

## SYMPOSIUM P

# Organic and Polymeric Materials and Devices—Optical, Electrical, and Optoelectronic Properties

April 1 – 5, 2002

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SESSION P1: DEVICE ENGINEERING AND  
PHYSICS

Chair: Shuit-Tong Lee  
Monday Afternoon, April 1, 2002  
Franciscan II/III (Argent)

**12:45 PM \*P1.1**

**HIGH-EFFICIENCY POLYMER-BASED ELECTRO-  
PHOSPHORESCENT DEVICES.** Xiong Gong, Jacek C. Ostrowski,  
Matthew R. Robinson, Daniel Moses, Guillermo C. Bazan, and Alan  
J. Heeger, Institute for Polymers and Organic Solids, University of  
California Santa Barbara, Santa Barbara, CA.

We report on the performance of two host / guest systems of new iridium complexes as the guest material. In the first system, a high efficiency yellow-green electrophosphorescent light-emitting organic diodes employing tris [9,9-dihexyl-2-(pyridinyl-2') fluorene] iridium(III) ([Ir(DPF)3]) doped into a blend of poly(vinylcarbazole) (PVK) with 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazol (PBD), was demonstrated. External quantum efficiencies up to 10% photon/electron and luminous efficiencies of 36 cd/A were achieved. The brightness depends on the doping concentration; for 1 wt.-% [Ir(DPF)3], the maximum brightness was in excess of 8300 cd/m<sup>2</sup>. The devices exhibited no emission from PVK or PBD even at 0.01 wt.-% [Ir(DPF)3] doping concentration. The second system was incorporated tris (2, 5 - bis - (2' - (9, 9' - dixhexylfluorene)) pyridine) iridium (III) ([Ir(DFP)3]) into a polyfluorene derivative. Red electroluminescence at 600 nm with quantum efficiencies of up to 3% photon/electron was observed. No energy transfer was evident from the data of photoluminescence. The brightness depends on the doping concentration; for 1 wt.-% [Ir(DPF)3], the maximum brightness was in excess of 1000 cd/m<sup>2</sup>. The data suggests that Förster energy transfer plays a minor role in achieving high efficiencies in these devices. Alternatively, the experimental data suggests that charge trapping and subsequent recombination are responsible for the high efficiencies of these devices. These results demonstrate that high efficiency electrophosphorescence can be obtained from polymer-based LEDs that are fabricated by processing the active materials from solution.

**1:00 PM \*P1.2**

**LASER-ASSISTED STM SPECTROSCOPY: A NEW TOOL TO  
PROBE PHOTOCARRIERS IN ORGANIC SEMICONDUCTORS.**  
Denis Fichou, Fabrice Charra, and Oleksandr Marchenko,  
CEA-Saclay, SPCSI-DREC-AM-DSM, Gif-sur-Yvette, France and  
Paris 6 Univ, Paris, FRANCE.

Charge transport in organic semiconductors strongly depends on the degree of molecular and crystalline ordering. But most studies have been performed on macroscopic dimensions leading to overall parameters. In order to reach the intrinsic behavior of highly organized materials, it is necessary to access defect-free nano-domains with the possibility not only to image passively it but also to submit it to electrical and optical excitations. The metallic tip of an STM can be used as a through-space nano-contact to a semiconductor sample. Tunnel current-voltage curves can then be recorded with the possibility to reach atomic spatial resolution. The influence of light is investigated by coupling the organic nano-junction to a laser beam through a prism in a pure optical way, thus reducing greatly thermal effects. Monitoring the tip-sample distance at the angstrom level allows to tune the I-V characteristics of these nanoscale organic tunnel MIS junctions. Beside continuous lasers, we also used a femtosecond pulsed laser, thus adding time resolution to spatial resolution. We report here on recent results obtained with various organic semiconductors using our light-assisted non-contact spectroscopy and show that it provides a new and powerful tool to study the physics of photocarriers in these materials.

**1:30 PM \*P1.3**

**MOLECULARLY ENGINEERED MATERIALS AND INTERFACES  
FOR ORGANIC LIGHT EMITTING DEVICES.** Zakya H. Kafafi,  
Naval Research Laboratory, Washington, DC.

Progress has been recently made in developing efficient organic light-emitting diodes based on molecularly engineered materials,(1,2) and electronically tailored organic/metal and organic/organic interfaces.(3) New molecularly engineered materials with enhanced carrier transport properties, and their incorporation in light-emitting devices will be reported. Different approaches taken for tuning the electronic structures of luminescent guest/host molecular systems for efficient energy transfer from host to guest and/or direct electron-hole recombination on the guest molecules will be discussed. In addition, the tailoring of organic/metal and organic/polymer interfaces via molecular engineering and energy level alignment for efficient charge injection and carrier transport will be reviewed.

1. L.C. Picciolo, H. Murata and Z.H. Kafafi, Appl. Phys. Lett. 78, 2378 (2001).
2. H. Murata, G.G. Malliaras, M. Uchida, Y. Shen, and Z.H. Kafafi,

Chem. Phys. Lett. 339, 161 (2001).

3. A. J. Mäkinen, I. G. Hill, T. Noda, Y. Shirota and Z.H. Kafafi, Appl. Phys. Lett. 78, 670 (2001).

**2:00 PM \*P1.4**

**INJECTION AND CHARGE TRANSPORT IN POLYFLUORENE  
POLYMERS.** Alasdair Campbell, Theo Kreouzis, Dmytro Poplavskyy,  
Jenny Nelson, Donal Bradley, Blackett Laboratory and Centre for  
Electronic Materials and Devices, Imperial College, London, UNITED  
KINGDOM.

This talk presents an overview of recent results concerning the injection and transport of both electrons and holes in a range of conjugated fluorene polymers. The polyfluorenes are one of the two main families of commercially significant materials under development for applications in plastic optoelectronic applications and are representative of the state of the art in terms of materials performance. Our results are specifically for samples provided by the Dow Chemical Company with whom we have been working for the past five years and include both homo- and co-polymers. We describe a range of experiments that probe the hole and electron transport characteristics of these materials and their dependence on chemical structure and polymer morphology. Current-voltage, dark injection transient and time-of-flight measurements are used to probe the detailed dependence of injection and transport on film thickness, applied voltage and sample temperature. We discuss our results in the context of current literature models.

Acknowledgements:

We thank Mark Bernius, Jim O'Brien and Mike Inbasekaran of the Dow Chemical Company for providing the polyfluorenes that we have studied. We also thank the Dow Chemical Company ("Polymer Semiconductors") and the UK Engineering and Physical Sciences Research Council (grants GR/M08011, GR/M45115 and GR/N34772) for supporting our programme. JN thanks the EPSRC for the award of an Advanced Fellowship and DP for a project studentship. We also thank Homer Antoniadis for his valuable contributions to this work.

**2:30 PM \*P1.5**

**ORGANIC THIN FILM TRANSISTORS - ELECTRONICS  
ANYWHERE.** Thomas Jackson, Pennsylvania State University,  
University Park, PA.

Conventional microelectronics has been spectacularly successful at providing increasingly complex digital processing and large-capacity digital memory. It has thus far been less successful at providing simple function at very low cost and there is increasing interest in thin film electronics as an alternative to conventional ICs for low cost or large area applications. Organic semiconductors are of particular interest because they can be deposited and processed at low temperature. Best organic thin film transistor (OTFT) device performance now rivals or exceeds that of amorphous silicon devices, and low OTFT process temperatures allow fabrication on a range of surfaces including polymeric substrates, cloth, or even paper. Although field-effect carrier mobility as low as about 10-2 cm<sup>2</sup>/V-s is adequate for some low-performance applications, field-effect mobility greater than 1 cm<sup>2</sup>/V-s has been reported for OTFTs, and may allow OTFT use in higher performance applications. Pentacene is of particular interest since field-effect carrier mobility near 2 cm<sup>2</sup>/V-s has been measured in this material [1,2]. We have fabricated pentacene-based organic thin film transistors on flexible low-temperature polymeric substrates with performance comparable to a-Si:H devices (field-effect mobility > 1 cm<sup>2</sup>/V-s, current on/off ratio > 108, and near zero threshold voltage). Using these devices we have fabricated digital and analog circuits, active matrix display pixel arrays, and integrated OTFT - organic light emitting diode active pixels. These results demonstrate OTFT utility for a variety of low-cost or large-area electronics applications. [1] C.D. Sheraw, J.A. Nichols, D.J. Gundlach, J. . Huang, C.C. Kuo, H. Klauk, T.N. Jackson, M. G. Kane, J. Campi, F.P. Cuomo, and B.K. Greening, "Fast organic circuits on flexible polymeric substrates," 2000 International Electron Devices Meeting Technical Digest, pp. 619-22, (December 2000). [2] J.H. Schön, and C. Kloc, "Fast Organic Electronic Circuits Based on Ambipolar Pentacene Field-Effect Transistors," Applied Physics Letters, 79, pp. 4043-4044 (December 2001).

