared to the bulk thin films. However, MEH-PPV/PFO blend nanofibers showed reduced energy transfer from PFO to MEH-PPV as compared to the corresponding thin films. Field-effect transistors based on the MEH-PPV/PHT blend nanofibers exhibited p-channel transistor characteristics with hole mobility in the range of $(0.05\text{-}1)\times10^{-4}$ cm^2/Vs. Our results demonstrate that conjugated polymer nanofibers are promising 1-D system to study confinement effects on charge transport and optical properties.

I6.4

A Self Aligned Fully Lithographic Process for Integrated OFETs. Ioannis Kymissis, Kevin Ryu, Akintunde I. Akinwande, Charles G. Sodini and Vladimir Bulovic; EECS, MIT, Cambridge, Massachusetts.

A self-aligned fully lithographic process for forming organic FET integrated circuits will be presented. The process uses pentacene as the semiconductor, and parylene, a CVD vapor deposited polymer, as the gate dielectric. The process has a maximum process temperature of 90 degrees C. Self-alignment is achieved through backside exposure through a high optical density gate pattern and a properly engineered semi-transparent gold source/drain layer. The process allows for the formation of vias, interconnect between source/drain and gate layers, lithographic isolation of the transistors, and the formation of both self-aligned and non-aligned transistors. The process provides for significantly reduced overlap capacitance (>50% for the self aligned process over a control process with a 5um design rule, <4pF typical on a 1000um wide transistor) as well as reduced gate dielectric leakage, with no measurable sacrifice in mobility or contact resistance over the control, non-self aligned process. In addition to discussing the process, material, and mask design strategies used, we will also discuss the device and circuit advantages of the self-aligned strategy.

I6.5

New Phenylene Vinylene Based 2-Dimensional Oligomers with Cyano Groups for Optoelectronic Applications. Yashpal J. Bhandari[1], Zukhra Niazimbetova[2] and Mary E. Galvin[1]; [1]Materials Science and Engineering, University of Delaware, Newark, Delaware; [2]Rohm and Haas Electronic Materials, LLC, Marlborough, Massachusetts.

The last two decades have seen a growing interest in the field of Organic Semiconductors specifically for applications in organic light emitting diodes (OLEDs), thin film transistors (TFTs), and organic photovoltaics (PVs). An OLED operates by the injection of electrons and holes into the emissive polymer layer by the application of voltage leading to formation of exciton and emission of light. On the other hand, in organic photovoltaics, the incident photon excites an electron from the π to π* orbital to form bound electron-hole pair which split at the interface formed between organic/organic or organic/metal electrode and migrate freely to generate electricity. In addition to the absorption in the red and infrared for photovoltaics, the two processes require a balanced charge injection and efficient carrier mobility. In polymers, hole mobility is more facile than electron mobility and hence polymers with improved electron mobility are required for high device efficiency. π-πstacking in semiconducting organic materials, induces a 2-D delocalization of charge and increases carrier mobility by decreasing the activation energy for interchain carrier hopping. In addition to carrier mobility, PLED efficiency depends on charge injection, which in turn depends on the barriers between the molecular frontier orbitals of the polymer (HOMO for hole injection and LUMO for electron injection) and the work function of the contact metal electrodes. The smaller the barrier the greater the charge injection. On the other hand electron accepting materials with smaller band gap and absorption in the red can be blended with electron donating materials like poly(3 hexylthiophene) to form donor-acceptor system for use in organic photovoltaics. We have developed an oligomer with an electron withdrawing cyano substituent CN-X, which has the potential for π-π stacking, 2-dimensional delocalization of charge, improved charge injection and absorbs in the red. The structure-property relationships and applications of CN-X in light emitting diodes and organic photovoltaics will be discussed.

I6.6

Novel Dielectric Materials for Organic Electronics. Antonio Facchetti, Myung-Han Yoon and Tobin J. Marks; Northwestern University, Evanston, Illinois.

We present are latest results on the design and fabrication of very high capacitance dielectric materials for organic field-effect transistors. We will show that utilization of appropriate self-assembling siloxane building blocks and polymer matrices allows solution-processed, pinhole-free organic dielectrics. Electrical (MIS, TFT) data demonstrate that these insulators can be efficiently integrated into large TFT structures. These devices function for both p- and n-channel semiconductors, the molecular components of which exhibit greatly different core structures and substituent functionalities. Substantial TFT response is achieved at very low operational biases (< 1V), without serious leakage currents (< 10-8 A/cm at 1V).

I6.7

Oriented Anthracene and Pentacene Thin Films. Randall L. Headrick[1], Hua Zhou[1], Binran Wang[1], Ricardo Ruiz[2], Alex C. Mayer[2], George G. Malliaras[2] and Alexander Kazimirov[3]; [1]Department of Physics, University of Vermont, Burlington, Vermont;

[2]Department of Materials Science and Engineering, Cornell University, Ithaca, New York; [3]Cornell High Energy Synchrotron Source, Cornell University, Ithaca, New York.

Azimuthally 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 parallel, oriented row like structures, which have identical crystallographic orientations. This is in contrast to films grown by conventional techniques that are oriented with (00L) planes parallel to the surface, but are composed of grains with random azimuthal orientations. Depending on the exact growth conditions, fine filaments, micron-wide rows, or fully continuous films are formed. Synchrotron x-ray diffraction studies confirm that the films are highly ordered and oriented. Pentacene epitaxial growth by vapor deposition atop oriented anthracene was studied using in-situ synchrotron x-ray 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.

I6.8

Modeling the Organic Thin Film Transistors. Viorel Olariu[1], Robert Rotzoll[1], Siddharth Mohapatra[2], Robert Wenz[2], Michelle Grigas[2], Oleg Shchekin[2], Klaus Dimmler[1] and Ananth Dodabalapur[2,3]; [1]Design, OrganicID, Inc., Colorado Springs, Colorado; [2]R&D Laboratory, OrganicID, Inc., Austin, Texas; [3]The 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 become 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 RFIDs for large volume supply chains. In order to develop 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 regularly operates in the inversion mode. Due to the molecular nature of the semiconductor, the carrier mobility is order of 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 possible 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 developing 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 developed model as well a comparison between the simulated data and the 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 cm^2/Vs.

I6.9

Direct Observation of a Molecular Junction Using High-Energy X-ray Reflectometry. Michael Lefenfeld[1,2], Julian Baumert[2], Eli Sloutskin[3], Moshe Deutsch[3], Colin Nuckolls[1] and Ben Ocko[2]; [1]Chemistry, Columbia University, New York, New York; [2]Physics, Brookhaven National Labs, Upton, New York; [3]Physics, Bar-Ilan University, Ramat-Gan, Israel.

Molecular electronics is broadly defined as electronic devices whose properties are dominated by both the molecule/metal 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 an incredible problem and once they are accomplished, it is still difficult to determine how the molecules are truly organized. Therefore, recent studies have begun to use SAM covered liquid mercury (Hg) electrodes complemented with either another Hg electrode or a conductive solid film. This paper presents a new X-ray scattering technique which allows high resolution studies 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.

I6.10

Inkjet Printing of PEDOT:PSS Films for Organic Electronics. Lee Smith[3,1], Erik Garnett[4], John Perkins[1], Alex Miedaner[1], Calvin Curtis[1], Tanya Kaydanova[1], Andrew Leenheer[3,1], Maikel Van Hest[1], Sean Shaheen[1] and David S. Ginley[1]; [1]PV&EM, NREL, Golden, Colorado; [2]PV&EM, NREL, Golden, Colorado; [3]Physics, Colorado School of Mines, Golden, Colorado; [4]Chemistry, University of California Berkeley, Berkeley, California.

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. Poly-3,4-Ethylenedioxythiophene (PEDOT): polystyrene sulfonate (PSS) films were inkjet printed on glass and other substrates with various surfactant additives 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 intial PEDOT:PSS from 4 S/cm to 133 S/cm. The surface roughness could be reduced to 86 angstrom rms roughness 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 power tool for exploring contact formation as well as for direct writing of contacts on a variety of important materials for organic devices.

I6.11

Design and Characterization of Noble Organic Heterojunction Photovoltaic Device. Changhee Ko, Yashpal Bhandari and Mary E. Galvin; Materials Science and Engineering, University of Delaware, Newark, Delaware.

Since the discovery of light emitting diodes in 1990, conjugated organic polymers (organic conducting material) have been vigorously used in various fields including OLEDs, FETs, artificial muscles and PVs. The merits of organic conducting materials are that they can be processed from solution and their energy gap can be easily tuned. Recently the use of electroactive organics in photovoltaic devices (PVs) has received more focus due to the high demand for alternative energy. Our research is focused on the development of high efficiency organic photovoltaic device (PVs) using novel organic hetero junction material systems. Our organic hetero junction systems are mainly composed of oxadiazole containing PPV and poly 3-hexylthiophene (P3HT). The oxadiazole moiety is an electron withdrawing group (n-type) which also has significant oxidative stability and P3HT has high carrier mobility. When the oxadiazole containing PPV is blended with P3HT, photoluminescence quenching is observed. The optical and morphological properties of these blends and PV device characteristics will be discussed. New material systems for PVs will also be discussed.

I6.12

Tuning of Metal Work Functions with Self-Assembled Monolayers. Bert de Boer, Afshin Hadipour, Magda M. Mandoc and Paul W. M. Blom; Molecular Electronics, Materials Science Centre / University of Groningen, Groningen, Netherlands.

We demonstrate the tuning of metal work functions by chemically modifying the metal surface through the formation of chemisorbed self-assembled monolayers (SAMs) derived from 1H,1H,2H,2H-perfluorinated alkanethiols and hexadecanethiol. The ordering inherent in the SAMs creates an effective, molecular dipole at the metal/SAM interface, which increased the work function of Ag ($\Phi_{Ag}\sim$4.4 eV) to 5.5 eV ($\Delta\Phi\sim$1.1 eV) for 1H,1H,2H,2H-perfluorinated alkanethiols. Hexadecanethiol on the other hand shifted Φ_{Ag} to 3.8 eV ($\Delta\Phi\sim$0.6 eV). On Au, the SAM of 1H,1H,2H,2H-perfluorodecanethiol raised Φ_{Au} (4.9 eV) with 0.6 eV to 5.5 eV, whereas hexadecanethiol decreased Φ_{Au} by 0.8 eV. These chemically modified electrodes were applied in the fabrication of polymer LEDs and the hole injection into poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene (MEH-PPV) was investigated. An Ohmic contact for hole injection between a silver electrode functionalized with the perfluorinated SAMs, and MEH-PPV with a HOMO of 5.3 eV was established. Conversely, a silver electrode modified with a SAM of hexadecanethiol lowered Φ_{Ag} to 3.8 eV blocked the hole injection into PPV, which enables studying the electron transport in composite devices. The electron-only current was measured in a polymer/polymer blend photovoltaic cell based on MDMO-PPV (as donor) and poly[oxa-1,4-phenylene-(1-cyano-1,2-vinylene)-(2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylene)-1,2-(2-cyanovinylene)-1,4-phenylene] (PCNEPV, acceptor). This method demonstrates a simple and attractive approach to modify and improve metal/organic contacts in organic electronic devices like LEDs, photovoltaic cells, and FETs.

I6.13

Organic Light-Emitting Field-Effect Transistors using Patterned Growth of two Organic Semiconductors.

Stijn De Vusser[1,2], Soeren Steudel[1,2], Stijn De Jonge[1], Jan Genoe[1] and Paul Heremans[1,2]; [1]MCP, IMEC, Heverlee, Belgium; [2]ESAT, KULeuven, Leuven, Belgium.

Organic semiconductors have been incorporated in a number of devices, such as organic thin-film transistors (OTFT's), organic solar cells and organic light-emitting diodes (OLED's). 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 α-5T (a p-type organic semiconductor) and N,N'-Ditridecylperylene-3,4,9,10-tetracarboxylic diimide (PTCDI-$C_{13}H_{27}$) (an n-type organic semiconductor) was used. OLEFET's might become an interesting structure, 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-$C_{13}H_{27}$. 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 particles, thus creating a shadow region 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 taken out of the deposition system. In an inert atmosphere, the sample was turned 180° on the sample holder. During the following deposition of PTCDI-$C_{13}H_{27}$, the previously uncovered electrode was covered, as well as part of the channel. Inside the channel, an overlapping region of tetracene and PTCDI-$C_{13}H_{27}$ 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 into the organic semiconducting 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.

I6.14

Conduction Polymer Peposition by Inkjet Printing.

Ely Antonio Tadeu Dirani[1,2], Adriana Fatima Ferreira dos Santos[1], Adnei Melges de Andrade[1], Fernando Josepetti Fonseca[1], Rodrigo Fernando Bianchi[1] and Helena Liberatori Gimaiel[1]; [1]Departamento de Engenharia de Sistemas Eletronicos, Universidade de Sao Paulo, Sao Paulo, SP, Brazil; [2]Departamento de Engenharia Eletrica, Pontificia Universidade Catolica de Sao Paulo, Sao Paulo, SP, Brazil.

This work describes polyaniline deposition process using a commercial and inexpensive printer - Epson Stylus Photo R200. Ink-jet printing was used to directly deposit patterned 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 that 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 single material or such that they form discrete unmixed layers. By fully utilizing these unique properties of microliquids, we have succeeded in fabricating gas sensors by direct patterning of polymer solutions.

I6.15

Patterning of Conjugated Polymer Films for Flexible Electrochromic Devices.

Avni A. Argun and John R. Reynolds; Chemistry, University of Florida, Gainesville, Florida.

Patterning of electronic devices is essential for fabrication of independently addressed displays with high resolution values. One of the greatest challenges in patterning of electrodes is the complexity of the process to obtain fine structures. Line patterning, which involves printing of patterns on a plastic or paper substrate using a commercial printer, is utilized for preferential deposition of transparent poly(3,4-ethylenedioxythiopene)-poly(styrene sulfonate) (PEDOT/PSS) or electroless gold films with lateral resolution values of ~30 μm. These electrodes were used to build laterally configured polymer and metallic interdigitated electrodes (IDEs) for electrochromic devices (ECDs). Complementary colored, dioxythiophene based electrochromic (EC) polymers were deposited on alternating fingers of gold coated IDEs. EC switching kinetics of 2-lane, 4-lane, and 6-lane ECDs have been studied by applying deep potential steps and monitoring the reflectance change as a function of time. The switching times to reach 85% of the full contrast are 4.3 s, 1.5 s, and 0.8 s for 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. We have also introduced the use of highly porous metallized membranes in patterned reflective ECDs which allows fast EC switching of dioxythiophene based polymers (5-10 Hz) with outstanding power efficiencies and long-term stabilities (180,000 switches). Using metallized porous electrodes, reflectance attenuation of up to 90% in the NIR and ~60% in the visible regions are obtained. These display devices operate at low voltages (±1 V) and have low energy requirements to switch (~0.67 mJ/cm^2). Finally, we have developed a method to electrically contact patterned electrodes on porous substrates where the contacts are hidden on the back of the substrates. This method permits increased density and more design flexibility for display type devices as compared to conventional front-side contact techniques. A numeric display ECD was designed and assembled to demonstrate the independent addressing of patterned electrodes with back-side contacts.

I6.16

Electropatterning 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 patterned network materials to electro-optical devices, e.g. polymer light emitting diode (PLED) devices and conducting nanowires will be described. We have recently reported the improved device performance on PLED devices (Al/PFO/PVK/ITO) by doping of the electrochemically crosslinked hole transport layers based on polycarbazole networks. Fermi level tuning was achieved based on the applied potential prior to device fabrication. We will report the use of polyfluorene precursors electrochemically patterned using soft-lithography and imprinting methods. The patterns show high resolution and well-defined size and height limits. In contrast, previously reported direct electrochemical methods using monomers do not show the same pattern fidelity at the micron level. Lastly, we will describe the use of electrochemical nanolithogrpahy (ECN) to pattern "features, words, and wires" at the submicron level on precursor polymer films. ECN involves applying a bias potential between the AFM tip and the substrate in an electrochemical environment. It is found that the parameters for patterning include, thickness, potential, writing speed, and the presence of humidity/electrolyte in the films. The potential for higher complexities in patterning with different precursor polymer material composition,design, and microstructure will be described.

I6.17

Synthesis and Electronic and Optical Properties of New High Electron Affinity Conjugated Polymers.

Yan Zhu[1], Cheng-Tyng Yen[1], Samson A. Jenekhe[1] and Wen-Chang Chen[2]; [1]Chemical Engineering, University of Washington, Seattle, Washington; [2]Chemical Engineering, National Taiwan University, Taipei, Taiwan.