**3:30 PM P1.6**

**TRIPLET EXCIMERS IN DOUBLE DOPED WHITE ORGANIC  
LIGHT EMITTING DEVICES.** Brian W. D'Andrade, Stephen R.  
Forrest, Princeton Univ, Dept of Electrical Engineering, Princeton,  
NJ; Jason Brooks, Vadim Adamovich, Mark Thompson, Univ. of  
Southern California, Dept of Chemistry, Los Angeles, CA.

Electrophosphorescent materials have attracted much attention for their use in organic light emitting devices (OLEDs) because they harness both triplet and singlet states, leading to OLEDs with internal quantum efficiencies approaching 100% [1]. For white OLEDs (WOLEDs), at least three electrophosphorescent dopants are required

to produce emission that spans the entire visible spectrum. A red dopant, in a multi-doped single host, is doped at <1 wt%, or it can be doped into a separate band to prevent quenching of higher energy emitters [2]. Here, we use two blue emitting phosphorescent organometallic materials [3] - iridium(III)bis(4,6-di-fluorophenyl)-pyridinato-N,C<sup>2'</sup>) picolinate (FIr(pic)), and platinum(II)(2-(4,6-difluorophenyl)pyridinato-N,C<sup>2'</sup>) (acetyl acetonate) (FPt(acac)) - simultaneously doped into a 4,4'-N,N'-dicarbazole-biphenyl (CBP) host to efficiently produce white light based on triplet excimer and direct phosphorescent emission. Both dopants can be doped at ~6 wt% into a single host because energy transfer to the unbound ground state of the red excimer is forbidden. Color optimization leading to a high color-rendering index of 78 was achieved by varying the concentrations of the dopants. A FPt(acac) concentration of >1 wt% was necessary to produce excimers with broad featureless emission between 500- and 800 nm. The device had Commission Internationale de l'Eclairage (CIE) coordinates of (0.37,0.43) at 10 mA/cm<sup>2</sup>, a maximum external quantum efficiency = (4.0 ± 0.4)% corresponding to (9.2 ± 0.9) cd/A, and a maximum luminance of (31 000 ± 3000) cd/m<sup>2</sup> at 16.6 V.

[1] C. Adachi, M.A. Baldo, M.E. Thompson and S.R. Forrest, J. Appl. Phys. 90, (2001).

[2] B.W. D'Andrade, M.E. Thompson and S.R. Forrest, Adv. Mater., in press, (2001).

[3] S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, R. Kwong, I. Tsyba, M. Bortz, B. Mui, R. Bau and M. Thompson, Inorg. Chem. 40, (2001) 1704.

### 3:45 PM \*P1.7

AMORPHOUS MOLECULAR MATERIALS FOR OPTO-ELECTRONIC AND PHOTONIC DEVICES. Yasuhiko Shirota, Hiroshi Kageyama, Junsheng Yu, Kenji Okumoto, Hidekaru Doi and Nobumichi Kamiyoshi.

Amorphous molecular materials have demonstrated their suitability and versatility for use in electronic, optoelectronic and photonic devices. Since the late 1980s, we have performed a series of studies on the creation of amorphous molecular materials and their structures, reactions, properties and applications [1]. We report here the synthesis and properties of new amorphous molecular materials for organic electroluminescent devices and photonic devices based on the photorefractive effect. The performance of these devices will be discussed.

[1] Y. Shirota, J. Mater. Chem., 10, 1 (2000) and references cited therein.

## SESSION P2: MATERIALS AND SYNTHESIS

Chair: Alan Sellinger

Tuesday Morning, April 2, 2002

Franciscan II/III (Argent)

### 8:00 AM \*P2.1

NEW HIGHLY LUMINESCENT MOLECULES FOR OPTO-ELECTRONIC DEVICES. Fred Wudl, Olivier Dautel, Michail Bendikov, Univ of California, Dept of Chemistry and Biochemistry, Los Angeles, CA; Teruyuki Mitsumori, Mitsubishi Ltd and Univ of California, Los Angeles, CA.

We will present our latest results of design and synthesis of very strongly green luminescent organic solids which rival Alq3 in luminescence. The photophysical characterization of the materials will also be presented. These are novel planar aromatic heterocycles which will be used as n- or ambipolar carriers. Results of device fabrication and performance will also be presented.

### 8:30 AM P2.2

HIGH PERFORMANCE LEDs USING NEWLY DESIGNED IRIDIUM COMPLEXES AS DOPANTS IN CONDUCTING POLYMERS. Matthew R. Robinson, Xiong Gong, Jacek C. Ostrowski, Daniel Moses, Guillermo C. Bazan, Alan J. Heeger, UC Santa Barbara, Department of Materials Engineering, Physics Department, Chemistry Department, Institute for Polymers and Organic Solids, Santa Barbara, CA.

We report the performance of two host / guest systems using new iridium complexes as the guest material. In the first system, we make use of tris (9,9-dihexyl-2-(pyrid-2'-yl) fluorene)iridium(III) as an emitter doped into poly (vinylcarbazole) and tert-butylphenyl-5-biphenyl-1,3,4-oxidiazol. In this system electroluminescence quantum efficiencies of up to 9% photons / electron and luminous efficiencies of up to 35 cd/A are observed. Maximum brightness of over 8300 cd / m<sup>2</sup> is also achieved. In another system, we dope tris (5-bis-(2'-(9,9'-dihexylfluorene)) pyridine) iridium(III) into a polyfluorene derivative. Red electroluminescence at 600 nm is observed despite no energy transfer observed in photoluminescence

studies. Förster energy transfer appears to play a minor role in these devices. The data suggest charge trapping and subsequent recombination results in highly efficient carrier recombination ultimately resulting in high efficiency light output.

### 8:45 AM \*P2.3

RATIONALLY DESIGNING LANTHANIDE COMPLEXES FOR ORGANIC ELECTROLUMINESCENCE. Jiafu Wang<sup>a,b</sup>, Zhiping Zheng<sup>a</sup>, Nassar Peyghambarian<sup>b</sup> and Ghassan E. Jabbour<sup>b</sup>.

<sup>a</sup>Department of Chemistry, University of Arizona, Tucson, AZ.

<sup>b</sup>Optical Sciences Center, University of Arizona, Tucson, AZ.

A series of lanthanide complexes have been prepared with judiciously designed b-diketonate ligands. The performance of such complexes as electroluminescent materials in organic light-emitting diodes has been evaluated. Significant progress has been made in developing stable and highly efficient green-emitting materials based on terbium(III) complexes utilizing b-diketonates functionalized with the electron-withdrawing oxadiazolyl substituent. Research highlights will be presented, and future directions in developing lanthanide-based electroluminescent materials will be discussed.

### 9:15 AM P2.4

CROSSLINKABLE BLENDED POLYMERS IN LIGHT EMITTING DIODE APPLICATIONS. L.D. Bozano, R. Di Pietro, V.Y. Lee, R.D. Miller, K.R. Carter, J.C. Scott, IBM Almaden Research Center, San Jose, CA.

We have studied the properties of blends of electron and hole transporting materials in single and bilayer structure for OLED applications. The materials considered were a blue emitting polyfluorene, poly(9,9-di-n-hexylfluorene) (DHF), and a hole transporting material, poly-[4-n-hexyltriphenylamine] (HTPA). We indicate with an x, the crosslinkable forms of the materials (x-DHF and x-HTPA), where the polymer chains are terminated with a styryl end-group. The single layer structure is ITO/PEDOT/polymer layer/Ca/Al, and the bilayer one is ITO/PEDOT/x-HTPA/Polymer layer/Ca/AL. The thicknesses of the polymer layers are 50-70 nm. We compared the steady state, transport and optical properties of devices based on crosslinkable blends with the same non-crosslinkable materials. The devices were fabricated with different blend concentrations and with different electrode contacts. The IV curves, the external quantum efficiencies and the optical spectra of the different cases are presented. The crosslinkable blends behave best at small concentrations of the hole transporting material. At these concentrations the single layer OLEDs reach efficiencies greater than 0.1% and are higher than for single layer x-DHF or the non-crosslinkable blend by more than an order of magnitude. The blended materials are then studied in bilayer structure where the results show efficiencies of 0.8% independent of the nature of the emitting layer. We interpret these data in terms of phase segregation in the non-crosslinkable blends.