New conjugated polymers with high electron affinity are of great interest for applications in photovoltaic devices and in n-channel thin film transistors. A series of poly(2,7-diphenylpyrazino(2,3-g) quinoxaline)s with phenylene, biphenylene, thiophene, and bithiophene linkages were synthesized and characterized, and their photophysical and electrochemical properties were investigated. These poly(pyrazinoquinoxaline)s had optical band gaps of 1.6-2.44 eV. They showed highly reversible electrochemical reduction with an electron affinity (LUMO level) of 3.6-3.9 eV. The electronic structures of the poly(pyrazinoquinoxaline)s were calculated by the density functional theory and compared with the experimental results. A large improvement in performance of poly(2-methoxy-5-(2'-ethyl-hexyloxy) -p-phenylene vinylene) based light emitting diodes (a luminance of up to 950 cd/$m^2$and an external quantum efficiency of up to 0.19 %) was observed by using poly(pyrazinoquinoxaline)s as the electron transport materials. The experimental and theoretical results demonstrated that the pyrazinoquinoxaline moiety is an excellent building block for realizing high electron affinity organic semiconductors for electronics.

I6.18

Conjugated Oligoquinolines: n-Type Organic Semiconductors for Highly Efficient Blue Electroluminescence.
Abhishek P. Kulkarni[1], Angela P. Gifford[2], Christopher J. Tonzola[2] and Samson A. Jenekhe[1,2]; [1]Chemical Engineering, University of Washington, Seattle, Washington; [2]Chemistry, University of Washington, Seattle, Washington.

Achievement of pure blue electroluminescence (EL) with high efficiency, color purity and stability remains a challenge in the path towards realization of full-color organic light-emitting diodes (OLEDs) for displays. Although blue OLED performances are gradually improving, there is a need to develop new thermally stable blue emitting materials that are also capable of facile electron injection and transport. Towards this goal, we report on a series of blue-light-emitting, thermally robust, n-type organic semiconductors based on the oligoquinolines. The new oligoquinolines emit blue light in thin films, show good thermal stability (glass transition temperature, Tg $>$ 100°C) and possess facile reversible electrochemical reductions (electron affinities $\sim$ 2.7 eV). Simple bilayer diodes of the type ITO/PEDOT/PVK/oligoquinoline/LiF/Al gave stable blue EL with maxima at 450-460 nm, CIE coordinates at (0.15, 0.12), luminances of 470-4000 cd/m2 and luminous efficiencies of 3.3-7.9 cd/A (at brightness $>$ 100 cd/m2). The observed high luminous efficiencies are one of the best blue OLED performances reported to date from non-doped, blue fluorescent organic emitters. The high Tgs render the materials very stable in the amorphous form leading to good EL spectral stability. These results demonstrate that oligoquinolines are promising as both blue emitters and electron transport materials for developing high-efficiency OLEDs with a simple architecture.

I6.19

Doping and Emission Profiles in Planar and Vertical Light-emitting Electrochemical Cell Architectures.
Janelle Leger and Sue Carter; Physics, UC Santa Cruz, Santa Cruz, California.

We study light-emitting electrochemical cells (LECs) 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 profile in reverse bias slowly as compared to devices employing an Al electrode. Devices also displayed 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 effect 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 irreversible 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 p-doping was observed at voltages below the bandgap 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 dipolar effects may be critical to understanding electron injection in LECs. We further studied the changes in the optical absorption spectra characteristic of p-doping in MEH-PPV. Noticeable color changes were observed in both device structures after testing, further supporting evidence for p-doping in these devices. For certain structures, electrochromic effects were observed at voltages below the band gap allowing the fabrication of a dual electrochromic and light-emitting device architecture.

I6.20

Advanced Characterization of the Electronic Structure of MEH-PPV. David Keith Chambers[1] and Sandra Selmic[1]; [1]Louisiana Tech University, Ruston, Louisiana; [2]Louisiana Tech Univeristy, Ruston, Louisiana.

The discovery of conducting and semi-conducting organic materials, especially polymers, portends a revolution in the manufacture of electronic devices. The possibility of cheaply manufactured materials with a wide gamut of properties has drawn increasing research 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, this promise has, to date, remained largely unfulfilled. Despite intensive research efforts, 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 fundamentals involved in device fabrication, operation 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/oral presentation, I will present novel research results that explore the basic molecular structure, orientation, and electrical properties of this popular light emissive 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). By 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 orientation on the surfaces by identifying characteristic electron energies associated with the bonds 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 indicating the role of defect states, extrinsic carrier involvement, and Fermi-level pinning at the interface are discussed.

I6.21

Blue Emitting Phosphorescent Metal Complexes and Their Electroluminescence Properties. Rupasree Ragini Das, Seok Chang, Jong Hyoup Lee, Younghun Byun, Yi Yeol Lyu, Heekyung Kim, EunSil Han and Lyong Sun Pu; Flexible OLED Team, Samsung Advanced Institute of Technology, Yongin City, Kyongi-Do, South Korea.

With the radical development in the organic light emitting devices, blue emitting phosphorescent metal complex is drawing immense attraction from the research schools based in the universities and industries. The heavy transition metals with large spin orbit coupling constants complexed with the strong field carbon coordinating ligands can furnish blue emission from the triplet metal-to-ligand-charge-transfer states. We would discuss some of such blue emitting mononuclear and polynuclear complexes and their device performances. These metal complexes exhibit phosphorescence peak emissions from 440 nm to 480 nm with CIE color coordinates in the range of (0.14, 0.12) and (0.18, 0.30), where as the EL devices utilizing these complexes show red shifts in the emission peaks.

I6.22

Induced Electronic States by Chemical Interaction at the Metal/Organic Interface. Tadanobu Ikame, Kaname Kanai and Kazuhiko Seki; Nagoya University, Nagoya, Japan.

TNAP(11,11,12,12-Tetracyanonaphtho-2,6-quinodimethane) is one of well-known strong acceptor molecule. We studied the electronic structure and morphology at the interface between TNAP and several metal substrates (Au, Ag and Cu) by UPS(ultraviolet photoemission spectroscopy) and IRRAS(infrared reflection absorption spectroscopy). The induced interface states were observed at the interface between the TNAP and Ag substrate. Both UPS and IRRAS spectra of the very thin film of TNAP deposited on the Au and Ag substrates are well explained by the simulated spectrum of TNAP and TNAP- anion, respectively. These spectra of TNAP on Ag substrate are changing to the one of TNAP with increasing the thickness of TNAP. This fact shows that the strong charge transfer interaction between the TNAP and Ag substrate generates the characteristic electronic states of interface, which is well localized at the interface. In all the case of the substrates, the work function of the substrate is increased by deposition of the TNAP, indicating the interface dipole formation, which negatively charges the surface of TNAP film. Several mechanism of the interface dipole formation at the interface between the metal substrate and organic molecule was proposed by Ishii et al.[1] These results can be interpreted by the dipole caused by the electron transfer from the substrates to TNAP. IRRAS spectra show that TNAP molecule on Au is lying, although the orientation of TNAP molecule is random on both Ag and Cu substrates. This indicates that the chemical interaction between TNAP and metal substrates has an impact on the morphology of the organic film. It will be discussed the effect of the charge transfer interaction between the molecule and metal substrate on the electronic structure and morphology of deposited organic film. [1] H. Ishii, et al., Adv. Mater. 11, 605 (1999).

I6.23

New Perfluorocyclobutane based Hole Transporting Polymers for Polymer Light-Emitting Diodes. Bogyu Lim, Doojin Vak, Jieun Ghim, Dong-Yu Kim and Jin-Taek Hwang; Dept. of Materials Science and Engineering, Gwangju Institute of Science and Technology (GIST), Gwangju, South Korea.

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(styrenesulfonate)] (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-tin-oxide (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. Hole transporting polymer requires good solvent 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. We synthesized new curable hole transporting materials containing perfluorocyclobutane units with no acidic groups. The monomers were pre-oligomerized and coated onto ITO, and then in situ thermally polymerized and cured under nitrogen. These polymers showed high transparency, high Tg, HOMO level tunability, excellent solvent 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.

I6.24

The Effect of Atmospheric Doping on the Interfacial Electronic Structure of Phthalocyanine Thin Films as Studied by UPS. Toshio Nishi[1], Kaname Kanai[1], Yukio Ouchi[1], Martin R. Willis[2] and Kazuhiko Seki[3,4]; [1]Department of Chemistry, Graduate School of Science, Nagoya University, Nagoya, Japan; [2]School of Chemistry, The University of Nottingham, Nottingham, United Kingdom; [3]Research Center for Materials Science, Nagoya University, Nagoya, Japan; [4]Institute 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 electrical conductivity 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 titanyl 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 semiconducting 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 the electronic levels on the film thickness probed by UPS was clearly different between the film deposited in UHV condition and in oxygen atmosphere. The film deposited in UHV condition showed an n-type alignment between the highest occupied molecular orbital (HOMO) and Fermi level (E_F) of the substrate, while the film deposited in oxygen atmosphere showed a p-type alignment. 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.

I6.25

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 using physical (sputtering and evaportaion), chemical (chemical vapor deposition and sol-gel method), and electrochemical (electro or electrophoretic depositon) processes. These methods are very useful to make bulk-type electrodes, but have also difficulties in control 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 electrostatice 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 are investigated as a function of deposition conditions. Their electrochemical and electrochromic properties are also discussed.

I6.26

Organic Thin Film Transistors Obtained using Atomic Layer Deposited Al_2O_3 as High-k Dielectric. Sandro Ferrari[1], Elisabetta Peron[1], Francesca Perissinotti[1], Giovanna Scarel[1], Dario Natali[2], Mario Caironi[2], Luca Fumagalli[2], Marco Sampietro[2], Alessandra Angiulli[3] and Paolo Di Gianvincenzo[3]; [1]Lab. MDM - INFM, Agrate Brianza (Mi), Italy; [2]Dipartimento di Elettronica e Informazione, Politecnico di Milano, Milan, Italy; [3]ISMAC-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 insulators helps decreasing the threshold gate voltage significantly, enabling low voltage operation of the devices. Among the high-k oxides, Al_2O_3 appears to be a good candidate, since it is low cost, non-toxic and easily processible. In this paper we report on transistors obtained using Al_2O_3 as gate dielectric deposited with Atomic Layer Deposition (ALD). The films were grown using $Al(CH_3)_3$ as Aluminum and Oxygen sources respectively. ALD allowed to obtain extremely smooth Al_2O_3 films with very good electrical properties in terms of high breakdown voltages, up to 8-10 MV/cm, and low leakage currents, in contrast to Al_2O_3 obtained by PVD or anodic oxidation. Using poly-3-hexyl-thiophene as active layer, Al_2O_3 was compared to SiO_2 as a dielectric for organic transistors. Hole carrier mobility resulted to be lower in Al_2O_3 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 was accomplished, by using regio-regular poly-alchil-tiophenes with and without substitution in the side chain to improve the affinity with the polar Al_2O_3 surface. Comparisons among the different techniques will be reported.

I6.27

Large-Area Wet Micro-Printing for Organic Device Patterning. Hongzheng Jin[1,2] and James C. Sturm[1,2]; [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 direction of droplet travel, 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 surface 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 device substrate, 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 needed in a full-color display can be printed in 3 successive steps, one step for each color. The technique has the potential advantages of low-cost and high-throughput and it avoids some of the practical problems associated with the design and operation of an ink-jet apparatus. Both single-color pixel arrays and 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-butylphenyl)-1,3,4-oxadiazole (PBD) for electron transport and the dyes nile red, 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 × 300 μm pixels were printed over an area of ∼ 2 × 2 cm. Monochrome OLED devices were tested for their electrical and electroluminescent 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-are 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, E.P. Dona, and M.E. Thompson, IEEE Trans. Elec. Dev. 44, pp. 1269-1281 (1997).

I6.28

Electronic Structure and Charge Transfer Dynamics of Alq3/Al and Alq3/LiF/Al Interfaces. Stina K. M. Jonsson[1], Michel P. de Jong[2], William R. Salaneck[2] and Mats Fahlman[1]; [1]Department of Science and Technology, Linkoping University, Norrkoping, Sweden; [2]Department of Physics and Measurement Technology, Linkoping University, Linkoping, Sweden.

An explanation for the fact that Alq3/LiF/Al structures exhibit better device performance than Alq3/Al structures is sought in the electronic structure and charge transfer dynamics 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 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 Á. 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, we present evidence that it is n-doped fac-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. This also is the first time the fac-Alq3 has been observed 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 is discussed. (1) Yokoyama, T., Yoshimura, D., Ito, E., Ishii, H., Ouchi, Y., Seki, K., 2003, Jpn. J. Appl. Phys. 1, 42, 3666. (2) Bruwiler, P.A. , Karis, O., Martensson, N., 2002, Rev. Mod. Phys. 74, 703.

I6.29

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 semiconducting materials, processable from solution via spin coating or ink jet printing techniques. The strategy we apply to achieve this goal consists of combining characteristic 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 various functionalized 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 polymers 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 constitution as well as the processing conditions. In practice, we developed a molecular building kit which allows the synthesis of various semiconducting molecules via Diels-Alder reactions followed by aromatization- and transition-metal catalyzed coupling steps. All the obtained materials were characterized with respect to their constitution, their electronic and solid state properties. The characterization showed that is possible to shift the HOMO/LUMO levels over a wide range. This allows adapting the organic semiconductors energy levels 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 motilities 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.

I6.30

Optimization of Organic Solar Cells and Photodetectors Based on Pentacene Thin Films. Seunghyup Yoo, Benoit Domercq and Bernard Kippelen; School of Electrical and Computer Engineering, Georgia Institute of Technology, Atlanta, Georgia.

Pentacene is a material widely investigated as a p-type semiconducting layer in organic field-effect transistors and it has been demonstrated that the carrier mobility in thin film of pentacene can be higher than ∼ 1 cm^2/Vsec in a direction parallel to the substrate [1]. However, its suitability for solar cells or photodetectors, in which carrier transport usually occurs in a direction perpendicular to the substrate, was unclear. Here, we report on the photovoltaic properties of multilayer devices based on pentacene thin films. Maximum power conversion efficiencies of 3.4 % have been demonstrated with our laboratory solar simulator. Further optimization of these pentacene-containing solar cells will be discussed. [1] T. W. Kelley, L. D. Boardman, T. D. Dunbar, D. V. Muyres, M. J. Pellerite, and T. P. Smith, J. Phys. Chem. B 107, 5877 (2003).

I6.31

Radiotracer Diffusion Measurements of Noble Metal Atoms in Semiconducting Organic Films. Michael Scharnberg[1], Joern Kanzow[1], Klaus Raetzke[1], Stefan Meyer[2], Jens Pflaum[2], Rainer Adelung[1] and Franz Faupel[1]; [1]Chair for Multicomponent Materials, Christian-Albrechts-University of Kiel, Kiel, Germany; [2]3. Physikalisches Institut, University of Stuttgart, Stuttgart, Germany.

The application of organic field effect transistors (OFETs) for large scale low-cost electronic devices has lead to intense research. Diindenoperylene (DIP) thin films on SiO2 are a prominent system due to their high structural out-of-plane order. While bottom contact OFET structures can be realized easily, preparation of top contacts might cause diffusion of metal atoms (typically Au) deep into the organic film changing the injection properties at the interface. These properties are of great importance for device fabrication. Therefore, only by understanding the diffusion behaviour of metals into the organic layer, formation of well defined interfaces and control of their properties will become possible. For a better understanding of the diffusion of noble metal atoms into crystalline organic films, a radiotracer technique has been used to obtain diffusion profiles for Ag and Au diffusion into crystalline DIP films. For Ag diffusion in DIP, the decrease in Ag concentration of four orders of magnitude within the first few nanometers indicates that most of the metal atoms remain near the surface while small amounts can penetrate deep into the thin film and can even accumulate at the interface between organic film and the silicon substrate. A comparison with diffusion profiles obtained for polymers indicates that the interplay between diffusion and immobilization by aggregation also determines the diffusion behaviour of metals into organic crystalline materials. Latest experiments support this interpretation of the diffusion profiles. Single atoms are highly mobile in the organic crystalline material due to the weak interaction between the metal and the organic material. Therefore, most of the single atoms that penetrate into the material do so during the intial phase of the deposition. When more and more atoms arrive at the surface cluster formation sets in. Due to the high cohesive energy of the metal the atoms can not leave the cluster and are immobilized. After deposition of a closed surface layer no further metal diffusion should be observerd. With the knowledge about the diffusion processes gained by the radiotracer measurements control of process parameters and development of barrier layers in sub-monolayer range should be possible.