### 9:30 AM \*P2.5

COLOR TUNING PLATINUM AND IRIDIUM PHOSPHORESCENT DOPANTS FOR HIGHLY EFFICIENT ORGANIC LIGHT EMITTING DIODES. Jason Brooks, Liza Babayan, Bert Alleyne, Peter I. Djurovich, Mark E. Thompson, University of Southern California, Department of Chemistry, Los Angeles, CA.

The incorporation of heavy-metal phosphorescent dopants as emissive materials in organic light emitting diodes (OLEDs) can lead to highly efficient devices which approach a quantum efficiency of 100%. This phenomena is based on the strong spin-orbit coupling from the heavy atom which readily intersystem converts all excitons to an emissive triplet state. A series of cyclometalated iridium and platinum complexes have been synthesized. These materials have high quantum yields of emission and have lifetimes in the microsecond range. The luminescence from these complexes originates predominantly from the <sup>3</sup>[π-π\*] ligand based lowest energy excited state mixed with a varying degree of metal-ligand charge transfer character. The nature of the cyclometalating ligand has a direct affect on the emissive color of the complex. For example, increasing the conjugation of a ligand system will generally lead to a red shift, and the use of different heterocycles will have even more profound effects on the emissive state. However, through the use of substituent effects, a single ligand system, such as 2-phenylpyridine, can be tuned throughout the visible spectrum. This is done by specific substitution of electron donating and withdrawing groups. These phosphors have been incorporated as emissive dopants in OLEDs. The synthesis, photophysical, electrochemical, and device performance data of these complexes will be presented.

### 10:00 AM P2.6

AROMATIC POLYIMIDES CONTAINING WELL-DEFINED CONJUGATION UNITS. Moonhor Ree, Tae Joo Shin, Hong Ki Park, Department of Chemistry, Center for Integrated Molecular Systems, BK21 Functional Polymer Thin Film Group, and Polymer Research

Institute, Pohang University of Science and Technology, Pohang, SOUTH KOREA.

A series of aromatic polyimides composed of well-defined conjugation units were synthesized from 5,5'-bis(4-aminophenyl)-2,2'-bifuryl (PFDA) and 2,2'-bis(furyl)benzidine (FurylBZ) with various dianhydrides. The synthesized polyimides emit blue to green light with a quantum yield of 7.3-14.9%, depending on the polymer backbone. In particular, PFDA-based polymers exhibit extremely narrow photoluminescence. The structure, thermal stability, refractive index and dielectric properties of the polymer films were also determined. Overall, these new polyimides have good properties performance as potential light-emitting and charge-transporting material candidates for fabricating optoelectronic devices. This study was supported in part by the Center for Molecular Integrated Systems (KOSEF) and the Korean Ministry of Education through the Postech Polymer Research Institute.

#### 10:30 AM **P2.7**

##### SYNTHESIS AND CHARACTERIZATION OF AIR STABLE N-DOPED POLYMERS BASED ON ALKYLATED POLY(P-PHENYLENEBENZOBISTHIAZOLE).

Max D. Alexander Jr. and Douglas S. Dudas, Polymer Branch, Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson AFB, OH.

Air stable n-doped polymers have long been a goal of many in the conducting polymer community. This goal has been difficult to achieve due to the intrinsic environmental instability of these 'reduced' systems. Upon exposure to water and/or oxygen many of the current and previously produced materials tend to re-oxidize, losing their conductivity. We have produced a family of environmentally stable polymers based on poly(p-phenylenebenzobisthiazoles). Alkylation of these systems was accomplished at room temperature yielding highly conductive materials that maintained their conductivity over long periods of time while exposed to the atmosphere. The resulting polymers were characterized by a variety of techniques including ESR, UV-Vis, FTIR, NMR, thermopower, AC and DC conductivity. Results of these studies will be reported as a function of dopant type and concentration.

#### 10:45 AM **\*P2.8**

##### SYNTHESIS AND CHARACTERIZATION OF NOVEL LIGHT-EMITTING POLYMERS. Alex K-Y. Jen, Xuezhong Jiang, Michelle Liu, and Petra Herguth, Department of MS&E, University of Washington, Seattle, WA.

A series of novel conjugated copolymers based on the fluorene/dicyanophenyl and fluorene/benzothiadiazole units were synthesized via the Suzuki coupling reactions. The incorporation of electron-deficient structures into polyfluorenes provides an effective mechanism to improve both charge injection and mobility of the polymers. Highly efficient LEDs that possess low turn-on voltage (2.2 V), high external quantum efficiencies (as high as 9.5%), and high brightness (~60,000 cd/m<sup>2</sup>) have been achieved using these polymers. In addition, very efficient and bright emission from exciplexes generated between hole-transporting amine derivatives and these polymers were observed. The best device derived from these exciplexes demonstrated a very low turn-on voltage (2.8 V), a high external quantum efficiency (0.91%), and a high brightness of 3370 cd/m<sup>2</sup>. The desirable properties of this device were attributed to the excellent charge transporting ability of these copolymers.

#### 11:15 AM **P2.9**

##### EFFECT OF COMPOSITION AND SEQUENCE DISTRIBUTION OF OXADIAZOLE MOIETIES ON LUMINESCENCE IN A POLY(PHENYLENE-VINYLENE DERIVATIVE). S. Vaidyanthan, M.E. Galvin, Dept of MS&E, University of Delaware, Newark, DE.

In order to realize the vast potential offered by semiconducting polymers in emissive display technologies, it is important to understand the structure-property relationships that govern their performance. This talk will focus on one such relationship in the most widely studied class of polymers viz. poly(phenylene-vinylene) (PPV) derivatives. We have synthesized a series of oxadiazole containing PPV copolymers varying the composition and sequence distribution of the oxadiazole moiety in the mainchain. We find that a statistically random copolymer performs 5-6 times better in EL efficiency and has a much lower turn-on voltage than a corresponding alternating copolymer with the same chemical composition. By studying the series of these copolymers, we gain insight into how the chemical composition and architecture of this class of material affects LED performance, and understand the science to design better materials for polymeric LEDs.

#### 11:30 AM **\*P2.10**

##### DESIGN OF CHEMICALLY AND MECHANICALLY RESPONSIVE

ELECTROACTIVE POLYMERS. Timothy M. Swager, Department of Chemistry and Center for MS&E, Massachusetts Institute of Technology, Cambridge, MA.

This presentation will describe the design of electroactive polymers as sensors and actuators. Highly conductive polymers containing transition metal complexes in the main chain will be presented. Redox matching, overlapping the metal and organic polymer redox waves, was found to promote much higher electroactivity and conductivity than had been previously observed in metal containing conjugated polymers. The integration of novel receptor functions can also be accomplished by incorporating tungsten calixarene moieties into poly(polythienyl phenylene)s. These materials have been shown to respond to p-xylene and small Lewis bases. Structures that can undergo conformational and/or structural changes that are triggered by oxidation and reduction will be presented. These structures are of interest in both the contexts of chemical sensors and artificial muscles.

#### SESSION P3: PATTERNING AND PRINTING

Chair: Ghassan E. Jabbour  
Tuesday Afternoon, April 2, 2002  
Franciscan II/III (Argent)

#### 1:30 PM **P3.1**

##### ANOMALOUS TEMPERATURE DEPENDENCE IN SOLVENT-ENHANCED DYE DIFFUSION IN POLYMER FILMS.

Troy Graves-Abe, Florian Pschenitzka, J.C. Sturm, Center for Photonics and Optoelectronic Materials (POEM), Department of Electrical Engineering, Princeton University, Princeton, NJ.