I6.32

Abstract Withdrawn

I6.33

Direct Tunneling Carrier Injection in Organic Diodes with an

Ultrathin SiO_2 Layer. Koshi Okamura[1], Masakazu Nakamura[2] and Kazuhiro Kudo[2]; [1]Graduate School of Science and Technology, Chiba University, Chiba, Japan; [2]Department 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 Al_2O_3, 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, that is 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 SiO_2 layer of about 2nm, an organic layer, such as CuPc, pentacene or Alq_3, 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 can 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 tunneling carrier injection and energy relaxation accompanying the light emission will be presented in the session.

I6.34

Spin-Conserving Carrier Recombination in Conjugated Polymers. Manfred J. Walter[1], M. Reufer[1], P. G. Lagoudakis[1], U. Scherf[2], J. M. Lupton[1] and J. Feldmann[1]; [1]Photonics and Optoelectronics Group, Physics Department and CeNS, Ludwig-Maximilians-Universitaet, Munich, Germany; [2]FB Chemie, Universitaet Wuppertal, Wuppertal, Germany.

According to simple spin 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 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 argumentation as η>25% holds only if a negligible energy difference between singlet and triplet PP-states is assumed [1]. However, little is known experimentally about the crucial exchange 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 polymeric material 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 PLEDs means that the goal of exceeding the spin statistical limit of 25% is most likely only surmountable 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] M. Wohlgenannt *etal.*, *Nature* **409**, 494 (2001). [2] J. M. Lupton *etal.*, *Phys.Rev.Lett.* **89**, 167401 (2002).

I6.35

Electronic Structure Calculation and Multiscale Simulation of Acene Functionalized Polyhedral Oligomeric Silsesquioxanes (POSS) Molecular Crystals. Feng Qi[1], Murat Durandurdu[1,2] and John Kieffer[1]; [1]Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan; [2]Department 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 silsesquioxanes (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 configurations have a similar band 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 semiconducting organic molecular materials, which have broad electronic applications. This work provides an example of the design and synthesis of new materials based on building block assembly.

I6.36

Trap-Assisted Hole Injection and Quantum Efficiency Enhancement in Poly(9,9' Dioctylfluorene-Co-Benzothiadiazole) Polymer Light-Emitting Diodes. Alexander Seeley[1], Richard Friend[1,2], Jeremy Burroughes[2] and Ji-Seon Kim[1]; [1]Physics, University of Cambridge, Cambridge, United Kingdom; [2]CDT Ltd, Cambridge, United Kingdom.

We report a reversible many-fold quantum efficiency enhancement during electrical driving of polymer light-emitting diodes (LEDs) containing poly(9,9' dioctylfluorene-alt-benzothiadiazole) (F8BT), developing over several minutes or hours at low applied bias and recovering on similar timescales after driving. This phenomenon is observed only 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(styrene-sulphonate)-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.

I6.37

All-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 [3]. In this paper we report an all-polymer n-channel field effect transistor fabricated by drop-on-demand inkjet printing technique. Semiconducting organic molecule PCBM (methanofullerene [6,6]-phenyl C61-butyric acid methyl ester) [4] is used as an active channel material, conducting polymer polypyrrole (PPY) is used as source, drain and gate electrodes and PVP as insulating layer. All these polymers were inkjet printed to form the n-channel field effect transistors. Initially FETs 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 were tested in the Keithley electric probe station at room temperature and air ambience. The measured field effect mobility of PCBM is in the range of 10^{-3} cm^2/Vs to 10^{-6} cm^2/Vs. With using low work function soluble polymer materials for source/drain electrodes, this organic n-channel FET performance is expected to be further improved. References: [1] Calvert P, //Inkjet Printing for Materials and Devices; Chemical Materials//, 2001, 13, 3299-3305. [2] Paul KE, Wong WS, Ready SE, Street RA, //Additive Jet Printing of Polymer Thin-Film Transistors//, Applied Physics Letters, 2003, 83(10), 2070-2072. [3] Sirringhaus H, Kawase T, Friend RH, //High-Resolution Ink-Jet Printing of All-Polymer Transistor Circuits//, MRS Bulletin. July 2001, 539-543. [4]Christoph Waldauf, Pavel Schilinsky, Mario Perisutti, Jens Hauch and Christoph J. Barbec, //Solution-Processed Organic n-type Thin Film Transistors//, Advanced Materials 2003, 15(24), 2084-2088.

I6.38

Sub-Microsecond Molecular Thermometry using Thermal Spin Flips. J. Stehr, J. M. Lupton, M. Reufer, Manfred J. Walter, G. Raschke, T. A. Klar and J. Feldmann; Photonics and Optoelectronics Group, Physics Department and CeNS, Ludwig-Maximilians-Universitaet, Munich, Germany.

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 passed through the material is converted into heat. Consequently, there is considerable interest in techniques for thermal measurements on organic devices. We recently presented a highly sensitive molecular thermometer based on dual emission from the commonly used organic semiconductor platinum octaethyl porphyrin (PtOEP). 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 PtOEP 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 activated 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 triplet to the singlet 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 *etal.*, *Adv.Mater.*, in press.

I6.39

Degradation of Ruthenium(II) Tris-bipyridine Light Emitting Devices. Jason Slinker[1], John DeFranco[1], Jonathan Rivnay[1], Jared Delcamp[1], Samuel Flores-Torres[2], Hector Abruna[2], Len Soltzberg[4] and George Malliaras[1]; [1]Materials Science and Engineering, Cornell University, Ithaca, New York; [2]Chemistry and Chemical Biology, Cornell University, Ithaca, New York; [3]Department of Chemistry, Princeton University, Princeton, New Jersey; [4]Department of Chemistry, Simmons College, Boston, Massachusetts.

Within the class of organic semiconductors, ionic transition metal complexes (iTMCs) such as ruthenium(II) tris-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 display 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) tris-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 to date. The presence of water has previously been shown to suppress the photoluminescence quantum yield of these devices. We have quantitatively investigated the influence of moisture on ruthenium(II) tris-bipyridine device performance. By running devices under controlled humidity levels, we have observed 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.

I6.40

Efficient RGB and White OLEDs Using Platinum Dinuclear Complexes as Phosphorescent Emitters. Biwu Ma[1], Peter I. Djurovich[2], Jian Li[2], Simona Garon[2], Arnold Tamayo[2] and Mark E. Thompson[2,1]; [1]Materials Science, USC, Los Angeles, California; [2]Chemistry, 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 intersystem converts all excitons to an emissive triplet state, leading the quantum efficiency close to the theory limit of 100%. Most of these metal complexes (such as iridium 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 bisacetylacetone-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 layers structure, a multiple-doped single emissive layer structure (both structures mixing emissions from different dopants) and 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.

I6.41

Correlating Structure Development to Performance Enhancement in Organic Semiconductor Films. Dean Michael DeLongchamp[1], Sharadha Sambasivan[2], Daniel A. Fischer[2] and Eric K. Lin[1]; [1]Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland; [2]Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithesrburg, 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 powerful tool 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 chemistry, substrate-relative orientation, and defect 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 will 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 outline motifs that can be fruitfully pursued to develop next-generation materials.

I6.42

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.

Polymeric light-emitting devices(PLEDs) using aluminum as the cathode normally have poor light-emitting efficiencies due to the high work-function of aluminum, which impede 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)nOH, PEG], 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 not 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. This suggested that interfacial reaction due to the strong coordinating power of the oxygen atom of PEG with Al(3+) ions play an important role in the enhancement mechanism. Different device configurations utilizing this enhancement mechanism have been investigated and will be discussed. In particular, we found that top-emission devices could favorably take advantage of this enhancement mechanism. 1. X. Y. Deng et al, Appl. Phys. Letts. 84, 3522(2004). 2. L. S. Hung et al, Appl. Phys. Letts. 70, 152(1997).

I6.43

New Thiophene-Linked Conjugated Poly(azomethine)s: Theoretical Electronic Structure, Synthesis, and Properties. Cheng-Liang Liu[1], Fu-Chuan Tsai[1], Chao-Ching Chang[1], Wen-Chang Chen[1] and Samson A. Jenekhe[2]; [1]Department of Chemical Engineering and Institute of Polymer Science and Engineering, National Taiwan University, Taipei, Taiwan; [2]Departments of Chemical Engineering and of Chemistry, University of Washington, Seattle, Washington.

We report a joint theoretical and experimental study of several new thiophene-based poly(azomethine)s. Hybrid density functional theory (DFT) method was used to calculate the optimized geometry and electronic structure of 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 group 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 the poly(azomethine)s. Five soluble new conjugated poly(azomethine)s derived from the polymerization of 2,5-diformyl-3-hexylthiophene (DFHT) with various diamines were prepared and characterized. 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 experimental 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.

I6.44

Photogeneration and Electronic Transport Mechanisms in Thin Films of Amorphous 2,4,7-Trinitro-Nine-Fluorenone. Ilia Mikhailovich Kachirski, Physics, Peoples Friendship University, Moscow, Russian Federation.

The photogeneration process in thin films of vacuum evaporated amorphous 2,4,7-trinitro-9-fluorenone (a-TNF) is investigated by steady-state photoconductivity 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 occures according to the Onsager mwchanism. 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 Photoconductivity methods. It was suggested that the transport of charge carriers in a-TNF is controlled by traps. Some parameters of traps were determined.

I6.45

Abstract Withdrawn

I6.46

Patterning Organics with Photolithography. John Andrew DeFranco[1], Brad Schmidt[2], Ricardo Ruiz[1], Michal Lipson[2] and George Malliaras[1]; [1]Materials, Cornell University, Ithaca, New York; [2]Electrical 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.

I6.47

Abstract Withdrawn

I6.48

Processable Dioxythiophene Based Polymers with Branched Substituents. Christophe R. G. Grenier, Benjamin D. Reeves, Avni A. Argun, Merve Ertas, Aubrey L. Dyer and John R. Reynolds; University of Florida, Gainesville, Florida.

We have developed a new family of branched dialkyl and dialkoxy substituted poly(3,4-propylenedioxythiophene)s (PProDOT-R_2) 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-(CH_2O-(2-ethylhexyl)$)_2$, PProDOT-(2-ethylhexyl$)_2$, PProDOT-(CH_2O-(2-methylbutyl)$)_2$, PProDOT-(2-methylbutyl$)_2$, PProDOT-(CH_2O-2-ethylbutyl$)_2$, PProDOT-(2-ethylbutyl$)_2$, PProDOT-(hexyl$)_2$ and PProDOT-($CH_2OC_{18}H_{37}$$)_2$. The polymers obtained have high molecular weights (M_n= 20,000-50,000 g mol^{-1}) and dispersities around 1.7. All of the polymers are highly soluble in chloroform, while the ethyl branched polymers, as well as the octadecyl substituted polymer, are also highly soluble in DCM, toluene and THF. The methyl branched derivatives, as well as polymers substituted with short linear alkyl chains have moderate solubility in these solvents. Solutions of these polymers display thermochromism and solvatochromism. Spray-cast films from polymer solutions are electroactive switching from a strongly absorptive blue-purple (alkyl) or reddish-purple (alkoxy) color in the neutral state to a highly transmissive sky-blue color. The optical bandgap varies between 1.84 eV to 1.96eV, which is typical of substituted PProDOT derivatives. The branched polymers films have unusual switching behavior with complete optical changes in a narrow range of potential (<200mV), and have a well resolved fine structure of the π-π^* transition. In the case of the linear substituted monomers, these optical changes occur over a much larger potential range ($\sim$600mV) and show only poorly resolved vibronic peaks. The polymer films presents electrochromic luminance contrast between 40 and 70% and have composite coloration efficiencies over 1000 cm^2/C, with subsecond switching rates, with the exception of the octadecyl polymer, having a switching time of 2.2s and a coloration efficiency of $\sim$500 cm^2/C. Using these sprayable polymers, we were able to build fast-switching, high contrast electrochromic devices such as dual-polymer electrochromic windows and reflective devices.

I6.49

High-Mobility Polymer Thin-Film Transistors and Solvent Effects. Joonhyung 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 cm^{2}V^{-1}s^{-1}, which is much higher than any mobility reported for polymer TFT with polymer dielectric. The solvent used in forming the active 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.

I6.50

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.

Photoactive organic field-effect transistors, photOFETs based on soluble semiconductors and dielectrics with top source and drain electrodes are fabricated and characterised in the dark and under illumination. Gate insulating layers are based on polymeric dielectrics that are spin coated on ITO coated glass substrates. The semiconducting layers of the transistors are based on conjugated polymers as electron donors and materials of high electron affinity as electron acceptors in bulk heterojunction and bilayer concepts. Although materials used for the active layers of transistors are known to be highly photoactive it was observed that the device performance under light is also strongly influenced by the gate-insulating layer.

I6.51

Polymer Gate Dielectric Formulation for Organic Thin-Film Transistors. S. Young Park, Joonhyung Park, M. Joon Kim, Tae 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 in which pentacene is the active material, polyvinylphenol (PVPh) 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 PVPh are retained while the hysteresis is eliminated with the presence of PVAc.

I6.52

Direct Measurement of Surface Complex Loading and Surface Dipole, and their Effect on Simple Device Behavior. Jing Guo[1], Norbert Koch[2], Jeffrey Schwartz[1] and Steven L. Bernasek[1]; [1]Chemistry, Princeton University, Princeton, New Jersey; [2]Physics, Humboldt University Berlin, Berlin, Germany.

Tin complexes of phenoxide ligands having a range of dipole moments were prepared on the surface of ITO. Surface complex loadings and stoichiometries were measured by Quartz Crystal Microgravimetry (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 effected by surface phenoxide complex introduction correlate with these surface complex dipole moments and with total surface dipole per unit area, and current densities in simple hole-only diode devices also correlate with these total surface dipoles.

I6.53

Feedback Enhancement in Photonic Crystal Lasers with an Organic Gain Material. Rik Harbers[1,2], Nikolaj Moll[2], Rainer F. Mahrt[2], Daniel Erni[1] and Werner Baechtold[1]; [1]Swiss Federal Institute of Technology, Zurich, Switzerland; [2]IBM 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 enlarge 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 the devices to be smaller as the interaction length needed to reach the lasing threshold is decreased. The introduction of high-index material also gives rise to new design criteria, which are investigated and employed to design a photonic crystal laser with an organic gain material. Calculations of the coupling constant of the laser show that using high-index materials results in much higher mode coupling and thus smaller devices. First vertical-emitting laser devices have been fabricated according to optimized parameters and the measured spectral features agree very well with the predictions of the simulations.

SESSION I7: Thin Film Transistors
Chair: Ana Claudia Arias
Thursday Morning, March 31, 2005
Room 2001 (Moscone West)

8:30 AM I7.1

Effects of Polarized Organosilane Self-Assembled Monolayers on Organic Single-Crystal Field-Effect Transistors. Jun Takeya[1], T. Nishikawa[2,3], T. Takenobu[2], S. Kobayashi[2], T. Mitani[3] and Y. Iwasa[2]; [1]Materials Science Research Laboratory, CRIEPI, Komae, Japan; [2]Institute for Material Reasearch, Tohoku University, Sendai, Japan; [3]JAIST, Tatsunokuchi, Japan.

Significant efforts are being made to bring organic field-effect transistors (OFETs) into practical use, taking advantages of their potential of low-cost production, mechanical flexibility and optical as well as chemical sensitivities. To promote the development, some basic questions are to be further elucidated, such as the intrinsic nature of the transport of charge induced at the surface of the organic semiconductors. Following this direction, we proposed a method of laminating organic crystals on SiO$_2$ / doped Si substrates by natural electrostatic force [1]. Four-probe measurements on the single-crystal devices revealed genuine transfer characteristics of the OFETs, free from parasitic contact effects. The laminated single-crystal devices are useful to examine whether new technologies in polycrystalline thin-film OFETs are intrinsic to the semiconductor-SiO$_2$ interface or are an artifact due to grain-boundaries, because the process of single-crystal device fabrication is identical to the commonly studied bottom-electrode thin-film OFETs. Self-assembled monolayers (SAMs) of neutral organosilane molecules are often incorporated in thin-film OFETs to passivate the SiO$_2$ surface before evaporating the organic semiconductor [2]. First, we examine the effect of the neutral SAMs with the single-crystal devices where the organosilane monolayers are carefully deposited before the crystal lamination. With the use of less than 100-nm thick SiO$_2$ and rubrene crystals, the subthreshold swing is reduced down to 0.11 V/decade, which is narrower than reported SiO$_2$-based thin-film FETs. The result is due to highly homogeneous interface, where surface trap density is estimated to be one-order smaller than typical thin-film FETs. Intrinsically high performance of organic FETs is guaranteed by this experiment. Secondly, stimulated by the recent report by Kobayashi et al. that threshold gate voltage V_{th} can be controlled by polarization of the SAMs molecules [3], we also prepared the single-crystal devices incorporating heavily polarized SAMs, With the polarized SAMs, the threshold of the pentacene single-crystal devices apparently shifts as compared with the FETs with unpolarized SAMs. Noting that the present four-terminal measurements on the single crystals are free from complications such as grain boundaries and parasitic contact effects, the V_{th} shift is due to an intrinsic charge-doping effect at the interface between the well-ordered SAM molecules and the almost perfectly ordered pentacene molecules. For rubrene single-crystal devices, however, the shift in V_{th} is only around 1/5 compared to the pentacene single-crystal FETs, indicating additional nanoscopic ionic-charge redistribution near the surface of the crystals [4]. [1] J. Takeya et al., J. Appl. Phys. 94, 5800 (2003). [2] D. J. Gundlach et al., IEEE Electr. Dev. Lett. 22, 571 (2001). [3] S. Kobayashi et al., Nat. Mat. 3, 317 (2004). [4] J. Takeya et al., Appl. Phys. Lett. in press.