Polymer-based Organic Light-Emitting Diodes (POLEDs) have shown much potential for use in flat panel displays. An important challenge in fabricating POLED displays is the development of an efficient process to locally dope the spun-on polymer film with emissive dyes to create pixels of different colors. One promising solution is to transfer the dye from a pre-patterned organic film onto the polymer surface by printing, and then diffuse the dye into the polymer in a solvent vapor environment [1]. Solvent vapor can be used to temporarily increase the diffusion coefficient of dye in the polymer, permitting room-temperature diffusion to avoid thermal degradation of the polymer. In this work, we have investigated the effect of temperature on solvent-enhanced diffusion of coumarin 6 (C6) into poly(9-vinylcarbazole) (PVK). After transfer of C6 onto the surface of the PVK, samples were placed on a heated stage in a chamber and exposed to a flow of nitrogen and acetone. The profile of the diffused dye was determined by depth-dependent photoluminescence measurements and Secondary Ion Mass Spectroscopy. We found that the amount of diffused dye decreased at higher temperatures, in contrast to conventional thermally-driven diffusion. At an acetone partial pressure of 120 torr, a two minute anneal at 20°C resulted in a nearly uniform distribution of C6, whereas there was no detectable movement of C6 in the system above 36°C. The results are understood by noting that the decrease in the polymer glass-transition temperature and the corresponding rapid increase in dye diffusivity depend on the quantity of solvent absorbed by the polymer, which decreases as the temperature of the polymer is raised. Since the solvent absorption causes an increase in film volume, we confirmed this effect with in situ measurements of polymer thickness by reflectometry, finding thickness increases that ranged from 23% at 20°C to 5% at 36°C.

This work is supported by DARPA, NJCST and NDSEG.

Reference:

[1] F. Pschenitzka and J.C. Sturm, Appl Phys Lett 78 (17) 2584 (2001).

#### 1:45 PM **P3.2**

##### LARGE AREA SCREEN PRINTABLE POLYMER-BASED OPTOELECTRONIC DEVICES. Sue Carter\*, Melissa Kreger\*, Sarah Tuttle, John Victor, Add-Vision, Scotts Valley, CA and \*Physics Department, University of California, Santa Cruz, CA.

I will give an overview of our efforts to make screen printed large area polymer-based light emitting devices and solar cells on flexible substrates for low information content display applications.

#### 2:00 PM **\*P3.3**

##### INKJET PRINTING OF BIOPOLYMERS, CONDUCTORS AND DIELECTRICS. Paul Calvert, Department of MS&E, Ghassan Jabbour and Yuka Yoshioka, Optical Sciences Center, University of Arizona, Tucson, AZ.

Inkjet printer have been explored as methods for depositing materials in order to build devices or structures. For multilayer printing we need to be able to deposit inks such that the new liquid ink does not mix with previous layers. If a single solvent, or dispersing medium,

such as water is to be used, we must be able to chemical solidify the early layers in order to print onto them. This might be done by thermal or photo-crosslinking or by codepositing two reactive inks. A necessary part of device building will be removal of unwanted reaction products by a washing step. This requires that the printed layers must also adhere to the substrate and each other. Printing has been carried out using both thermal and piezoelectric printheads attached to a computer-controlled 3-axis (xyz) stage. This paper will describe efforts to print and immobilize dielectrics, metallic conductors and polymer gels. Within the gels we have immobilized fluorescent biopolymers and have studied diffusive loss from these layers into water. Polymers of molecular weight from 19,000 Daltons upwards were trapped within a codeposited printed hydrogel.

### 2:30 PM \*P3.4

**ACTIVE MATRIX OLED DISPLAY BACK PLANES ON FLEXIBLE SUBSTRATES.** Daniel Toet, Teruo Sasagawa, Patrick M. Smith, Paul G. Carey, and Paul Wickboldt, FlexICs, Inc., Milpitas, CA.

We have developed an ultra-low temperature (sub-100 °C) process to fabricate high performance polycrystalline silicon (poly-Si) devices on flexible substrates. Our process enables the fabrication of active matrix displays on inexpensive transparent plastic materials such as polyethyleneterephthalate (PET) and polyester (PET). Such displays, besides being compatible with non-planar viewing surfaces, are also more rugged and lighter than conventional displays built on glass. Furthermore, plastics are compatible with roll-to-roll manufacturing, implying a significant reduction in the production costs. Lastly, poly-Si technology allows for the integration of driver circuitry on the display panel, reducing system complexity and manufacturing costs, and for the use of organic light emitting diodes (OLEDs), which provide a substantial performance advantage over conventional liquid crystal technology.

Active matrix OLED display back planes using top-gate self-aligned p-type poly-Si thin film transistors (TFTs) were fabricated on PEN substrates as well as on glass substrates using a plastic compatible process. The poly-Si was obtained by pulsed laser crystallization of a-Si thin films. This method, which is the only poly-Si process compatible with plastic, yields films with large, virtually defect free grains. Gate oxides with capacitance-voltage and breakdown characteristics close to those of thermal oxides were subsequently deposited at temperatures below 100 °C. The final stage of the fabrication process consisted in the room temperature deposition and patterning of a low resistivity indium tin oxide layer ( $r < 1 \text{ m}\Omega\text{cm}$ ), which forms a transparent bottom electrode for the OLEDs. Electrical measurements on individual TFTs made in Si deposited on glass by plasma enhanced chemical vapor deposition show that our process yields high quality devices: mobilities around 100  $\text{V}\cdot\text{s}/\text{cm}^2$ , ON-OFF ratios greater than 2.106 and threshold voltages above 5V are obtained.

### 3:15 PM P3.5

**TEMPLATED GROWTH OF CRYSTALLINE ORGANIC FILMS ON NANO-PATTERNED SUBSTRATES.** Debra J. Mascaro, Massachusetts Institute of Technology, Dept of MS&E, Cambridge, MA; Timothy M. Swager, Massachusetts Institute of Technology, Dept of Chemistry, Cambridge, MA; Henry I. Smith and Vladimir Bulovic, Massachusetts Institute of Technology, Dept of Electrical Engineering and Computer Science, Cambridge, MA.

We use nano-patterned substrates as templates for the growth of polycrystalline thin films consisting of organic small molecules such as pentacene, tetracene, and 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA). This templated growth promotes molecular ordering within the van der Waals-bonded thin films, leading to enhanced charge carrier mobilities that will benefit applications such as organic thin film transistors. We pattern our substrates using optical interference lithography, a maskless, planar, large-area technique with attainable periodicities ranging from 100 nm to one micron. Topographical patterns are fabricated by standard etching techniques, and chemical patterns are obtained using self-assembled monolayer chemistries and processes. The organic small molecules are vacuum evaporated onto thermally controlled substrates. Characterization of the resulting thin films by AFM and SEM reveals elongated grains with distinct facets as compared to the disordered, sometimes dendritic grains observed on unpatterned surfaces. Faceted grains on the plateaus of topographically patterned substrates exhibit preferred alignments with respect to the underlying template. Preliminary TEM, polarized fluorescence microscopy, and glancing incidence x-ray diffraction results indicate that the nano-patterned substrates induce preferential molecular orientations and facilitate molecular ordering.

### 3:30 PM P3.6

**AGILE PHOTONIC BAND GAP LASING STRUCTURES.** Rachel Jakubiak, University of Dayton Research Institute, Dayton, OH; L.V. Natarajan, Vincent P. Tondiglia, Mark Schmitt and Steve Siwecki, Science Applications International Corporation, Dayton, OH;

Timothy J. Bunning and Richard A. Vaia, Air Force Research Laboratory, Materials and Manufacturing Directorate, Wright-Patterson AFB, OH.

Photonic band gap (PBG) materials that allow for coherent localization of light hold considerable promise for the emerging generation of nano- and mesoscale optoelectronic components. Holographic photopolymerization offers a highly versatile approach to integrate highly fluorescent materials into well-defined polymer networks to make one-, two- or three-dimensional photonic band gap materials. This work describes the fabrication and characterization of inorganic-organic PBG materials using switchable holographic reflection gratings derived from polymer-dispersed liquid crystals (PDLCS). The grating consists of distinct polymer and liquid crystal domains that give rise to a periodic index of refraction profile and control of optical feedback. Inorganic and organic fluorescent species reside within the liquid crystal domains and when optically excited gain amplification occurs. An electric field applied across the grating aligns the directors of the liquid crystal and the refractive index profile disappears, as does the lasing action. Possible applications for this technology include optoelectronic displays, compact sensor packages and read-write optical heads for data storage.

### 3:45 PM P3.7

**ORIENTATION, PHOTOPOLYMERIZATION, AND PHOTOPATTERNING OF NOVEL PHTHALOCYANINE MOLECULES.** Carrie L. Donley, Rebecca A.P. Zangmeister, Wei Xia, Anthony Drager, David F. O'Brien, Neal R. Armstrong, University of Arizona, Department of Chemistry, Tucson, AZ.

Two novel phthalocyanine molecules peripherally substituted with side arms containing ethylene oxide and terminal styryl groups (abbreviated styryl CuPc and cinnamyl CuPc, respectively) have demonstrated the ability to self-assemble into columnar aggregates with coherence lengths approaching 100 nm. The orientation of these molecules in thin films formed either on a Langmuir-Blodgett (LB) trough or by spin-coating has been determined through a combination of polarized IR and UV/Vis spectroscopies indicating that the spin coated films adopt a more flat lying orientation than those formed on a LB trough. In addition, the styryl functionality in the side arms of these molecules allows for photodimerization of adjacent styryl groups by [2+2] cycloaddition to form cyclobutane rings when these groups are appropriately spaced and oriented. Extensive photodimerization can lead to polymerization as the side arms in one molecule photodimerize with molecules above and below it, tying the molecules within a column together. Photopolymerization of the cinnamyl CuPc results in a sufficiently insoluble form of this molecule as to allow for photopatterning on the micron scale of thin films of this material deposited either from an LB trough or by spin-coating. Initial studies incorporating these and other novel phthalocyanines in photovoltaic cells will also be presented.

### 4:00 PM P3.8

**PHOTO-ASSISTED MATERIAL MIGRATION IN NANO-HYBRID FILMS.** Takashi Ubukata, Masahiko Hara, Frontier Research System, RIKEN, Wako, JAPAN; Takahiro Seki, Chemical Resources Laboratory, Tokyo Institute of Technology, Yokohama, JAPAN.

During the past several years, it has been shown that thin films of azobenzene functionalized polymers (azo polymers) form regular surface modification under the irradiation with an interference pattern of coherent light. Such photogeneration of surface relief gratings (SRGs) on azo polymers has attracted much attention not only from academic interests but also from a viewpoint of practical use for optical device applications. Recently, we have shown our new proposal that nano-hybrid films composed of azo polymers and other guest molecules provide interesting SRG systems. First, a low-molar-mass liquid crystal material was incorporated into the azo polymers in an expectation that rapid polymer chain migration should be achieved due to the increased fluidity. Due to the cooperative nature involved in this binary molecular system, this may be dubbed a host-guest supramolecular SRG material. It is suggested that various kinds of functional molecules can be drifted and placed in a photo-patterned way in this process. For one example, a dichroic dye was incorporated as the guest. This ternary component hybrid film was also investigated. In this film, lateral photo-transfer of the dye was actually induced by the polymer chain migration, resulting in a patterned and oriented crystallization of the dyestuff.

SESSION P4: POSTER SESSION  
ORGANIC BASED MATERIALS AND DEVICES I

Chair: Rudy Schlaf  
Tuesday Evening, April 2, 2002  
8:00 PM  
Metropolitan Ballroom (Argent)

#### **P4.1**

**POLY(3-HEXYLTHIOPHENE) TRANSISTORS AT HIGH CARRIER DENSITIES.** D. Natelson, B. Hamadani, L.H. Yu, Rice University Dept. of Physics and Astronomy, Houston, TX; C. Winkler, J. Lu, S. Stemmer, Rice University Dept. of Mechanical Engineering and Materials Science, Houston, TX.

At very high gated carrier densities field effect transistor (FET) structures using poly(3-hexylthiophene) exhibit remarkable properties, including a metal-insulator transition and a low temperature superconducting state (Schön et al., Nature **410**, 189 (2001)). We report current progress in attempts to examine electronic transport in this regime, with a focus on temperature-dependence of channel and contact resistances in multiterminal structures.

#### **P4.2**

**DOPANT PAIRING IN A MOLECULAR SEMICONDUCTOR.** Howard M. Branz, Brian A. Gregg, National Renewable Energy Laboratory, Golden, CO.

Recent doping experiments in n-type perylene diimide semiconducting thin films showed an unexpected quadratic dependence of electrical conductivity upon dopant molecule concentration.[1] In this paper, we propose a model of doping efficiency which explains this result. By computing electrostatic energies in a realistic geometry, we show that pair associations between dopant molecules can reduce the first ionization energy by about 115 meV, compared to unpaired dopants. A semiclassical treatment of electron polarization effects suggests their influence on the binding energy reduction is negligible. We propose that singly-ionized dopant pairs outnumber the ionized unpaired dopants and dominate conductivity. Random association into dopant pairs during spin-coating explains the quadratic dependence of conductivity. Our model agrees with the measured conductivity activation energy and magnitude, assuming a typical electron mobility in the liquid crystal. Because dopant pairing in the crystal raises the total electrostatic energy by about 80 meV, the random distribution of dopants implies a weaker interaction during the spin-coating process than in the solid. Until nearly all the solvent is evaporated, the electrostatic interaction between dopants is screened by the solvent and the intermolecular distances are large. The last stage of crystallization evidently is too rapid for separation of randomly-paired low-mobility molecules.

We expect dopants to pair in other organic semiconductors.

Near-quadratic dependences of conductivity on dopant concentration are observed in p-type phthalocyanine [2] and polythiophene [3]. Finally, a simple model of doping in polymers suggests pairing reduces the dopant ionization energy by about 1/6.

[1] B.A. Gregg and R.A. Cormier, JACS, **123**, 7959, 2001.

[2] M. Pfeiffer et al., APL, **73**, 3202, 1998.

[3] Reedijk, et al, PRL, **83**, 3904, 1999.

#### **P4.3**

**COMPARISON OF BLENDED VERSUS LAYERED STRUCTURES IN POLYMER-BASED PHOTOVOLTAICS.** Stephanie Chasteen and Sue A. Carter, University of California Santa Cruz, Physics Dept., Santa Cruz, CA; H. Tillmann and H.-H. Horhold, INNOVENT Technologieentwicklung, University of Jena, GERMANY.

We report comparisons of the photovoltaic response of layered versus blended sandwich photovoltaic devices of Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-ethynylene-2,5-dimethoxy-1,4-phenylene-ethynylene](M3EH-PPV) with either the electron-accepting Poly[oxa-1,4-phenylene-1,2-(1-cyano)-ethynylene-2,5-dioctyloxy-1,4-phenylene-1,2-(2-cyano)-ethynylene-1,4-phenylene] (CN-Ether-PPV) or a hole-accepting phenylamino-p-phenylenevinylene derivative (PA-PPV), with the goal of improving exciton dissociation and charge transport. M3EH-PPV provides a well-characterized semiconducting polymer for photovoltaic applications. In single-layer devices it exhibits a quantum efficiency of less than 1%, which increases to nearly 10% with the addition of a titanium dioxide (TiO<sub>2</sub>) layer. Past research has demonstrated that more efficient devices can be fabricated from blends of electron- and hole-accepting polymers, yielding quantum efficiencies of about 25%. However, it is difficult to control the internal morphology of blended devices. In contrast, the device structure of layered devices is quite easy to control. Thus, multilayered devices could provide a favorable alternative to blends. We will compare these two types of devices architectures (blends vs. layers) in order to understand how device morphology affects charge transport and dissociation processes in polymer photovoltaics. We will discuss how these results can be used in the design of more efficient polymer photovoltaics.

#### **P4.4**

**ELECTRON TRANSFER DYNAMICS IN CONJUGATED POLYMER/NANOCRYSTALLINE SEMICONDUCTOR INTERFACE.** Neil Anderson, Xin Ai, Tianquan Lian, Emory University, Department of Chemistry, Atlanta, GA.

Electron transfer property between conjugated organic polymer and semiconductor (or metal) interface plays an important role in the function of polymer-based devices such as light-emitting diode and solar cells. Solar cells based on thin films of conjugated polymer/nanocrystalline semiconductor composites are a promising technology of future generation photovoltaics. We have undergone a series of studies to investigate both forward and backward electron transfer dynamics in a variety of conjugated polymer/nanocrystalline semiconductor thin film electrodes using femtosecond infrared spectroscopy. In these studies, both the infrared absorption (positive polarons and IRAV) in conjugated polymer and injected electrons in semiconductor nanoparticles are directly monitored to enable the assignment of interfacial electron transfer process. We found that forward electron transfer from MEH-PPV to metal oxide (TiO<sub>2</sub> and SnO<sub>2</sub>) occurs on the sub-picosecond time scale, while the backward electron transfer occurs on the micro to milli second time scale. We observed interesting trend of electron transfer rate rate in different metal oxide TiO<sub>2</sub>, SnO<sub>2</sub> thin films. In this talk, I will summarize the results from these studies and discuss the dependence of charge transfer dynamics on the property of the semiconductor, polymer, and their interaction.