8:45 AM I7.2

Charge Carrier Mobility Measurements in Tetracene Single Crystals. Jens Pflaum, Jens Niemax 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 crystals of tetracene were grown from purified material by sublimation 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 platelett-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 polymeric PPX-gate insulator, we could achieve an electrical breakdown-field strength of 3MV/cm. For holes a defined TOF transient is observed along the c'-direction of the crystals, whereas the electrons obey a strongly dispersive transport behavior caused by deep-level trapping. 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 $\sim$1.0cm^2/Vs. Fitting the experimental data by a model suggested by Hoestery-Letson (1), the density of traps as well as their respective energy could be adjusted. By complementary Laue diffraction and gas-chromatography (GC) studies the structural and the chemical imperfections related to the observed traps can be distinguished. From these data we can conclude that trapping is mainly caused by chemical inhomogeneities in the molecular crystals. From FET measurements, a multiple-trapping and release transport is observed for holes moving in the (ab)-crystal surface. The maximum mobility of $\sim$0.8cm^2/Vs at RT agrees well with the one obtained by TOF. Again, GC of the chemical composition of the cyrstal surface indicates a 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 polyacenes and we will suggest possible approaches towards a reduction of electrically active traps in the bulk as well as on the surface of crystals and films. Financially supported by the OFET-DFG project (project no. Ka 427/8). (1) D.C. Hoestery, G.M. Letson, J. Phys. Chem. Solids, 24 (1963) 1609

9:00 AM I7.3

Organic Based Magnetic Thin Films by Low Temperature CVD. R. Shima Edelstein[1], J. W. Yoo[1], N. P. Raju[1], J. D. Bergeson[1], K. I. Pokhodnya[1,2], Joel S. Miller[2] and Arthur J. Epstein[1]; [1]Department of Physics and Department of Chemistry, Ohio State University, Columbus, Ohio; [2]Department of Chemistry, University of Utah, Salt Lake City, Utah.

Spintronic devices[1] 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 interfaces[2]. 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 $Co_2(CO)_8$ / TCNE system to form cobalt tetracyanoethylene [Co(TCNE)$_x$, x$\sim$2] - a paramagnetic compound. This work then has been implemented for the $V(CO)_6$ / TCNE system to form vanadium tetracyanoethylene [V(TCNE)$_x$, x$\sim$2]. Thick ($\sim$5-10 μm) CVD made films were reported[3] to be ferrimagnetic with an ordering temperature T_c of up to $\sim$400K, and room temperature conductivity $\sigma_{RT}\sim 10^{-4}$ S/cm. In this work we report how the process parameters are controlled to make thin films ($\sim$0.05-0.5 μm) of known composition (and room temperature conductivity $10^{-4} < \sigma_{RT} < 10^{-3}$ S/cm) which may be incorporated in spintronic devices. Supported in part by DARPA Grant No. N00014-02-1-0593, U.S. Army Research Office Grant No. DAAD19-01-1-0562, and DOE Grant Nos. DE-FG02-01ER45931 and DE-FG02-86ER45271. References: 1. Wolf; J. Supercond. **13**, (2000), p. 195. 2. Prigodin, et al; Adv. Mat. **14**, (2002), p. 1230. 3. Pokhodnya, et al; Adv. Mater. **12**, (2000), p. 410.

9:15 AM I7.4

A New Architecture for Nanoscale Field-Effect Transistors. Daniel Fine, Liang Wang and Ananth 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 followed by the deposition or growth of 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, to below 10 nm. The semiconductor is then deposited above the gate insulator and connects 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 deposited 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 AlxOy 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. The new device architecture that we have 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 to realize a truly molecular transistor. With channel dimensions that can be near 5 nm, it will be possible to cause some directed macromolcular 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 *I7.5

π-Stacked N-Channel Organic Semiconductors with High Electron Mobilities in Organic Thin Film Transistors. C. Daniel Frisbie, 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 structure, crystal packing, and thin film morphology- on critical device parameters such as the electron mobility, the threshold voltage for conduction, and the on-to-off current ratio. In our best devices based on pi-stacking perylene diimide derivatives, we achieve saturation electron mobilities over 1 cm^2/Vs and on-to-off current ratios above 10^7. We use a four-pronged strategy for the development of n-channel organic semiconductors, involving (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 touch on each of these components and will emphasize recent success we have had with pi-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 O_2/H_2O sensitivity.

10:15 AM I7.6

Transport in Polycrystalline Polymer TFTs. Bob Street, John Northrup and Alberto Salleo; Palo Alto Research Center, Palo Alto, California.

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 extract 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.

10:30 AM *I7.7

Recent Advances in Organic Field Effect Transistors. Domenico Cupertino, Simon Ogier, Veres Janos, Stephen Leeming and Giles Lloyd; Research, Avecia, Manchester, United Kingdom.

Today, at least on the laboratory scale, organic thin film transistors (OTFT's) have reached a level of performance suggesting that polymer electronics will become a reality[1,2]. However, there are many critical factors which need to be considered so that we may merge the realities of electronics and manufacturing with the basic physics and chemistry of new materials before true, low cost flexible and large area devices can be commercialized. E.g. Suitable substrates need to be compatible with the active materials and manufacturing production. A number of organic semiconductor materials have now emerged in the field which offer good performance in simple OFET devices. As a step towards simpler processing, we have developed a range of amorphous polymeric semiconductors with mobilities reaching $>0.01\ cm^2V^{-1}s^{-1}$. Being amorphous, they are insensitive to many of the deposition conditions and hence offer greater flexibility to vary the device structure. One of the most exciting advantages is that these materials can be made exceptionally stable and easy to work with under ambient conditions. The polymers can be coated from common organic solvents in light and air onto plastic substrates, such as PET or PEN and the organic transistors can be stored unencapsulated for months, or even years, without any significant degradation. This in turn enables simplification of fabrication processes, for example roll-to-roll printing. In test devices, the semiconductors give reliable, robust performance and are remarkably stable in operation, which is a considerable advantage for low cost production. In this talk we discuss the development of high purity polytriarylamine (PTAA) materials and formulations. Results on improvements in device stability on storage and in continuous operation, achieved through optimisation of gate dielectric materials, will be presented. Hysteresis and bias stress are also discussed as important considerations for high quality devices. The robustness of operation is illustrated in the dynamic characteristics of simple circuits, e.g. inverters. 1 J. Veres, S.D. Ogier, S.W. Leeming, D.C. Cupertino, and S. Mohialdin Khaffaf, Adv. Funct. Mat., 13, 199-204, 2003 2. J. Veres, S.D. Ogier, S.W. Leeming, D.C. Cupertino, S. Mohialdin Khaffaf, G. Lloyd, Proc. SPIE, 2003, San Diego

11:00 AM I7.8

Fabrication of Organic Electronic Devices using Inorganic-Organic Hybrid Materials as Gate Dielectrics.

Ruth Houbertz[1], Gerhard Domann[1], Angelika Schmitt[1], Michael Popall[1], Barbara Stadlober[2], Anja Haase[2] and Ursula Haas[2]; [1]Hybrid Polymers for Microsystems, Fraunhofer-ISC, Wuerzburg, Germany; [2]Joanneum Research Forschungsgesellschaft, Weiz, Austria.

Information technology is the impetus of today's life, where integrated organic electronics, optoelec-tronics, 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 tran-sistor (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 film-deposited organic semiconductors, and it is more 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 pentacene, but also by the dielectric layer due to sev-eral reasons. Beside general growth conditions (e.g. substrate temperature, deposition rate), the growth is also dependent on the substrate material, its surface roughness and chemistry, and 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 de-vice. 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 expoxy 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 materials show permittivities between 4 and 6 (125 kHz) and dielectric strengths of up to 400 V/micro-m. They can be thermally cured at low temperatures between 80 and 150 C, enabling one to use thermally sensitive materials such as PET substrates. In addition, their processing is very flexible: a large variety of application and patterning methods can be applied [1,2]. The fabrication of OFETs using pentacene deposited on various ORMOCER thin-film dielectric lay-ers will be presented. OFETs in top-contact geometry show a charge carrier mobility up to 0.25 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 influ-ence of the dieletric ORMOCER layers will be discussed

11:15 AM I7.9

Morphological Effects on Charge Transport in Conjugated Polymers.

R. Joseph Kline[1], Michael D. McGehee[1] and Michael F. Toney[2]; [1]Material Science and Engineering, Stanford University, Stanford, California; [2]Stanford 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 materials property limiting the performance of both of these devices. 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/mole to 36,000 g/mole. We find that the mobility also increases with MW in diodes, but only by a factor of 15. 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 constant MW. We have used atomic force microscopy (AFM), x-ray diffraction and grazing incidence x-ray scattering (GIXS) to measure changes in the crystallinity and crystal orientation, and have correlated this to temperature dependent mobility measurements. AFM images of low-MW films show a nanorod 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 GIXS results show that at a constant MW in both low- and high-MW films, the mobility correlates to the strength of in-plane π-stacking, agreeing with results previously reported by Sirringhaus for variations in regioregularity and casting solvent. When comparing different MWs, however, this correlation breaks down. The case where a low- and high-MW film have received the same annealing treatment shows the high-MW film to have a mobility higher by a factor of 80, despite the fact that the low-MW film has substantially stronger in-plane π-stacking. These results strongly suggest that the mobility suppression in low-MW films is 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.

11:30 AM *I7.10

Stable Semiconducting Thiophene Polymers and their Field Effect Transistor Properties.

Iain McCulloch[1], Clare Bailey[1], Mark Giles[1], Martin Heeney[1], Maxim Shkunov[1], David Sparrowe[1], Masayoshi Suzuki[2] and Robert Wagner[3]; [1]Merck Chemicals, Southampton, United Kingdom; [2]Merck Japan, Atsugi, Japan; [3]Merck KGaA, Darmstadt, Germany.

Combining high charge carrier mobility and ambient air stability is a major challenge in the design of solution processable organic semiconducting polymers. Thiophene polymers have demonstrated the highest p-type field effect mobility of any solution processed polymer to date. One drawback of this class of polymers however, is that they can possess a relatively low ionisation potential, which in the presence of oxygen, often results in spontaneous p-type doping. As a result, in some transistor device configurations, the transistor properties can change with time, leading to a lower current modulation caused by higher off currents. In this work, we explore strategies to chemically modify the thiophene backbone structure, which leads to changes in both the backbone conformation and microstructure, as well as the electronic energy levels of the molecular orbitals. A series of terthiophene polymers were synthesised, and their physical and electrical properties reported. The effects of changes in molecular structure on transistor performance and air stability are discussed.

SESSION I8: Morphology, Interfaces and Devices

Chair: John Emerson
Thursday Afternoon, March 31, 2005
Room 2001 (Moscone West)

1:30 PM *I8.1

N- and P-type Electrical Doping in Organic Thin Films.

Antoine Kahn, Princeton University, Princeton, New Jersey.

Doping has been shown to improve the performance of organic devices, in particular light emitting diodes [1]. By increasing conductivity and reducing contact resistance, the drive voltage of devices can be dramatically reduced. We examine here the n- and p-type doping of several organic materials of interest. P-doping of small molecule hole-transport materials like ZnPc and α-NPD by co-evaporation with the high electronegativity molecule F_4-TCNQ is best understood at the present time. The energetics of doping, i.e. energy levels of dopant vs. host, have been determined by ultra-violet and inverse photoemission spectroscopy (UPS, IPES) and show a small dopant ionization energy, consistent with efficient doping [2]. High film conductivity and injection enhancement by carrier tunneling through a narrow depletion region were demonstrated [2]. F_4-TCNQ was also recently used to dope the standard polymer poly(9,9-dioctylfluorenyl-2,7-diyl) (PFO). In this case, the doped films were formed by spin-casting a co-solution of polymer and dopant molecules. In spite of a less favorable energy match for doping, as seen by UPS and IPES, i.e. the polymer ionization energy is $\sim$0.55 eV higher than the dopant electronegativity, a net Fermi level movement toward the polymer highest occupied molecular orbital (HOMO) is measured, evidence of p-doping. An order of magnitude increase in current density is also obtained at high bias, indicating reduction of the effective injection barrier. N-doping 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). Dopants must have very low ionization energy and are thus inherently instable and difficult to handle. Alkali metals 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 atom leads to a fairly tightly bond cation-anion pair with 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-evaporated with NTCDA. The energetics of this organic system are investigated with UPS and evidence of n-doping is obtained both with UPS and current-voltage measurements. Finally, we report on on-going measurements of n-doping with Li stabilized with a crown ether molecule. The position of the alkali cation in the crown ether in principle reduces its diffusivity and increases its distance to the acceptor (host) molecule, allowing higher delocalization of the electron. 1. J. Blochwitz J et al. Organic Elect, 2 97 (2001); X. Zhou et al, Appl. Phys. Lett., 78 410 (2001) 2. W. Gao et al., Appl. Phys. Lett. 79, 4040 (2001); W. Gao at al, J. Appl. Phys. 94, 359 (2003)

2:00 PM I8.2

Charge Carrier Transport Studies of Organic Single Crystal Field-Effect Transistors using Nondestructive, Reversible Methods. Mang-mang (Mike) Ling, Alejandro L. Briseno and Zhenan Bao; Chemical Engineering, Stanford University, Stanford, California.

Organic semiconductor single crystals are ideal systems for charge transport studies. However, due to their fragileness it is challenging to fabricate and characterize these devices. In this talk, we report methods for organic 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-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 I8.3

Interfacial Effects in Polymeric Thin Film Transistors Studied Using Laminated Films. Michael Chabinyc[1], Alberto Salleo[1], Yiliang Wu[2], Ping Liu[2], Beng Ong[2], Martin Heeney[3] and Iain McCulloch[3]; [1]Electronic Materials Laboratory, PARC, Palo Alto, California; [2]Xerox Research Centre of Canada, Mississuaga, Ontario, Canada; [3]Merck Chemicals, Southampton, United Kingdom.

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 semiconducting polymers. Interpretation of these studies is complicated by the fact that transport occurs within $\sim$ 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 modified dielectrics. We have laminated supported films of semiconducting 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 cm^2/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 that differ by more than a factor of 100. These results directly demonstrate that the lower mobility obtained for semiconducting films spun on bare silicon dioxide is likely due 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 I8.4

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 larger compensation of carrier traps. Comparing the four-probe FET channel conductance to the one deduced from two probe conductance measurements reveals the metallic electrode-polymer interfacial contact resistance at various temperatures. We will discuss the implications of our data to the insulator-metallic transition in RR-P3HT.

2:45 PM I8.5

Mechanical and Charge Transport Properties of Self Assembled Organic Monolayers. Imma Ratera[1], Jeong Y. Park[1], Jeff Neaton[2], Gerard Smidth[1], Alexander Liddle[1], D. Frank Ogletree[1] and Miquel Salmeron[1]; [1]Materials and Surface Science, Lawrence Berkeley National Laboratory, Berkeley, California; [2]University 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, complex molecule-substrate, intermolecular interactions and 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 molecules. Traditionally electrical measurements have been conducted on molecular structures and nano-objects situated between metal electrodes with large aspects 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 provide a unique way to control the quality and structure of the molecular films between nanoelectrodes because due to the coplanarity of the electrodes ($<$ 1nm) the molecules are accessible at the nanoscale to an STM/AFM tip and thus it allows to clarify the ambiguities of the unknown contact structure that plague this field. An understanding of how electrons flow through organic molecules is important in several areas: rationalizing electron transfer in organic and biological molecules; fabricating molecular electronic devices, such as oLEDs and also for developing molecular devices.

3:15 PM I8.6

Interface and Gate Bias Dependent Response of Sensing Organic Thin-Film Transistors. Maria Cristina Tanese[1], Daniel Fine[2], Ananth Dodabalapur[2] and Luisa Torsi[1]; [1]Chemistry, Universita di Bari, Bari, Italy; [2]PRC/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 remarkable response repeatability [2]. The response is reproduced, within 2%, for 420 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 already implemented 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 OTFT compatibility to microfluidics, opens wide horizons for the use of OTFT in compact 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 organic semiconductors active layers, 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 are 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 a doping or of a trapping process of the organic active layer. The occurrence of these two effects, that can also coexist, depend on the gate-dielectric/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 sensor operated in the enhancement mode 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 in a resistor-type sensor. [1] L. Torsi, A. Dodabalapur, L. Sabbatini, P.G. Zambonin, Sensors and Actuators B., 67, 312, 2000. [2] B. Crone, A. Dodabalapur, A. Gelperin, L. Torsi, H.E. Katz, A.J. Lovinger, and Z. Bao, Appl. Phys. Lett., 78, 2229, 2001 [3] B. K. Crone, A. Dodabalapur, R. Sarpeshkar, A. Gelperin, H.E. Katz, Z. Bao, Journal of Applied Physics, 91, 10140, 2002.

3:30 PM I8.7

Investigation of Annealing Effects and Film Thickness Dependence 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 RR-P3HT:methanofullorene [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) 1:1 wt-ratio blend were studied. 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 device performance were studied for devices annealed before and after cathode deposition. Thermal annealing shows significant improvements in the performance of both types of devices, with post-production annealing being slightly better. In devices with 43 nm active layer, maximum power conversion efficiency (PCE) of 3.1% and fill factor (FF) up to 67% was observed under AM1.5, 100 mW/cm2 illumination. By keeping optimized thermal annealing condition and varying active layer thickness, devices with PCE up to 3.98% were fabricated. Atomic force microscopy (AFM), UV-Vis and Raman spectroscopy were conducted on the P3HT:PCBM films to explain the effect of thermal annealing.

3:45 PM *I8.8

Self-Organisation of Nanocrystals in Polymer Brushes: Application in Heterojunction Photovoltaic Diodes. Richard Friend[1], Henry Snaith[1], Gregory Whiting[2], Neil Greenham[1] and Wilhelm Huck[2]; [1]Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom; [2]Department of Chemistry, University of Cambridge, Cambridge, United Kingdom.

Heterostructures formed between electron and hole-accepting molecular semiconductors are generally required for active photovoltaic device structures. We have developed the growth off transparent conducting electrodes of films of polyacrylate brushes, with triarylamine side groups as hole-transporting components. Solution-processing a second component with favourable enthalpic interactions does not gives 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 2:1 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 are particularly suited for photovoltaic devices, since they provide the correct length scale for migration of photogenerated excitons 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 nanoscale-ordered composites.

4:15 PM I8.9

Micro-Structural Effects on the Optical and Charge Transport Properties in Poly (9,9-Dioctylfluorene-co-Benzothiadiazole). Carrie L. Donley[1], Jana Zaumseil[1], Jens W. Andreasen[2], Martin M. Nielsen[2], Ji-Seon Kim[1] and Richard H. Friend[1]; [1]Department of Physics, University of Cambridge, Cambridge, United Kingdom; [2]Risoe National Laboratory, Roskilde, Denmark.

Spin-coated poly (9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) films of different molecular weights (M_n = 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 crossed 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. Annealing films to sufficiently high 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 ("alternating structure"). A similar transition between these two micro-structures is also observed in pristine films as a function of molecular weight. Changes in the vibrational transitions indicate a change in the torsion angle between the F8 and BT units as a function of molecular weight and different annealing conditions, which may be correlated to the micro-structural changes described above. This restructuring is dictated by the strong localization of electron density on the BT units in F8BT, which subsequently affects the efficiencies of both interchain electron transfer and exciton migration. Films exhibiting the "alternating structure" show significantly lower electron mobilities than films exhibiting the "non-alternating structure", due to a decrease in the efficiency of interchain electron transport in this structure. In addition, interchain exciton migration to low energy weakly emissive states is also reduced for these "alternating structure" films, as observed in their luminescence spectra, resulting in higher luminescence efficiencies.

4:30 PM I8.10

Effects of Various Types of Doping on the Electronic Structure of Organic Interfaces. Kazuhiko Seki[1,2], Toshio Nishi[3], Senku Tanaka[3], Tadanobu Ikame[3], Hisao Ishii[4] and Kaname Kanai[3]; [1]Research Center for Materials Science, Nagoya University, Nagoya, Japan; [2]Institute for Advanced Research, Nagoya University, Nagoya; [3]Dept. Chemistry, Graduate School of Science, Nagoya University, Nagoya, Japan; [4]Research Institute of Electro Communication, Tohoku University, Sendai, Japan.

Recently there is much interest in the electronic structure of the organic/metal interfaces. About phenomena within a few molecular layers at the contact, the major subject is dipole layer formation, about which we now have some sound insight [1-5]. There are also phenomena extending into thicker region, such as the Fermi level (E_F) alignment, but they still remain unexploited. Here we report our recent efforts for understanding them, with special attention to electrical doping. Most organic materials in devices are used undoped. This is in contrast to inorganic semiconductors, which are almost always doped. The dopants (a) fix E_F of the matrix at some energy in the bandgap, and (b) causes band bending leading to E_F alignment by forming space charge. Thus we have questions: (1) Can we expect band bending leading to E_F alignment for "undoped" organic layer? (2) Can we expect p-doping by O_2 as the origin of the well-known conductivity enhancement by O_2? and (3) Can we find good organic dopants for controlling the electronic structure? As for (1) and (2), we discriminate between clean ultrahigh vacuum (UHV) and more conventional atmosphere. Under UHV, some well-purified compounds like TPD [6] or *p*-sexipheny[7] do not show alignment of metal E_F with E_F of organics at fixed position [8]. Some materials, e.g. C_{60} [9] or F_{16}ZnPc [10], contain residual impurities, which align the metal E_F with fixed E_F of the organic layer with band bending. In these cases, the impurity dominates the interfacial electronic structure. As for the atmospheric effect (2), we studied the interfaces of titanyl phthalocyanine (TiOPc), for which Tada et al.[11] reported the change of the FET properties from n-type in UHV to p-type after O_2 exposure. We observed corresponding change of the band bending [12], demonstrating that ambient gases do able to bend the band in the organic layer by bulk doping. We also found that O_2 pins the E_F position, which was not found for films prepared under UHV. As for (3), various p-type organic dopants (e.g. F_4TCNQ) [3,13] and metal n-dopants were reported, but n-type organic dopants are still to be explored. We found that tetrathianaphthacene (TTN) is a reasonably good n-dopant when doped in F_{16}ZnPc [10]. [1] H. Ishii et al., Adv. Mater. 11 (1999) 605. [2] W.R. Salaneck et al. (Eds), Conjugated Polymers and Molecular Interfaces, Marcel Dekker, New York, 2002; [3] W. Gao & A. Kahn, J. Phys., C15 (2003) S2757. [4] M. Fahlman & W. R. Salaneck, Surf. Sci., 500 (2002) 904. [5] H. Vazquez et al., Appl. Surf. Sci., 234, 107 (2004). [6] N. Hayashi et al., Synth. Metals 121 (2001) 1717.. [7] H. Oji et al., unpublished. [8] H. Ishii et al., Phys. Stat. Solidi (a) 201 (2004) 1075. [9] N. Hayashi et al., J. Appl. Phys.92 (2002) 3784. [10] S. Tanaka et al., Synth. Metals, submitted. [11] H. Tada et al., J. Appl. Phys. 76m 873 (2000). [12] T. Nishi et al., Synth. Metals, submitted. [13] J. Blochwitz et al., Org. Electronics 2 (2001) 97.

4:45 PM I8.11

Surface Structure of Conjugated Polymer Thin Films: The Measurement of Surface Dichroic Ratios by NEXAFS and their Correlation with Field-Effect Conduction Properties.

Peter Ho[1], Lay-Lay Chua[1,2], Xingyu Gao[1,3], Dongchen Qi[1,3], Swee-Ching Tan[1,3], Andrew Wee[1,3], Jui-Fen Chang[2] and Richard Friend[2]; [1]Dept of Physics, National University of Singapore, Singapore, Singapore; [2]Cavendish Laboratory, University of Cambridge, Cambridge, United Kingdom; [3]Singapore Synchrotron Light Source, Singapore, Singapore.

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 over the field-effect mobility of charge carriers which reside in a thin (2 nm thick) field-effect conduction channel there in top and bottom-gated organic FETs respectively. However very little is known about the structure of these frontiers layers although consideration of the dis-equilibrium that pervades throughout solvent drying, as well as the presence of the energy-mismatched interfaces, suggests that these structures must vary considerably from the bulk. Previous studies however have largely relied on the use of X-ray scattering for the bulk structure and assumed that these results carry over to the surface layers. Here we report new insights obtained by direct measurement of the surface dichroic ratios of the top surface and bottom surfaces (exposed by delamination) of regioregular poly(3-hexylthiophene) thin films using near-edge X-ray absorption fine structure (NEXAFS) spectroscopy exciting the C1s core level. The NEXAFS experiments were conducted at the Singapore Synchrotron Light Source (SSLS). C1s NEXAFS has the appropriate surface sensitivity (2 to 3 nm) and allows direct probing of the pi-star and sigma-star transition dipole directions that yield 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 interfaces, 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 structures evaluated by photoluminescence and absorption spectroscopies. Solvent treatment and careful annealing therefore provide ways to optimize the field-effect properties.

SESSION I9: Poster Session: Organic Based Materials and Devices

Chairs: Ana Claudia Arias, Lukas Burgi, John Emerson
and Nir Tessler
Thursday Evening, March 31, 2005
8:00 PM
Salons 8-15 (Marriott)

I9.1

Polymer FET with Enhanced Performance by Inkjet Printing Modified PEDOT-PSS as S/D Electrodes. Fengliang Xue, Zhengchun Liu, Yi Su and Kody Varahramyan; Institute for Micromanufacturing, Louisiana Tech University, Ruston, Louisiana.

Inkjet printing enables a low-cost and simple process for the fabrication of polymer electronic devices. Metal nanoparticles and salts, and conducting polymers can be used for contact electrodes using inkjet printing technique. Inkjet printed metals has high conductance but requires relatively high temperature (270 °C) for decomposition, while inkjet printed conducting polymers has low conductance at low temperature printing process (80 °C) . Conducting polymer PEDOT-PSS is the most intensively used material for contact electrode by means of inkjet printing. However, spin coated conducting polymer PEDOT-PSS gives a conductivity of around 0.1 S/cm in our experiment. Addition of polar solvents into commercial PEDOT-PSS solution is able to enhance conductivity of conducting polymers[1,2]. The residual polar solvent in the dried PEDOT-PSS thin film is thought to be the cause of the enhanced conductivity [1]. It is unknow whether the enhanced conductivity has long term stability. In our experiments, we modified the commercial PEDOT-PSS with polar solvent DMSO. The conductivity of spin cast PEDOT-PSS was measured by Hall Effect measurement system. The unmodified PEDOT-PSS was studied for comparison. The conductivity of unmodified and modified PEDOT-PSS was measured to be 0.07 S/cm and 30 S/cm, respectively. The conductivity of unmodified and modified PEDOT-PSS degraded to be 0.033 S/cm and 20.8 S/cm in 75 days, respectively. The change of conductivity for both materials becomes saturated after 75 days. The modified PEDOT-PSS has been used in a polymer FETs by inkjet printing. P3HT was used as a FET channel material, which can be dissolved in THF, Chloroform, Chlorobenzene, P-xylene and Toluene. Chloroform is most commonly used and gives highest mobility of resulted transistors. But the solution is not suitable for inkjet printing due to printer nozzle cloging. We use P3HT in Toluene as an ink for inkjet printing. The solution was printed on the 25 μm long channels defined by inkjet printed PEDOT-PSS source/drain electrodes. n$^+$-Si was used as the substrate and gate electrode and 100 nm thick SiO2 as gate dielectric. All devices were prepared and characterized in the air ambient at room temperature. The polymer FETs work in accumulation mode and have good I-V characteristics. Without considering the series resistances, the saturation mobility is calculated to be 0.01 cm^2/Vsec and the on-off ratio at saturation region is $2.87\cdot10^3$. Polymer FETs with unmodified PEDOT-PSS as S/D electrodes were also fabricated for comparison. The experimental results show that the saturation mobility is $2\cdot10^{-4}$ cm^2/Vsec and the on/off current ratio is 46. Both devices had negligible degradation in a week. In conclusion, modified PEDOT-PSS has been used for inkjet printed electrodes for improving polymer FETs performance. References [1] J.Y. Kim, et al. Synth. Met. 126 (2002) 311 [2] S.K.M. JÖnsson, et al. Synth. Met. 139 (2003) 1.

I9.2

Dielectric Constant and Breakdown Field Studies of Electrostatic Self-Assembled (ESA) Materials. Ramazan Asmatulu, Brian Geist, William B. Spillman and Richard O. Claus; FEORC, Virginia Tech, Blacksburg, Virginia.

Nanostructured polymeric films were fabricated on gold-coated glass slides using the electrostatic self assembly (ESA) method. The thicknesses of the films were in the range of 120 nm to 630 nm and obtained by depositing different of numbers bilayers of negatively charged Poly s-119 (PS-119) or heparin and positively charged poly(diallyldimethylammonium chloride) (PDDA). Measurement electrodes were fabricated on the ESA films using silver grease and a brass bar. Capacitance measurements were conducted to determine the dielectric constant of the ESA films over various temperature and frequency ranges at 1 mV and 15% relative humidity, while electric field breakdown tests were performed at 1000 Hz, 15 % relative humidity and varying temperatures and voltages. The test results showed that dielectric constant values were between 1.8 and 2.4 and breakdown field values were approximately 9 kV/mm. Based on 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 nanostructured ESA films.

I9.3

Dual-Gate SiO$_2$/P3HT/SiN$_x$ OTFT. Flora Li, Sarswati Koul, Yuri Vygranenko, Peyman Servati and Arokia Nathan; University of Waterloo, Waterloo, Ontario, Canada.

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 a low-temperature amorphous silicon nitride (SiN$_x$) as the gate dielectric. This design provides a means of characterizing the density of states of the bottom P3HT/SiO$_2$ and top P3HT/SiN$_x$ interfaces, to evaluate the interface integrity and provide insight into the underlying transport mechanisms. 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.

I9.4

Fabrication of RR-P3HT-based TFTs using Low-temperature PECVD Silicon Nitride. Sarswati Koul, Yuriy Vygranenko, Andrei Sazonov, Flora Li and Arokia Nathan; Electrical and Computer Eng., Waterloo University, Waterloo, Ontario, Canada.

Regioregular poly(3-hexylthiophene) (RR-P3HT) is a commercially available semiconducting (conjugated) polymer with a field effect mobility ranging between 0.01-0.1 cm^2/V-s, depending on processing technique and device structure. RR-PRHT films can be deposited by chemical-vapor deposition or other coating techniques, based on which a variety of TFT structures in staggered and inverted staggered configurations have been demonstrated. The most commonly used gate dielectric materials for organic TFTs are SiO$_2$, Al$_2$O$_3$ and Ta$_2$O$_5$. In this work, we report for the first time a fully encapsulated RR-P3HT-based TFT structure with a SiN$_x$ as a gate dielectric and passivation material. The fabrication process reported here enables a realization of discrete transistors or transistor circuits on glass, Si/SiO$_2$ wafers, or any appropriate plastic substrates, using consecutive photolithographic steps. We will present the critical technological issues such as a substrate surface treatment (which should be carried out for good interface stability), polymer spin coating, and preparation of device quality a-SiN$_x$ films by 75^{o}C PECVD.

I9.5

The Effect of Gate Dielectric Surface Energy on Pentacene Morphology and OFET Characteristics. Sang Yoon Yang, Kwonwoo Shin and Chan Eon Park; Polymer Research Institute, Chemical Engineering, Pohang University of Science and Technology, Pohang, Gyungbuk, 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(imide-siloxane)s 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 grain size (~300 nm) and decreased ordering of pentacene molecules vertical to the gate dielectric with low surface energy, the mobility of low surface energy gate dielectric FETs is larger by a factor of about 5 compared to their high surface energy counter parts. In pentacene growth on the low surface energy gate 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 FET 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 transport of charge carriers and cause lower carrier mobility in spite of the formation of large grains (~1.3 μm).