#### **P4.5**

**THE CREATION OF A HYBRID PROTEIN/CONDUCTIVE POLYMER THERMOSENSOR.** Lawrence L. Brott, Rajesh R. Naik, Morley O. Stone, US Air Force Research Laboratory, Materials & Manufacturing Directorate, Wright-Patterson Air Force Base, OH.

The use of thermal sensors and imaging devices has become so widespread that numerous applications ranging from military sensors to firefighting equipment rely heavily upon this technology. There is a desire, however, to improve upon the sensitivity of uncooled sensors while reducing the complexity of their fabrication. Our research takes a biomimetic approach through the incorporation of a thermosensitive protein to enhance the properties of the infrared sensing device. The TipA protein of *Salmonella* is a natural choice since it shows an incredibly fast response time, exhibits large conformational changes in response to slight variations in temperature, and most importantly, exhibits rapid, renaturation uncharacteristic of a protein response. By integrating this protein into a crosslinked matrix of poly(vinyl alcohol) doped with conducting carbon black, a relatively simple, reliable and stable thermal sensor can be fabricated.

#### **P4.6**

**PROBING THE CONFORMATION OF OLIGO(PHENYLENE-VINYLENE) CHROMOPHORES USING SINGLE MOLECULE SPECTROSCOPY AND GAS-PHASE ION CHROMATOGRAPHY.** Melissa A. Summers, John E. Bushnell, Paul R. Kemper, Michael T. Bowers, Guillermo C. Bazan, Steven K. Buratto, Dept of Chemistry & Biochemistry, University of California Santa Barbara, Santa Barbara, CA; Matthew R. Robinson, Department of Materials, University of California, Santa Barbara, Santa Barbara, CA.

We have performed single molecule spectroscopy on a series of oligo(phenylenevinylene) (OPV) chromophores adsorbed to a glass surface. Unlike other small well-defined organic chromophores, we observe a wide range of polarization anisotropies from samples of oligomers with chains of either 5 or 6 phenyl rings. We show that we are able to distinguish the orientation and conformation of these single molecules based on their response to modulated polarization. We categorize the oligomers into three classes of shapes based on their polarization anisotropy: elongated, slightly bent, and kinked. Gas-phase ion chromatography measurements in combination with AMBER force-field calculations were used to determine the detailed conformations adopted by the oligomers. The gas-phase conformations show that the number and position of cis defects dictate the overall shape of the molecules. We show that the correlated results from the single molecule experiments and the gas-phase conformation calculations allow us to directly compare a single molecule's shape with its luminescence properties. This information gives us unprecedented insight into the function of molecular shape and conformation in the optical properties of organic thin films. Furthermore, we can relate our findings on these oligomers to related materials used in organic light-emitting diode (OLED) applications, including the tetrahedral oligo(phenylenevinylene) molecules, and other PPV-based oligomers and polymers.

#### **P4.7**

**PHOTOPHYSICS OF CONJUGATED POLYMERS IN MIXED SOLVENTS: EFFECT OF PHASE SEGREGATION ON DEVICE PERFORMANCE.** Anoop Menon, Mary E. Galvin, University of Delaware, MS&E, Newark, DE; Christopher J. Collison, Lewis J. Rothberg, University of Rochester, Department of Chemistry, Rochester, NY.

We report transient and steady state photoluminescence results along

with absorption and NMR data to support the existence of two distinct morphological species in a solution of PPV pentamer, PPV and a blend of the two. NMR data provide evidence for the close packing of polymer chains, a consequence of solvent quality reduction. These data are correlated with optical properties of the aggregated species in poor solvents and the isolated chains in good solvents. The increase in the steric hindrance of backbone leads to an increase in effective conjugation length, which in turn leads to a spectral red shift in absorption and emission spectra. At the same time, interchain excitations with negligible luminescence lead to a dramatic reduction in quantum yield. We attempt to correlate these effects to photophysical properties in films and address the issue of phase segregation in bad solvents. The relevance of these studies to film formation will be discussed and the corresponding effect on performance of a light emitting diode will be presented.

#### **P4.8**

STUDIES OF AlQ/Mg:Ag INTERFACE IN ORGANIC LIGHT-EMITTING DIODES BY XPS. X.D. Feng, D. Grozea, A. Turak and Z.H. Lu Department of MS&E, University of Toronto, CANADA; H. Aziz and A.M. Hor, Xerox Research Centre of Canada, CANADA.

The organic/cathode interface plays an important role in device degradation of organic light-emitting diodes (OLEDs). The interface between 8-hydroxyquinoline aluminium (Alq) and Mg: Ag cathode in OLEDs, operated for some time, was characterized using X-ray photoemission spectroscopy (XPS). An in-vacuum peeling-off method was used to avoid additional oxidation of the surfaces. XPS results indicate that Alq molecules break down, so that Al is rich at the interface. It is also found by XPS depth-profiling results that Al can diffuse into Mg: Ag electrode, and that the degree of oxidation of cathode diminishes gradually from the interface to deeper metallic layer.

#### **P4.9**

INFRARED EMISSIONS OF THE DEVICE BASED ON RARE EARTH COMPLEXES. F.F. Zang, Z.R. Hong, W.L. Li, H.Z. Wei, D.Y. Wang, M.T. Li, R.G. Li, B. Chu, D. Fan, Laboratory of Excited States Processes, Chinese Academy of Sciences, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, PR CHINA.

IR(infrared) emissions of electroluminescent (EL) devices with rare earth complex have been investigated. Our group have found the IR emission of the Yb<sup>3+</sup>, Pr<sup>3+</sup> of organic diodes with Yb(DMN)<sup>3</sup> bath and Pr(DMN)<sup>3</sup> bath complexes, respectively. However, IR emissions form in the diodes with the RE complexes have not yet been investigated to our knowledge. We observed IR emission for Ho<sup>3+</sup> and Dy<sup>3+</sup> resulted from the diodes with Dy- and Ho-complexes respectively. 986nm radiation corresponding to 5F<sub>5</sub>—5I<sub>7</sub> transition of Ho<sup>3+</sup>, and 1198 nm and 1496 nm radiations corresponding to 5I<sub>6</sub>—5I<sub>8</sub> and 5F<sub>6</sub>—5I<sub>6</sub> transition of Dy<sup>3+</sup> in the EL devices, respectively, were achieved. The visible EL emissions also measured in addition to the IR radiations and the relationship between IR emission and visible one also discussed is affected by both the ligand and HTL. More research have been done to analyze the relationship between the center ion and ligands, some results have been got. In addition, some experiment has been done to study the superficial characteristics of rare earth complexes using different ligands.

#### **P4.10**

EFFECTS OF AN Al<sub>2</sub>O<sub>3</sub> BUFFER LAYER ON THE CHARACTERISTICS OF ORGANIC LIGHT EMITTING DIODES WITH SPUTTER-DEPOSITED CATHODES. Samil Kho, Sungjun Bae and Donggeun Jung, Department of Physics, Physics Research Division and Institute of Basic Science, Sungkyunkwan University, Suwon, REPUBLIC OF KOREA.

The advantages of sputter deposition of electrodes of organic light emitting diodes (OLEDs) include simplicity of the deposition process, large area uniformity of the deposited films and improved adhesion between the deposited materials and the substrates. However, preparation of OLED cathodes using sputtering is quite challenging because organic thin films are sensitive to the radiation damage accompanied by the sputtering process. In this work, we report that an Al<sub>2</sub>O<sub>3</sub> buffer layer prevented the emitting layer from degradation during the sputter deposition of the cathode. For the OLEDs used in this work, indium-tin-oxide (ITO), N,N-diphenyl-N,N-bis(3-methylphenyl)-1,1-diphenyl-4,4-diamine (TPD), tris-8-hydroxyquinoline aluminum (Alq<sub>3</sub>) and aluminum (Al) were used as the anode, the hole transport layer, the emitting layer, and the cathode, respectively. The Al<sub>2</sub>O<sub>3</sub> buffer layer was formed on top of the Alq<sub>3</sub> emitting layer by thermal evaporation of Al and subsequent oxidation of the deposited Al into Al<sub>2</sub>O<sub>3</sub>. The Al electrode was formed by r.f.-magnetron sputter deposition. The OLEDs with sputter deposited Al cathodes showed much lower current, luminance, and luminescence efficiency than the

OLEDs with thermally evaporated Al cathodes. Insertion of an Al<sub>2</sub>O<sub>3</sub> buffer layer between the Alq<sub>3</sub> emitting layer and the sputter deposited Al cathode, however, improved the current, luminance, and luminescence efficiency notably.