I9.6

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 material and process, inorganic and organic insulators 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 have investigated different electrolytes: Hydrogen peroxide 30% H2O2 (Al and Ta), Aq. sol. with 0.01% citric acid (Ta), Ethylene glycol sol. with NH4B5O8 (Al) From Kiessig interferences (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 breakthrough 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 Ta2O5 mobilities in the range of 10-̂2cm2̂/Vs and threshold voltages -4.8V could be achieved. VDS was at -5V.

I9.7

Analysis of Current-Voltage Characteristics of Dual-gate Organic Thin Film Transistors. R. Coehoorn, G. H. Gelinck and E. van Veenendaal; Philips Research Laboratories, Eindhoven, Netherlands.

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 single bottom gate (BG) organic transistor. The electrically active layer, made of 50 nm thick pentacene, and the insulator layers are all solution processed. The electrodes are made of gold. DG-OTFT technology is of great interest for applications, because these devices have a larger on-current and a steeper sub-threshold slope than conventional OTFTs, and the application of TG voltage makes it possible to actively control the threshold voltage. In this paper we analyze the linear transfer characteristics of DG-OTFTs in the BG and TG mode (the current as a function of the BG (TG) voltage, for fixed TG (BG) voltages). We show that the transfer characteristics can be adequately described in terms of a semi-empirical model. In this model, the current in the accumulation region is described using the Vissenberg-Matters (VM) model for the field-effect mobility [2]. The subthreshold conduction is described by a phenomenological expression, and the conductance in the off-state is taken to be ohmic. The main effect of a TG voltage, in the BG mode, is to change the threshold voltage and to open a second accumulation channel at the top interface. The mobility in this channel is a factor of 104 smaller than in the bottom channel. We attribute this to the relatively high roughness of the interface between pentacene and the top insulator. To analyze these results in more detail, we developed a second model which extends the microscopic VM model [2] to the case of a dual gate transistor. First, the hole and electron carrier densities across the polymer layer are calculated, and subsequently the conductance is calculated by taking the integral of the conductivity across the layer. In contrast to the VM model, we consider systems with a finite organic layer thickness, with a possible gradient of energetic disorder across that thickness, and with a finite band gap (thereby including screening by the low-mobility electrons). We show that the layer thickness is still much larger than the widths of the accumulation channels (apart from the situation close to threshold), give an assessment of the effect of various types of gradients of the disorder, and reveal the effect on the threshold voltage due to screening of a positive second gate voltage by electrons. In conclusion, the second gate voltage in DG-OTFTs provides an important novel degree of freedom, that makes it possible to investigate the physics of the transport process in much more depth than in the case of a conventional single gate transistor. [1] G.H. Gelinck, E. van Veenendaal, R. Coehoorn, in preparation. [2] M.C.J.M. Vissenberg and M. Matters, Phys. Rev. B57, 12964 (1998).

I9.8

High Performance and High Stability of Lead Phthalocyanine Thin-Film Transistors in Ambient Air. Hiroaki Tachibana[1], Hiromi Iwazumi[1] and Yoshinori Tokura[1,2]; [1]Correlated Electron Research Center (CERC), AIST, Tsukuba, Japan; [2]University of Tokyo, Tokyo, Japan.

Metal phthalocyanines (Pc's) 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 Pc 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 cm^{2}V^{-1}s^{-1} and on/off current rations greater than 10^5. Among many Pc families, lead phthalocyanine (PbPc) with a shuttlecock-shaped molecule structure exhibits unique properties such as one-dimensional conduction nature, electrical switching, and high sensitivity to gas. These properties depend on the film structures, because two phases, monoclinic phase and triclinic phase, exist in the crystal structures. In the monoclinic crystal phase, lead atoms form a one-dimensional 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 SiO$_2$/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 TFT were measured using a HP 4155A semiconductor parameter analyzer in ambient air. The mobility of the PbPc TFT strongly depends on the substrate temperature for deposition. When deposited onto octadecyltriethoxysilane-treated substrate at room temperature or lower, the mobility of the PbPc TFT is less than 10^{-5} cm^{2}V^{-1}s^{-1}. However, the mobility increases with increasing the substrate temperature. At temperature around 140 °C, the mobility becomes larger than 10^{-3} cm^{2}V^{-1}s^{-1}. In addition, the mobility of the PbPc TFT strongly depends on kinds of self-assembled monolayer (SAM) on the surface of SiO$_2$ layer. Alkylsilane layers with different alkyl chain length on SiO$_2$ were prepared. We investigated the effect of alkyl chain length of SAM on the PbPc TFT performance. The mobility increases with increasing the alkyl chain length. The PbPc TFTs fabricated on triacontyltrichlorosilane-treated substrate have field-effect mobility larger than 0.1 cm^{2}V^{-1}s^{-1} and current on/off ratio greater than 10^5. Furthermore, the mobility of the PbPc TFT shows high stability in air, where it does not almost change after exposure to air more than three months.

I9.9

Flexible Pentacene/PMMA Thin-Film Transistors Fabricated on Aluminium Foil Substrates. Joaquim Puigdollers, Cristobal Voz, Isidro Martin, Albert Orpella, Michael Vetter and Ramon Alcubilla; Enginyeria Electronica, Universitat Politecnica Catalunya, Barcelona, Spain.

Pentacene thin-film transistors (TFT) were fabricated on aluminium foils using the polymer polymethyl methacrylate (PMMA) as a gate dielectric. Then, the aluminium substrate acts as a gate electrode itself. A bottom gate, inverted structure, was 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 Ás-1 and substrate temperatures below 100 °C. The maximum process temperature was 170 °C, corresponding to the baking of polymethyl methacrylate. 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 600 mm, respectively. Devices show p-type characteristics with on/off ratios over 10^3 for VGS ranging from -30 to + 30V. The field-effect mobility and threshold voltage were around 0.01 $cm^2V^{-1}s^{-1}$ and -15 V, respectively. It is important to point out that these devices are 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 ($-CH_3$) 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 inexpensive substrates (plastic, aluminum foil...), (b) the methyl ending groups improve the pentacene ordering like a SAM does. In this paper, the influence of 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. Orpella, R. Quidant, I. Martin, M. Vetter, R. Alcubilla, Organic Electronics 5(1-3), 67 (2004).

I9.10

Evaluation of the Self-Assembly and Transistor Performance of a Soluble Oligothiophene Series. Amanda R. Murphy[1], Jean M. J. Frechet[1], Paul C. Chang[2], Vivek Subramanian[2] and Dean M. DeLongchamp[3]; [1]Chemistry, UC Berkeley, Berkeley, California; [2]Electrical Engineering and Computer Science, UC Berkeley, Berkeley, California; [3]Polymer Division, National Institute of Standards & Technology, Gaithersburg, Maryland.

A series of symmetrical α,ω-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 processed 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 spun-cast films. The larger oligomers were found to self-assemble into crystalline terraces after thermolysis, resulting in high charge mobilities as measured in top-contact thin film transistors.

I9.11

Room Temperature Deposition of TiO2 Thin Films on PET(poly-ethyleneterephthalate) by using UV-enhanced Atomic Layer Deposition. Moon C. Kang, Byoung H. Lee and Myung Mo Sung; Chemistry, Kookmin University, Seoul, South Korea.

We have deposited titanium dioxide thin films on PET(poly-ethyleneterephthalate) 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 precusor gases onto the substrate surface and subsequent chemisorption 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.

I9.12

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.

High performance organic active matrix pixel is fabricated by using a metal oxide (V2O5) 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 $\sim$ 0.1 to 0.5 square centimeters per volt second and ON/OFF current ratios >1000. 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.

I9.13

Optical Interference as a Tool to Describe the Spectral Changes Created by a Tunable and Controllable Excitons Confinement. Fery Christophe[1], Drazic Valter[1], Geffroy Bernard[2], Denis Christine[2] and Maisse Pascal[2]; [1]Thomson R&D, Cesson-Sevigne, France; [2]Laboratoire 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 level of excitons confinement, can be controlled and tuned thanks to the presence of a thin hole-blocking layer (BCP) 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 Alq3 thickness was varied from 60nm up to 180nm. 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 BCP 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.

I9.14

Highly Transparent and Conductive CdO Thin Films as Anodes for Organic Light-Emitting Diodes. Film Microstructure Morphology and Effects on Performance. Yu Yang, Qinglan Huang, Andrew W. Metz, Shu Jin and Tobin J. Marks; Chemistry, Northwestern University, Evanston, Illinois.

Highly conductive and transparent CdO thin films have been grown on glass and on single-crystal MgO(100) by MOCVD 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.

I9.15

Efficient and Stable Organic Light-Emitting Diodes using Carbon Nanotube-Surfactant Layer at Metal-Organic Interface. Sumit Chaudhary[1], Krishna Veer Singh[2] and Mihrimah Ozkan[1,2]; [1]Electrical Engineering, UC Riverside, Riverside, California; [2]Chemical and Environmenal 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 aluminum cathode-emissive polymer interface. This layer was spin-coated from aqueous solvent. 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 ampiphilic nature of the film.

I9.16

Single-Walled Carbon Nanotube Composites as Hole Injection Layer for Organic Light Emitting Diode Applications. Ching Ching Oey[1], Aleksandra B. Djurisic[2], Chung Yin Kwong[1], Chi Hang Cheung[2], Wai Kin Chan[3] and Po Ching Chui[1]; [1]Dept. of Electrical and Electronic Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong; [2]Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong; [3]Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong.

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 some other attractive properties over inorganic ones. 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 poly(3,4-ethylene dioxythiophene):polystyrene sulfonic acid (PEDOT:PSS) were investigated as hole injection layers in OLEDs consisting of N,N'-di(naphthalene-1-yl)-N,N'-diphenylbenzidine (NPB) as a hole transporting and tris-(8-hydroxyquinoline) aluminum (Alq_3) as electron transporting and emitting layer. The devices were characterized by electroluminescence and current-voltage measurements. By comparing the performance of devices fabricated using different surfactants (polyethyleneimine (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 OLEDs performance. Improved efficiency was obtained for optimized SWCNTs concentration compared to the devices with pure PEDOT:PSS, although maximum luminance is lower. The PEDOT:PSS:SWCNT nanocomposite layers are characterized and the reasons for the improved OLED performance are discussed.

I9.17

Syntheses of White-Light-Emitting PAI-Conjugated Polymers and their Application to OLEDs. Junji Kido, Masataka Iwasaki, Takayuki Ito and Hsing-Lin Lan; Polymer Science and Engineering, Yamagata University, Yonezawa, Yamagata, Japan.

Copolymers consisting of blue-emitting 9,9-dioctylfluorene units (PF) and orange-emitting units, {2,6-bis(2-phenyl-vinyl) -pyran-4-ylidene}malonitrile (BPPM), were prepared using the Suzuki coupling method. The BPPM contents of the copolymers were varied from 0.2 to 1.0 percent. All the copolymers exhibited blue photoluminescence in the solutions and in the films. However, OLEDs with a structure of ITO/PEDOT/Copolymer/Ca/Al showed white emission with CIE coordinates of, for example, x=0.33, y=0.31 for the polymer with 0.2 percent BPPM. The emission mechanisms are assumed to include the carrier trapping and recombination at the BPPM sites results in the addition of a broad band in orange region of the visible spectrum.

I9.18

Spectroscopic Ellipsometry of the Optical Functions of Some Widely Used Organic Light Emitting Diodes (OLEDs) Materials. Zhengtong Liu[1], Ching Ching Oey[2], Aleksandra B. Djurisic[1], Chung Yin Kwong[2], Chi Hang Cheung[1], Wai Kin Chan[3] and Po Ching Chui[2]; [1]Department of Physics, The University of Hong Kong, Pokfulam Road, Hong Kong; [2]Dept. of Electrical and Electronic Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong; [3]Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong.

Organic light emitting diodes (OLEDs) have attracted a great deal of attention in both academic and commercial fields because of their potential applications for the next generation flat panel color displays. In order to further understand the device physics as well as efficiently model and design OLEDs, it is essential to know the optical functions of each layer of the devices. In this work, optical functions of some widely used OLEDs materials (N,N'-di(naphthalene-1-yl)-N,N'-diphenylbenzidine (NPB), tris (8-hydroxyquinoline) aluminum (Alq_3), 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), poly(3,4,-ethylene dioxythiophene):polystyrene sulfonic acid (PEDOT:PSS), and indium tin oxide (ITO)) were studied using spectroscopic ellipsometry (SE) in the spectral range from 1.55 eV to 4.1 eV (wavelength range of 300nm to 800nm). The samples were prepared either by thermal evaporation in high vacuum or spin-coating of thin films onto glass and silicon substrates. For determination of the optical functions of ITO, commercial ITO glass was used. Measurements at different incident angles were performed to determine whether the samples can be considered isotropic. The absorption spectra were also measured. The optical functions were modeled by point-to-point fit, as well as the conventional oscillator model and modified oscillator model. The results obtained by the different models are compared and discussed.

I9.19

Synthesis of Fluorene-Containing Arylamine and its Application to OLEDs. Junji Kido, Jiro Asaka, Takashi Yamamoto, Kinh Luan Thanh Dao, Takayuki Ito and Hsing-Lin Lan; Polymer Science and Engineering, Yamagata University, Yonezawa, Yamagata, Japan.

A fluorene-containing arylamine (DFPA) was synthesized, which can be spin-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, TBPAH, 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 3.2 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.

I9.20

Tuning the Emission Wavelength of Heteroleptic Iridium Complexes by Varying the pKa of the Ancillary Ligands. Tae-Hyuk Kwon[1], Myoung Ki Kim[1], Su Jin Park[2], Dong Hyun Jung[2], Seok Jong Lee[2] and Jong-In Hong[1]; [1]School of Chemistry, Seoul National University, Seoul, South Korea; [2]Coperate 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. Herein, 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 isoquinolinecarboxylic acid, pyrazolecarboxylic acid, and oxazolecarboxylic acid. Emission wavelength of the iridium complexes seems to well correlate with the pKa value of the ancillary ligands, which was further supported by extensive DFT calculations.

I9.21

Photoelectron Spectroscopy of Organic Polymer/Metal Interfaces For OLEDs. Korhan Demirkan, Anoop Mathew, 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′-ethylhexoxy)-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 for designing higher efficiency organic electronic devices.

I9.22

Modified HOST Materials having Higher Energy Band Gap in Organic Light Emitting Diodes (OLEDs): Synthesis of CBP Derivatives through the Buchwald Reaction. Tae-Hyuk Kwon[1], Hyo Soon Cho[1], Su-Youn Choi[1], Myoung Ki Kim[1], Kwan Hee Lee[2], Su Jin Park[2] and Jong-In Hong[1]; [1]School of Chemistry, Seoul National University, Seoul, South Korea; [2]Corporate R&D Center, Samsung SDI, Seoul, South Korea.

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 method. Phosphorescent spectra at 77 K shows that the designed host materials show the higher triplet energy band gap compared to CBP host. Herein, we report the synthesis of host materials, UV, fluorescence, solution PL (298 K and 77 K), film PL data of the phosphorescent dopant-host mixture and EL data.

I9.23

Inorganic Nanowire Light-Emitting Diodes in Organic Films.

Rolf Koenenkamp, Robert Word and Christoph Schlegel; Physics, Portland State University, Portland, Oregon.

We report room-temperature, white-color electroluminescence in ZnO nanowires embedded solidly in organic thin films. Excitonic luminescence around 380 nm is observed as a shoulder on a broader, defect-related band covering all of the visible range and centered at 620 nm. The ZnO nanowires are grown in a low-temperature process employing a technique that is suitable for large-area applications. The nanowires are robustly encapsulated in organic films deposited from high-molecular-weight solutions. Electron injection occurs through a transparent SnO2 layer, while hole injection is mediated by a p-doped polymer and an evaporated Au-contact. Stable device operation is observed at ambient conditions without further encapsulation on the time scales of 1 hour.

I9.24

Effects of Tertiary-Butyl Transport and Luminescence Properties of Anthracence-Based Blue Host Materials for OLEDs.

S. K. So[1], S. C. Tse[1], M. Y. Yeung[2], C. F. Lo[2], S. W. Wen[3] and C. H. Chen[3]; [1]Department of Physics and Centre for Advanced Luminescence Materials, Hong Kong Baptist University, Hong Kong, Hong Kong; [2]Department of Physics, The Chinese University of Hong Kong, Hong Kong, Hong Kong; [3]Department of Applied Chemistry and Microelectronics & Information Systems Research Center, National Chiao Tung University, Hsinchu, Taiwan.

The charge conduction and luminescence properties of a series of tertiary-butyl (t-Bu) substituted anthracene derivatives (ADN), critical blue host materials for organic light-emitting diodes, have been investigated experimentally and computationally. All ADN compounds exhibit ambipolar characters. The hole and electron mobilities, as deduced from time-of-flight measurements, and have values in the range 2-5x10^{-7} cm^{2}V^{-1}s^{-1} under an external applied field of about 1 MV cm^{-1}. Un-substituted ADN has the highest carrier mobilities while heavily substituted ADN has the least. The fluorescent lifetimes of the ADN compounds were also measured. The un-substituted ADN has the shortest lifetime while the heavily substituted is the longest. The transport and luminescence properties of are consistent with *abinitio* calculation, which indicates that the frontier orbitals are localized mainly on the anthracence moiety. We also attempt to correlate the relative magnitudes of μ_e and μ_h with the reorganization energies of the molecules. The results demonstrate that t-Bu substitution is an effective means of engineering the conductivity of organic charge transporter for OLED applications.

I9.25

Abstract Withdrawn

I9.26

High Efficiency Homojunction OLEDs using Aromatic Ring-Oxadiazole-Triphenylamine Based Compounds.

K. L. Tong[1], S. K. So[1], Tik H. Lee[2], L. M. Leung[2], M. Y. Yeung[3] and C. F. Lo[3]; [1]Department of Physics and Centre for Advanced Luminescence Materials, Hong Kong Baptist University, Hong Kong, Hong Kong; [2]Department of Chemistry, Hong Kong Baptist University, Hong Kong, Hong Kong; [3]Department of Physics, The Chinese University of Hong Kong, Hong Kong, Hong Kong.

The charge transporting and electroluminescence (EL) properties of a series of aromatic ring-oxadiazole-triphenylamine (ROT) based compounds with different aromatic ring substitutes (e.g. phenyl, naphthalene, anthracene, and pyrene) were studied. From time-of-flight (TOF) technique, the ROT compounds were found to be ambipolar with comparative hole and electron mobilities of about 10^{-6} cm^2/Vs at room temperature under the electric field of 0.5MV/cm. The frontier orbitals were examined computationally by an initio method. It was found that the highest occupied molecular orbital (HOMO) is localized on the phenylamine 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 constructed 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 spectra of the ROT devices vary from 440-520nm. The maximum luminance reaches 7500cd/m^2, and the current efficiency ~2.5cd/A. ROT materials can be used to fabricate efficient homojunction OLEDs with a very simple architecture.

I9.27

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

Kinh Luan Thanh Dao, Hsing-Lin Lan and Junji Kido; Polymer Science and Engineering, Yamagata University, Yonezawa, Yamagata, Japan.

Organic LEDs having triphenylamine tetramer (TPT) doped with hexacyano-quinodimethane (CN2-TCNQ) as a hole injection layer were fabricated by vacuum deposition. The OLED structure was ITO/ TPT doped with CN2-TCNQ/NPD/Alq/LiF/Al. The drive voltages are lowere 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.

I9.28

Transverse Electrical Transport in Pentacene Photodiodes.

Cristobal Voz[1], Joaquim Puigdollers[1], Isidro Martin[1], Albert Orpella[1], Michael Vetter[1], Francisco Fabregat[2], Germa Garcia[2], Juan Bisquert[2] and Ramon Alcubilla[1]; [1]Enginyeria Electronica, Universitat Politecnica de Catalunya, Barcelona, Spain; [2]Ciencies Experimentals, Universitat Jaume I, Castello, Spain.

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 coplanar to the substrate have been intensively studied. However, although pentacene has evidenced significant photosensitivity, 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 distinguised. 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, 640 and 100 nm in that order. Dark current-voltage characteristics evidence forward/reverse ratios over 10^3 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 around 1.3×10^{15} cm^{-3}. On the other hand, external quantum efficiency curves show a broad response band related to direct photogeneration of free carriers, but also clear antibatic features which evidence transverse exciton 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. [1] M. Shtein, J. Mapel, J.B. Benziger, S.R. Forrest, Appl. Phys. Lett. 81, 268 (2002). [2] J. Lee, S.S. Kim, K. Kim, J.H. Kim, S. Im, Appl. Phys. Lett. 84(10), 1701 (2004).

I9.29

Photovoltaic Cells Based on Multilayers of Ionic Poly(p-phenylene ethynylene)s and a Water-Soluble Fullerene Derivative.

Jeremiah Mwaura, Mauricio Pinto, Nisha Ananthakrishnan, David Witker, Kirk S. Schanze and John R. Reynolds; Chemistry, Center for Macromolecular Science and

Engineering, University of Florida, Gainesville, Florida.

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 cationic fullerene (C_{60}) derivative as acceptor. LBL film deposition was found to be linearly related to the number of bilayers 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 photon to current conversion efficiency (IPCE) 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/cm^2.The power conversion efficiencies measured at AM1.5 solar conditions (100 mW/cm^2) were as high as 0.04% for the best performing cells and similar to the IPCE results, the efficiency is a function of the thickness of the PV active layer.

I9.30

Electrical Properties of ITO/CdSe/P3OT/Au Heterojunction. Oscar Hilario Salinas[1], Cecilia Lopez-Mata[1], Hailin Hu[1], Ma. Elena Nicho-Diaz[2] and Oscar Gomez-Daza[1]; [1]Solar Materials, CIE-UNAM, Temixco, Morelos, Mexico; [2]CIICAp - UAEM, Cuernavaca, Morelos, Mexico.

Conducting polymer based heterojuntions 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 poly3octylthiophene (P3OT) by casting a chemically synthesized P3OT solution onto screen printed CdSe coatings. P3OT was obtained by oxidative polymerization of 3octylthiophene with FeCl3 as a catalyst/oxidant. The obtained polymer product was in intrinsic or undpoed 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 P3OT were deposited on top of the CdSe coatings. Since the screen printed coatings are quite porous, the solution of P3OT 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-P3OT 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 P3OT, 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 P3OT also reduces notably the forward current of the junction. The rectifying behavior should be related with the heterojunction because both ITO/P3OT and Au/P3OT form ohmic contacts.

I9.31

Photovoltaic Devices Based on a Donor/Sensitizer/Acceptor Architecture Utilizing Phthalocyanine Dye 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 nanoscale controlled placement of function. Poly (p-xylenetetrahydrothiophenium chloride) is co-deposited with poly (styrenesulfonate). The pair can be thermally converted to produce self-doped conducting poly (p-phenylenevinylene). Poly (butyleneviologen) dibromide is a polycationic salt that is used as the electron conducting layer. Copper (II) phthalocyanine-tetrasulfonic acid is used in increase photon absorption in the photovoltaic devices. Deposition conditions have been 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). Photovoltaic devices are 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 components could be mixed by changing polyelectrolyte in alternate layers. Devices were constructed with a salt/ methylviologen 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.

I9.32

Interface and Bulk Contributions of Metal/Polyaniline/Metal Structures. Rodrigo Fernando Bianchi[1,2], Helder Nunes da Cunha[3], Guilherme Fontes Leal Ferreira[1] and Joao Mariz Guimaraes Neto[3]; [1]Departamento de Fisica e Ciencia dos Materiais, Universidade de Sao Paulo, Sao Carlos, Sao Paulo, Brazil; [2]Departamento de Engenharia de Sistemas Eletronicos, Escola Politecnica, Sao Paulo, Sao Paulo, Brazil; [3]Departamento 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 to occur when Al was used as electrode. A phemomenological model employing the the Cole-Cole dielectrical 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 polarization and temperature are found to being in good agreement with experimental data. From the theoretical-experimental fittings were able to separate the bulk and the interface contributions to the complex impedance, as well as the evaluation of the PANI/Al interfaces thickness and resistivity, around 10 nm and 10Î3 Ohmm, respectivelly. Fapesp and MCT/IMMP from Brazil sponsored this work.

I9.33

Evaluation of Resistivities and Polaron Delocalization Lengths in Highly Conjugated (Porphinato)zinc(II) Oligomers. Paul R. Frail[1,2], Kimihiro Susumu[1], Jennie Fong[4], Paul J. Angiolillo[3,1], J. M. Kikkawa[2] and Michael J. Therien[1]; [1]Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania; [2]Physics, University of Pennsylvania, Philadelphia, Pennsylvania; [3]Physics, Saint Joseph's University, Philadelphia, Pennsylvania; [4]Chemistry, University of San Diego, San Diego, California.

A series of meso-to-meso ethyne-bridged (porphinato)zinc(II) oligomers have been synthesized from dimer through heptamer. The electronic absorption spectra of these species feature $S_0 \rightarrow S_1$ transitions that progressively red-shift (600-870nm) and increase dramatically in oscillator strength with increasing oligomer length with respect to the benchmark monomeric building block. The optical band gaps of these materials range from 2.0-1.3 eV, and parallel closely the corresponding potentiometrically determined HOMO-LUMO gaps. EPR analysis of the radical cation states of these conjugated oligomers shows a diminishing linewidth with increasing oligomer length, indicating polaron delocalization lenghts 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 solublilizing grous 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} Ωcm) for a given conjugation length. These changes in resistivity correlate with the nature of oligomer-oligomer intermolecular interactions made possible in the bulk phase.

I9.34

Programmable Conductance Switching and Negative Differential Resistance in Nanoscale Organic Films. Troy Graves-Abe[1,2] and J. C. Sturm[1,2]; [1]PRISM, Princeton University, Princeton, New Jersey; [2]Department 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 $Cu(ClO_4)_2$, 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 μm^2. 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 10^4 A/cm^2. The NDR peak was reproducible over multiple scans, although some hysteresis was observed and peak currents and voltages could vary 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 not observed. The devices' low-voltage conductivity could be varied by up to a factor of 10^3 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. Voltages below ~2 V did not change the devices conductivity 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 degrading. Similar electrical characteristics have been observed previously, primarily in electroformed inorganic insulating films [2]. Other observations of bistable switching in organic devices [3] have been attributed to stored charge [4]. We will present evidence that for the system we have studied, a mechanism based on the formation and destruction of conducting filaments [5] is more appropriate. [1] S.D. Evans et al, J. Am. Chem. Soc. **113** 5866 (1991). [2] A.K. Ray and C.A. Hogarth, Int. J. Electronics **57** 1 (1984). [3] L. P. Ma, J. Liu, and Y. Yang, App. Phys. Lett. **80** 2997 (2002). [4] L. P. Ma et al, App. Phys. Lett. **82** 1419 (2003); L. D. Bozano et al, App. Phys. Lett. **84** 607 (2004). [5] G. Dearnaley, A. M. Stoneham, and D. V. Morgan, Rep. Prog. Phys. **33** 1129 (1970).

I9.35

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

Polyethylene dioxythiophene doped with polystyrene 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, write-once-read-only 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 intermediating 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). Appling +4.0 V induces a "low" conductance state while applying -4.0 V switches the device back to the "high" conductance state. The current 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 bottom electrode material 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 Al/PEDOT:PSS interface. The charges are stored there and will resist later-on charge injection, resulting in the "low" conduction state. The negative voltage pulse can remove the stored charges and recover the device back to "high" conduction state. Reference: [1] C. C. Huang, H. F. Meng, and G. K. Ho et al, Applied Physics Letters, 84, 1195-1197 (2004). [2] S. E. Shaheen, R. Radspinner, and N. Peyghambarian et al, Applied Physics Letters, 79, 2996-2998 (2001). [3] J. Lu, N. J. Pinto, and A.G. MacDiarmid, Journal of Applied Physics, 92, 6033-6037 (2002). [4] S. Moeller, C. Perlov, W. Jackson, C. Taussig and S. R. Forrest, Nature, 426, 166-169 (2003).

I9.36

Charge Mobility Engineering of Organic Co-Host using Triphenylamine- and Rubrene-Mixed Alloy. H. H. Fong[1,2] and S. K. So[1,2]; [1]Physics, Hong Kong Baptist University, Hong Kong, Hong Kong; [2]Centre 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 luminous efficiency and the device stability. Recent research on the co-host OLED (e.g. Alq_3 : polycyclic aromatic hydrocarbon-based transporter) show that mixing the organic host transporters not only alter the charge recombination of the light-emitting region but also the overall 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 OLED applications, N, N'-diphenyl-N, N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) functions as a triphenylamino hole transporter while rubrene (RB) is an effective sensitizer. Previously, time-of-flight (TOF) mobility measurements show that both TPD and RB exhibit high hole mobilities of $\sim 10^{-3}$and $\sim 10^{-2}$cm^{2}V^{-1}s^{-1} respectively [H.H. Fong *etal*, *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 reduction in the 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 channels along RB molecules are established and become effective.The threshold hopping distance 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.

I9.37

Investigation of Bipolar Carrier Transport Properties in Pentacene by Admittance Spectroscopy. Jin An[1,2], Stephen S. W. Tsang[1,2] and J. B. Xu[1,2]; [1]Dept. of Electronic Engineering, Chinese University of Hong Kong, Hong Kong, Hong Kong; [2]Materials Science and Technology Research Center, Chinese University of Hong Kong, Hong Kong, Hong Kong.

In the area of organic field-effect transistors (OFETs), pentacence has been widely studied[1]. The reported field-effect hole mobility is as high as 1cm^2/V·s. From the application point of view, pentacene is believed to be one of suitable candidates used to fabricate organic integrated circuit to replace the traditional technology based on silicon. On the other hand, different studies have been performed to investigate the molecular structural effects on carrier mobility. Therefore, exploration of intrinsic carrier mobility of pentacene is highly desired. However, due to the high material cost and the large film thickness (5μm) 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[2] and Alq_3[3] with thinner organic films (<500nm). 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/Al configurations. They are used to study the unipolar (hole) and bipolar transport properties. The characteristics of field- and temperature-dependent hole mobility are comparable in two different structures. The zero-field hole and electron mobilities are above 10^{-4}cm^2/V·s, and 10^{-7}cm^2/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 charge carrier density in an OFET configuration[4] is not negligible. 1. Lin, Y.Y., et al., IEEE Transactions on Electron Devices, 1997. 44(8), p. 1325-1331. 2. Martens, H.C.F., J.N. Huiberts, and P.W.M. Blom, Applied Physics Letters, 2000. 77(12), p. 1852-1854. 3. Berleb, S. and W. Brutting, Physical Review Letters, 2002. 89(28): p286601. 4. Tanase, C., et al., Physical Review Letters, 2003 91(21), p. 216601.

I9.38

Abstract Withdrawn

I9.39

Bis-Heterocycle-Phenylene based Polymers for Optoelectronic Devices. Emilie Galand, Barry C. Thompson and John R. Reynolds; Department of Chemistry, Center for Macromolecular Science and Engineering and the George and Josephine Butler Polymer Research Laboratory, University of Florida, Gainesville, Florida.

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) [PBTB(OR)$_2$] and poly{1,4-bis[2-(3,4-ethylenedioxy)thienyl]-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. They are easily fabricated into films by either drop 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 regiosymmetry on charge transport for electrochemical 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 2-2.2eV 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 photovoltaic systems.

I9.40

Formation of Self-Assembled Multi-layers by using Molecular Layer Deposition. Byoung H. Lee, Moon C. Kang and Myung Mo Sung; Chemistry, Kookmin University, Seoul, South Korea.

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, microelectromechanicalsystems (MEMS) lubrication, protection of metal corrosion, and low dielectric layer. We have been studied the formation of organic-inorganic hybrid self-assembled multi-layers using molecular layer deposition. The multi-layers have been investigated by X-ray photoelectron spectroscopy (XPS), contact angle analysis, atomic force microscopy(AFM) and transmission electron microscopy (TEM). The results showed that these self-assembled multi-layers have high efficiency.

I9.41

New Conjugated Polymers Derived from Carbazole as Thermoelectric Materials. Isabelle Levesque[1,2], Xing Gao[1], Dennis D. Klug[1], Christopher I. Ratcliffe[1], John Tse[1,4], Mario Leclerc[2], Alboni Paola[3] and Terry M. Tritt[3]; [1]Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada; [2]Chemistry, Universite Laval, Quebec, Quebec, Canada; [3]Physics and Astronomy, Clemson University, Clemson, South Carolina; [4]Physics, University of Saskatchewan, Saskatoon, Saskatchewan, Canada.

Conjugated polymers and oligomers derived from 2,7-carbazole have been first 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 charge transport properties of these novel materials. Theoretical calculations performed on these polymers and other conjugated polymers have shown that their electron band structures are adequate for thermoelectric materials. An efficient thermoelectric material must possess a large Seebeck coefficient ($\Delta V/\Delta T$), 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 favourable 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 electrical properties of the pure and doped 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.