#### **P4.11**

BAND FILLING AND DEPLETION THROUGH THE DOPING OF POLYANILINE THIN FILMS. Bo Xu, Peter A. Dowben, University of Nebraska-Lincoln, Department of Physics & Astronomy, Lincoln, NE; Jaewu Choi, Louisiana State University, Center for Advanced Microstructures & Devices, Baton Rouge, LA.

The effects of doping in vapor deposited polyaniline thin films were studied by angle-resolved photoemission, XPS and inverse photoemission spectroscopy. The valence bands, conduction bands as well as the characteristic core levels show consistent shifts to the higher binding energy with sodium doping. Sodium, as an electron donor, when added to the polyaniline system, results in increased electron populations in the polyaniline bands - effectively filling the almost completely filled band. In the case of iodine doping, all the states shifted to lower binding energy. Iodine, as an electron acceptor, effectively depletes the electron population in the occupied bands polyaniline. No new state is induced by doping near Fermi level, suggesting that while the polyaniline system is sufficiently conducting to suppress the formation of Hubbard bands, correlation may, nonetheless, play a role. These results demonstrating band filling and depletion are similar to the results recently obtained in the doping of multi-wall carbon nanotubes [1], another potential one-dimensional conductor.

[1] Jaewu Choi, Iran Amildo Samayoa, Seung-Chu Lim, Chulsu Jo, Young Chul Choi, Young Hee Lee and P.A. Dowben, submitted to Physics Letters.

#### **P4.12**

HARDNESS DEPTH PROFILING OF ION-IMPLANTED POLYMER THIN FILMS. Gunnar Suchanek, Margarita Guenther, Gerald Gerlach, Dresden University of Technology, Institute for Solid State Electronics, Dresden, GERMANY; Bodo Wolf, Dresden University of Technology, Institute for Crystallography and Solid State Physics, Dresden, GERMANY.

Depth-sensing nano-indentation is a powerful technique for determining the hardness, i.e. the resistance to penetration, and the elastic modulus. In the case of ion-implanted polymer thin films, the hardness variation with depth follows the trend of the linear energy transfer (LET) for ionization due to the resulting cross-linking in the polymer film. Various possibilities for the measurement of hardness depth profile are known: The cross section technique, the layer removal technique, and the load variation technique where the indenter penetration depth is varied by changing the applied load. For the first two techniques, the influence of the coverage layers and the substrate on the measurement data is minimized, but sample preparation is very expensive. In the last case, the sample properties are not affected by sample preparation procedures. However, when a film on a substrate is indented, both the film and the substrate deform elastically, even at small penetrations of the indenter. Thus, the load variation technique determines a composite (non-homogeneous polymer film plus substrate) hardness and the hardness profile of the polymer film must be determined by a suitable data processing. In this work, the hardness and the elastic modulus profile of boron implanted polyimide films were determined both by the layer removal and the load variation techniques. Profiles were obtained in dependence on ion energy and implantation dose. The depth of the ion-modified surface layer was determined using the load variation technique from the depth dependence of the power law coefficient of the unloading curve. The reconstruction of the hardness profile by the deconvolution of load variation data is demonstrated. Suitable for film hardness and elastic modulus calculation weight functions are discussed.

#### **P4.13**

NONLINEAR SATURATION AND LASING CHARACTERISTICS OF GREEN FLUORESCENT PROTEIN. David J. Pikas, Sean M. Kirkpatrick, Erin Tewksbury, Lawrence L. Brott, and Rajesh R. Naik, Morley O. Stone, Materials and Manufacturing Directorate, Air Force Research Laboratory, WBAFB, OH; William M. Dennis, Department of Physics and Astronomy, University of Georgia, Athens, GA.

Green fluorescent protein (GFP) has been of interest to researchers recently due to its use in nonlinear microscopy and biomedical applications. Through the use of nonlinear characterization, GFP has been previously shown to exhibit saturable nonlinear absorption. This nonlinear saturation suggests the possibility of a two-photon induced population inversion in GFP, which can lead to the use of GFP as a frequency upconversion laser material, particularly for bioMEMS devices. Here, we explore this population inversion and report on the ultrafast two-photon pumped lasing properties of GFP. Specifically, we report on the lasing threshold, spectral features and output-input

energy characteristics. This is the first demonstration of ultrafast two-photon pumped lasing in a biological chromophore.

#### **P4.14**

**SIMULATION STUDY ON STRUCTURE AND ELECTRICAL CONDUCTIVITY OF AROMATIC MOLECULES FOR NANOSCALE DEVICE.** Hiroshi Mizuseki<sup>1</sup>, Chiranjib Majumder<sup>1</sup>, Rodion V. Belosludov<sup>1</sup>, Amir Farajian<sup>1</sup>, Jian-Tao Wang<sup>1</sup>, Hao Chen<sup>1,2</sup>, Yoshiyuki Kawazoe<sup>1</sup>. <sup>1</sup> Institute for Materials Research, Tohoku University, Sendai, JAPAN. <sup>2</sup> Physics Department, Fudan University, Shanghai, PR CHINA.

Recently, the molecular electronics has attracted strong attention as a "post-silicone technology" to realize a future nanoscale electronics device. A quarter century ago Aviram and Ratner (1) have first demonstrated how an organic molecule could function as a molecular rectifying diode. Further this has been supported by many experimental results. Aromatic molecules have  $\sigma$ - $\pi$ -conjugation systems through which electrons can flow easily. By substituting different functional groups on an aromatic system it is possible to increase or decrease the  $\sigma$ - $\pi$ -electron density and thereby creating acceptor (p-type) and donor (n-type) molecular subunits. Therefore, a rectifier could be built by combining these two molecular subunits between two electrodes in which electrons can flow from cathode to the acceptor or from donor to the anode (2). However, to avoid the reverse direction of flow one should decouple the direct interaction between donor and acceptor by an insulator like aliphatic functional groups. In the present work we present an ab-initio electronic structure calculations of a polyphenyl based molecular rectifier diode. The model system has been constructed from different type of donor, acceptor and the chemical bound rectifier molecular. The electronic structures of these molecules have been calculated and the molecular orbital energy level diagram has been analyzed. Moreover, from application areas of electronics, these wires have to be covered by other insulator molecule such as Cyclodextrins (CDs) (3). Although, electrical conducting wire itself have a good conductivity, the conducting wire in CDs is transformed and a conductivity is very sensitive of molecular structure. In order to examine the structure of conducting wire, we calculate the energies of various structures of conductive polymer in framework of CD molecules and investigate the conductivity using Greens function method. This study was performed through Special Coordination Funds of the Ministry of Education, Culture, Sports, Science and Technology of the Japanese Government.

(1) A. Aviram and M.A. Ratner, Chem. Phys. Lett. Vol. 29, 277 (1974).

(2) C. Majumder, H. Mizuseki, and Y. Kawazoe, J. Phys. Chem. A, Vol. 105 (2001) 9454-9459.

(3) R.V. Belosludov, H. Mizuseki, K. Ichinoseki, and Y. Kawazoe, Jpn. J. Appl. Phys., in press.

#### **P4.15**

**DEVELOPMENTS OF NEW OLED WITH SAMARIUM COMPLEX AS EMISSION LAYER.** R. Reyes, E. Hering, M. Cremona, Depto. de Física, Pontifícia Universidade Católica do Rio de Janeiro, PUC-Rio, BRAZIL; C.F.B. da Silva, H.F. de Brito, Instituto de Química, Universidade de São Paulo, BRAZIL; Sung Hoon Kim, Dept. of Dyeing and Finishing, College of Engineering, Kyungpook National University, KOREA.