I9.42

Water-Soluble Paracyclophane Chromophores with Large Two-Photon Action Cross Sections. Han Young Woo[1,2], Alexander Mikhailovsky[2], Dmitry Korystov[2] and Guillermo C. Bazan[1,2]; [1]MC-CAM, University of California, Santa Barbara, California; [2]Chemistry, 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 TPM 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 ($\delta\eta = \sim 10$ GM). In this contribution, we report molecular design and chracterization of TPM-specific chromophores based on [2.2]paracyclophane with exceptionally large $\delta\eta$. Different substituents were chosen to modulate the strength of the donor nitrogen groups 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,N-bis(6”-chlorohexyl)-4’-aminostyryl]-[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,N-bis(4”-(6”’-chlorohexyl)phenyl)-4’-aminostyryl]-[2.2]paracyclophane (3N). The charged species are: 4,7,12,15-tetra[N,N-bis(6”-(N,N,N-trimethylammonium)hexyl)-4’-aminostyryl]-[2.2]paracyclophane octaiodide (1C), 4,7,12,15-tetra[(N-(6”-(N,N,N-trimethylammonium)hexyl)carbazol-3’-yl)vinyl]-[2.2]paracyclophane octaiodide (2C). 4,7,12,15-tetra[N,N-bis(4”-(6”’-(N,N,N-trimethylammonium)hexyl)phenyl)-4’-aminostyryl]-[2.2]paracyclophane octaiodide (3C). The overall set of compounds series allows the examination of solvent influence and donor strength effects on $\delta\eta$. Two-photon excitation spectra, measured using TPIF technique, show δ values of 1290 $\sim$ 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 $\delta\eta$ 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 $\delta\eta$ 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 $\delta\eta$.

I9.43

Thin Films of Phthalocyanine/Perylene Tetracarboxyldiimide Blends for Organic Solar Cell Devices. Alexandru Vlad[1], Pascal Viville[2], Dana Serban[1], Vinciane De Cupere[3], Gael Zucchi[3], Vincent Bayot[1], Roberto Lazzaroni[2] and Yves Geerts[3]; [1]DICE, Universite catholique de Louvain, Louvain-la-Neuve, Belgium; [2]SCMN, Universite de Mons-Hainault, Mons, Belgium; [3]LCP, Universite Libre de Bruxelles, Bruxelles, Belgium.

The performances of organic photovoltaic (solar cells) devices 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 discotic-like phthalocyanines (PcH2) and electron acceptor calamitic-like perylene tetracarboxyldiimide (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 organization at ambient temperature that can favor the vertical migration of the charges 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 roughness, the 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.

I9.44

Supramolecular Organization of Thiophene-based Oligomers: From Solution to Solid-state Nanostructures. Philippe Leclere[1,2], Mathieu Surin[1], Gwennaelle Derue[1], W. James Feast[3], Pascal Jonkheijm[2], Albertus P. H. J. Schenning[2], E. W. (Bert) Meijer[2] and Roberto Lazzaroni[1]; [1]University of Mons-Hainaut, Mons, Belgium; [2]Eindhoven University of Technology, Eindhoven, Netherlands; [3]IRC, 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 molecular and supramolecular architectures. The role of self-assembling processes (pi-pi interactions, hydrogen bonding) of these systems is demonstrated here for disubstituted oligothiophene derivatives ($n = 5$, 6 and 7). This approach appears to be very promising to conjugated 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 and can be clearly pinpointed. Depending on the interactions between the molecules and the substrate, one-dimensional (nanowires) or two-dimensional (platelets) objects can be generated (1). Here, Atomic Force Microscopy (AFM) is used to investigate the morphologies of thin deposits made from assembly of thiophene-based oligomers starting from molecularly dissolved solutions or aggregates already formed in solution. For the later situation, Circular Dichroism (CD) analysis is helpful for the description of the thermodynamics of the aggregate formation in solution. 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 semi-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 circuits, through surface patterning with nanometer-sized objects. They can provide control of the organization of the nanostructures following predefined architectures as well as the characterization of the electrical properties on the local scale. (1) Ph. Leclere, M. Surin, P. Viville, R. Lazzaroni, A.F.M. Kilbinger, O. Henze, M. Cavallini, F. Biscarini, W.J. Feast, A.P.H.J. Schenning, and E.W. Meijer, Chemistry of Materials (Special Issue on Organic Electronics).

I9.45
Synthesis and Properties of Polycyclosilanes.

Christoph Marschner, Andreas Wallner and Judith Baumgartner; Institut fuer Anorganische Chemie, Technische Universitaet Graz, Graz, Austria.

Polysilanes are a well studied class of inorganic polymers. Their most interesting feature is that of σs-bond delocalisation. 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 polybicyclosilanes may be attractive materials. These compounds would be rigid rod like structures with the main chain consisting of oligosilane cages. Recent synthetic efforts have provided us with a simple access to bicylo [2.2.2] oligosilanes. These compounds can be converted into dianions which are versatile 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 silane cages will be the subject of discussion.

SESSION I10: LEDs
Chair: Ghassan Jabbour
Friday Morning, April 1, 2005
Room 2001 (Moscone West)

8:30 AM I10.1
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 two decades and currently organic materials have found promising applications, such as display and transistors. To enhance the performance of organic LEDs, doping technology and graded-mixed junction structure by co-evaporation method have been extensively adopted in formation of organic thin films.[1-3] 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 solid 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, 143. 2. A.B. Chwang, R.C. Kwong, and J.J. Brown, Appl. Phys. Lett. 2002, 80, 725. 3. D. Ma, C.S. Lee, S.T. Lee, and L.S. Hung, Appl. Phys. Lett. 2002, 80, 3641.

8:45 AM *I10.2
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 discuss the issues that need to be addressed for these materials to succeed in display and lighting applications.

9:15 AM I10.3
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 film allows unique approaches to study the mechanisms of these devices$^{1-3}$ 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 5% 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 symposium we report planar LECs with up to 53 simultaneously formed p-n junctions in series between two electrodes 0.5 cm apart, which offer uniform light emission and an open circuit voltage of 63.5V. 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 Interelectrode Spacing", J. Gao and J. Dane, Appl. Phys. Lett. 83: 3027-29(2003) 2. "Visualization of electrochemical doping and light-emitting junction formation in conjugated polymer films", J. Gao and J. Dane, Appl. Phys. Lett. 84: 2778-80(2004) 3. "Imaging the degradation of polymer light-emitting devices", J. Dane and J. Gao, Appl. Phys. Lett., in press Oct.25 (2004)

9:30 AM I10.4
High Efficiency Blue-Emitting OLED using Wide-Gap Arylamines.

Junji Kido^{1,2}, Daisaku Tanaka^{2}, Yuya Agata^{2} and Hitoshi Shimizu^{2}; ^{1}Polymer Science and Engineering, Yamagata University, Yonezawa, Yamagata, Japan; ^{2}Optoelectronic 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 emission 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 ITO/p-doped buffer layer/wide-gap arylamine hole-transporting layer/ blue-emitting FIrpic layer doped into carbazole-containing quaterphenyl 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.

9:45 AM I10.5

OLED Degradation Described by Using a One-Free-Parameter Time-Dependent Diffusion Model.

Benoit Racine, Salvatore Cina, Armand Bettinelli and Henri Doyeux; 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, showing in excess of 100Kh at 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 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 degradation, normally observed during the 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. Furthermore the same results were also analyzed by using various fit 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 real experimental values. Using our model produces a far smaller error, despite having a single fit parameter, therefore allowing for reliable estimation of the lifetime, vital when testing new materials or new device architectures.

10:00 AM I10.6

Molecular-Scale Electronic Processes across Organic-Organic Intra- and Inter-Chain Semiconductor Interfaces.

Linus P. H. Lu, Paiboon Sreearunothai, Alexander Seeley, Richard H. Friend and Ji-Seon Kim; Physics, University of Cambridge, Cambridge, United Kingdom.

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 particular formed between polymer chains (inter-chain) and within a polymer chain (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-dioctyl-fluorene-co-N-(4-butylphenyl)-diphenylamine) 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 inter- or intra-chain interfaces with different length-scales. In particular, the F8BT shows the effects of intra-chain heterojunction state (formed by random copolymerisation 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 photovotaics. 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 roles and implication of 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 studied.

10:30 AM I10.7

Light-Emitting Liquid Crystals: From Red, Green and Blue Light-Emitting Materials to Full Color and Polarised OLEDs.

Adam E. A. Contoret[1], Simon R. Farrar[1], W. Chung Tsoi[1], Kai L. Woon[1], Mary O'Neill[1], Matthew P. Aldred[2], Panos Vlachos[2] and Stephen M. Kelly[2]; [1]Department of Physics, University of Hull, Hull, United Kingdom; [2]Department 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 photopolymerization using ultraviolet light [1]. Here we report new material and device developments to show that liquid crystal polymer networks provide a practical alternative to the standard polymer and small molecule approaches to Organic Light-Emitting Displays (OLEDs). We describe the design and synthesis of novel polymerizable 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 luminance up to 560 cd m-2 at 10 V. Efficacies up to 2.2 cd A-1 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 photoalignment layers for OLEDs with lithographically patternable polarized emission. Illumination with polarized ultraviolet light induces 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 electroluminescence with a polarization ratio of 13:1 is demonstrated. [1] A. E. A. Contoret et al. Adv. Mater., 12 971 (2000).

10:45 AM *I10.8

New Materials for High Performance Organic Light Emitting Diodes for Displays and Lighting.

Samson A. Jenekhe[1,2], Abhishek P. Kulkarni[1], Tae Woo Kwon[2], Maksudul M. Alam[1], Christopher J. Tonzola[2], Yan Zhu[1] and Angela P. Gifford[2]; [1]Chemical Engineering, University of Washington, Seattle, Washington; [2]Chemistry, University of Washington, Seattle, Washington.

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 6,6′-bis(4-phenylquinoline) core has been synthesized and used as emissive and electron transport materials for blue OLEDs. Pure blue 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 n-type light-emitting conjugated dendrimers based on a benzene core, poly(phenylenevinylene) dendrons, and diphenylquinoline peripheral groups has been synthesized, characterized and used as emissive and electron 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-phenylene vinylene) (MEH-PPV) as the emissive layer increased with generation and number of electron-acceptor peripheral groups, reaching 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 aluminum cathode. White OLEDs were fabricated from blends or multilayers based on poly(9,9dioctylfluorene) (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 Walzer, Qiang Huang, Gufeng He, Rico Meerheim, Gregor Schwartz, Karsten Fehse, 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 emission zone. Red and green emission is obtained from triplet emitters, while fluorescent emitter materials are used for blue. A well-balanced carrier ratio inside the emission zone is achieved by different means, such as the use of appropriate matrix materials and the application of widened 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 of comparable architecture leads to device lifetimes of 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 Leadbeater, Ilaria Grizzi and Carl Towns; CDT Ltd., Cambourne, 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 very little work to address the direct fluorenone incorporation effect on the optoelectronic properties of other 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 new low-intensity red peak (640nm) appeared in the driven devices, which 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 Fluorine-Free Organic Small Molecules - A New Route to Saturated Blue Phosphorescence. Russell J. Holmes[1,2], Stephen R. Forrest[1,2], Tissa Sajoto[3], Arnold Tamayo[3], Xiaofan Ren[3] and Mark E. Thompson[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; [3]Department 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 fluorine atoms, necessary to blue shift molecular phosphorescence. We have developed a new class of materials capable of saturated blue electrophosphorescence without the need to attach fluorine atoms. Organic light emitting devices were constructed using the blue-green phosphor fac-tris(1-(9′, 9′ dimethyl-2′-fluorenyl)pyrzaolato, N, C^2)iridium(III) (FlZIr), doped into host matrices of N,N′-dicarbazolyl-3,5-benzene (mCP) and p-bis(triphenylsilyly)benzene (UGH2). Peak quantum and power efficiencies of (6.1 ± 0.6)% and (11.3 ± 1.1)lm/W in mCP, and (5.7 ± 0.6)% and (10.5 ± 1.1)lm/W in UGH2 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 Afternoon, April 1, 2005
Room 2001 (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 realising functional electronic devices by depositing materials from the liquid form using drop on demand piezoelectric inkjet head 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 and 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 dispersions 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 interactions between adjacent layers in the device. The interfaces in the transistor device such as those between the semiconductor and 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 on-off 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

A Rapid Evaluation Method to Assess Organic Film Uniformity in Roll-to-Roll Manufactured OLEDs. Svetlana Rogojevic, Tami Faircloth, Maria M. Otero, James C. Grande, Robert W. Tait, Joseph Shiang and Anil R. Duggal; GE Global Research Center, Niskayuna, New York.

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 cost. In order to do 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 evaluating 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 so 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 files. 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/PET 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 5 nm. We show examples of non-uniformity analysis and how it relates to OLED performance.

2:15 PM I11.3

Printable Optoelectronics: Understanding Light-Emitting Electrochemical Cells On Flexible Substrates. Melissa Ann Kreger[1], Matt Wilkinson[1], Eric Jones[1], Janie Jo Breeden[1] and Sue Carter[2]; [1]Add-Vision, Inc., Scotts Valley, California; [2]Physics, University of California Santa Cruz, Santa Cruz, California.

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 examine how the electroluminescence (EL) properties depend 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 charge 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 EL uniformity, the turn-on time, the device efficiency and stability. The dopants induce phase separation, of various degrees, within the printed LEP, which affects the film morphology and proves to be intricately related to the EL properties. The luminance output shows an inverse relationship between doping levels and EL quenching. Lower dopant concentrations optimize 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 dopant levels promotes faster p-I-n junction 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 indium 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 I11.4

Integrated Organic Semiconductor Optics for Miniaturised Analysis. Oliver Hofmann[3], Paul Miller[1], Xuhua Wang[3], Jingsong Huang[2], Donal D. C. Bradley[2,3], Andrew J. de Mello[1,3] and John C. de Mello[1,3]; [1]Department of Chemistry, Imperial College London, South Kensington, United Kingdom; [2]Department of Physics, Imperial College London, South Kensington, United Kingdom; [3]Molecular 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, proteomics, 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 instrumental footprints and can be fabricated at low unit cost, they 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 in place of the conventional macroscale 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 chips, allowing for the creation of fully integrated, precise analytical devices in a disposable credit card format. 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 *I11.5

Polymer Based Rectifiers and Integrated Circuits for Printable 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 (3-alcylthiophene) as semiconductor as well as polymer 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 recent developments in this field as well as the roadmap towards printed electronics for low cost RFID tags and other applications.

3:45 PM I11.6

13.56 MHz Organic Transistor based Rectifier Circuits for RFID Tags. Robert Rotzoll[2], Siddharth Mohapatra[1], Viorel Olario[2], Robert Wenz[1], Michelle Grigas[1], Oleg Shchekin[1,3], Klaus Dimmler[2] and Ananth Dodabalapur[1,3]; [1]Organic ID, Austin, Texas; [2]Organic ID, Colorado Springs, Colorado; [3]The 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 attractiveness of organic transistor-based circuitry for this highly 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 part of a tuned circuit. The frequency of this is standardized and 13.56 MHz is the preferred frequency for item level tags. Organic transistor circuits have hitherto not operated at this high frequency. In this presentation we show that by operating pentacene transistors in the non-quasi-static (NQS) 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 0.1-1.5 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 I11.7

High Performance Organic Schottky Diode. Soeren Steudel[1,2], Martijn Lenes[1], Carsten Deibel[1], Stijn De Vusser[1,2], Jan Genoe[1] and Paul Heremans[1]; [1]Polymer and Molecular Electronics, IMEC, Leuven, Belgium; [2]E.E.Dept, K.U.Leuven, Leuven, Belgium.

With ongoing improvements in the performance of small molecule organic thin film transistors (OTFT) and the first demonstrations of inverters 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 herby is the rectification stage that rectifies the incoming high frequency signal, preferable at the commercially used base carrier frequency of 13.56MHz, to power the signal modulation circuitry. We would like to present an organic Schottky diode based on pentacene that shows a superior performance to previous organic diodes as well as compared to amorphous 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 as 6MHz, supplying a DC voltage of 10V. Those finding represent an important 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 I11.8

Fabrication of OLED Displays on a Dome using a Deformable Polymeric Hole Injecting Anode. Rabin Bhattacharya[1], Sigurd Wagner[1], Yeh-Jiun Tung[2], Jim Esler[2] and Mike Hack[2]; [1]Electrical Engineering, Princeton University, Princeton, New Jersey; [2]Universal 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/m^2. 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 I11.9

Ambipolar Organic Transistors and Complementary-Like Logic Circuits.

Thomas Dimitrios Anthopoulos[1], Dago M. de Leeuw[1], Sepas Setayesh[1], Cristina Tanase[2], Jan C. Hummelen[2] and Paul D. M. Blom[2]; [1]Philips Research Laboratories, Eindhoven, Netherlands; [2]Molecular 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).