Organic light emitting diodes (OLEDs) represent today an active and promising area for the development of new optoelectronic devices. In this work the results of the growth and of the electrical and optical characterization of a new emitting OLEDs produced in our laboratory are presented. The devices are formed using a heterojunction between three organic molecular materials: a 40 nm thickness film of 1-(3-methylphenyl)-1,2,3,4 tetrahydroquinoline-6-carboxyaldehyde-1,1-diphenylhydrazone, working as a hole transporting molecular layer (HTL), a 40 nm thick layer of samarium complex, tris( $\alpha$ -thenoyl-trifluoroacetato)bis(triphenylphosphine oxide) samarium (Sm(TTA)<sub>3</sub>(TPPO)<sub>2</sub>) working as light-emitting layer and finally by another 45 nm thick layer of tris 8-hydroxyquinoline aluminum (Alq<sub>3</sub>), which is the electron transport layer (ETL). The device is grown in high vacuum environment ( $6 \times 10^{-6}$  Torr) on glass substrates coated with an hole injecting indium tin oxide (ITO) transparent layer. Finally, an electron injecting Al electrode (150 nm) is deposited onto the system. Polarizing the ITO as anode and the Al as cathode it was possible to observe the electroluminescence (EL) of the device at room temperature and to built the EL curve as a function of the applied bias voltage. Due to the Sm, the EL is peaked around 600 nm and the OLED red/orange light emission is almost linear with the current density. The I-V curves show an exponential dependence of I as a function of the applied voltage, as it is expected for a semiconductor diode. Measurements of optical absorption and photoluminescence (PL) as a function of different excitation wavelengths were performed in the OLED device and in the single layers of HTL, emission layer samarium complex and ETL. An investigation about the device

degradation as a function of the environmental conditions and optical and electrical excitation is also reported.

This work is supported by PADCT-CNPq, FAPERJ and FAPESP.

#### **P4.16**

**FULLY CONJUGATED 3-SUBSTITUTED POLYTHIOPHENE MATRICES FOR INORGANIC NANOPARTICLES.** Shaun Wright, Peter Skabara, Department of Chemistry, The University of Manchester, Oxford Road, Manchester, UNITED KINGDOM.

Nanoparticles of inorganic semiconductors, Quantum Dots (QD's), have emerged as potential materials for electronic and optoelectronic devices. QD's consist of an inorganic core which is passivated by an organic Lewis base group, i.e. tri-n-octylphosphine oxide (TOPO), to avoid degradation and agglomeration of the particles. Due to the physical nature of the particles device fabrication is difficult and expensive, requiring techniques such as MOCVD to form epitaxially grown layers of crystalline material. An alternative method is to incorporate the quantum dots within a supporting conjugated polymer matrix allowing films to be cast from solutions or melts whilst maintaining charge conduction through the bulk material. Well defined polymers based on 3-substituted thiophenes conduct electricity, whilst remaining stable to oxygen and moisture in both the doped and undoped states. Substitution at the 3-position not only increases solubility of the polymer but also allows the incorporation of Lewis base groups, i.e. phosphonates, which are able to replace the organic capping groups on the nanoparticles.

#### **P4.17**

**STUDY OF THE ELECTRONIC TRANSPORT OF PENTACENE FILMS BY PHOTOCONDUCTIVITY AND PHOTO THERMAL DEFLECTION SPECTROSCOPY.** Dietmar Knipp, Xerox Palo Alto Research Center, Palo Alto, CA; Reinhard Carius, Josef Klomfass, Research Center Juelich, Institute of Photovoltaics, Juelich, GERMANY.

The performance of pentacene TFTs is strongly affected by defects. The origin of the defects is not completely understood. Photoconductivity (PC) and photo thermal deflection spectroscopy (PDS) are powerful tools to study the band structure and defects in thin films. From sub band gap absorption information about defects and ordering of the material can be derived, which is of particular interest for electronic properties of the films. In particular, photoconductivity spectroscopy provides information about the transport and recombination of optically excited carriers. The method is therefore sensitive to all optical transitions in the band and in the sub band gap region that provide mobile carriers. Photo thermal deflection spectroscopy is based on the measurement of the heat created by the light absorbed in the sample and equally sensitive to all optical transitions. It is therefore complementary to photoconductivity and a combination of both methods gives additional insight into electronic processes in this material. We have applied these methods to study polycrystalline pentacene films with mobilities between  $10^{-3} \text{cm}^2/\text{Vs}$  and  $0.5 \text{cm}^2/\text{Vs}$ . Pentacene films with different grades of impurity were prepared between room temperature and  $80^\circ\text{C}$ . The thermal evaporated films exhibit four distinct absorption bands in the vicinity of 2.0eV in PC and PDS similar for all samples. The absorption coefficient is on the order of  $3\text{-}8 \times 10^4 \text{cm}^{-1}$ , which is similar to other materials of interest for thin film electronics or optoelectronic applications. At lower energies the absorption drops by more than three orders of magnitude independent of the deposition temperature, which indicates low levels of impurities in the material. The quantum efficiency of the photoconductivity is almost identical for all characterized samples and in good agreement with the PDS measurements, i.e. all optical excited carriers contribute to the photocurrent spectrum.

#### **P4.18**

**EDMR OF MEH-PPV LEDs.** George B. Silva, Carlos F.O. Graeff, DFM-FFCLRP-USP, Ribeirão Preto, BRAZIL; Lucas F. Santos, Roberto M. Faria, IFSC-USP, São Carlos, BRAZIL.

Light-emitting diodes (LEDs) based on conjugated polymers have advanced rapidly as a viable and valuable application to display technologies. In this work, electrically detected magnetic resonance (EDMR) is used to study the electronic transport properties of LEDs based on poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) (MEH-PPV). The LED consisted of ITO-coated glass, spin coated MEH-PPV using chloroform, and thermally evaporated Al. Typical MEH-PPV film thickness was around 360 nm. In an EDMR experiment, microwave-induced changes in the conductivity are measured as the sample is subjected to a swept dc magnetic field. The measurements were done using a modified, computer interfaced Varian E-4 X-Band spectrometer in the temperature range of 145 K to 300 K. Seven diodes ITO/MEH-PPV/Al have already been investigated with different emission efficiency. The EDMR signal is found to be composed of two lines, a lorentzian with peak-to-peak linewidth of 5



G, and a gaussian with peak-to-peak linewidth of 24 G. The g-factor of both components is about 2.002. The EDMR signal amplitude is typically  $10^{-5}$ , and only observed at forward bias, for  $V > 10$  V. The signal is a quenching, and assigned to the spin-dependent fusion of two like-charged polarons to spinless bipolarons. The relative amplitude of those components was found to be dependent on light emission efficiency of the diode. The lorentzian, which is dominant for bad emitter, is proposed to come from positive polarons, while the gaussian line to negative polarons. The attribution is based on lineshape analysis, polaron mobility, and temperature dependence of the EDMR signal. Results of EDMR performed on LEDs with different cathodes (Al, Ca, Mg and Ag) will also be presented. The process of carrier injection and polaron transport will be discussed. FAPESP and CNPq support this work.

#### **P4.19** ANISOTROPY OF PHYSICAL PROPERTIES AS THE PRINCIPAL CHARACTERISTIC OF POLYMER COMPOSITES.

A.T. Ponomarenko, A.V. Buts, V.G. Shevchenko, Enikolopov Institute of Synthetic Polymeric Materials RAS, Moscow, RUSSIAN FEDERATION; V.S. Travkin, UCLA, Los Angeles, CA; A.L. Gusev, All-Russian Institute of Experimental Physics, Sarov, RUSSIAN FEDERATION.

A great amount of accumulated experimental data shows that one of the principal characteristics of different types of materials is the anisotropy of the properties of their components and resulting anisotropy of the properties of the material itself. In both homogeneous and heterogeneous systems, it is practically always possible to single out different types of anisotropy at consecutive levels of hierarchy. In investigation of anisotropy hierarchical approach is especially applicable to composite materials from polymers and different fillers, such as chemical fibers with high concentration of hexaferrites of different structural types and natural ferromagnetic resonance frequency in the range 1-40 GHz. In magnetic composites the properties are complex functions of volume fraction of magnetic component, its particles size, shape and distribution in the matrix volume. The effect of spinning conditions and concentration of ingredients on the structure, mechanical and electrodynamic properties of composite fibers is described in detail. High tensile strength of the fibers is reached by optimizing spinning conditions for the type, content and dispersion of filler. Important parameters, which determine the properties of composite are discussed, such as the type of crystallographic magnetic anisotropy and the size of filler particles, affecting the stability of spinning process, uniformity, porosity, magnetic texture of the fibers, as well as their mechanical and electrophysical properties. Additional treatment of drawn fibers reduces their porosity and significantly increases magnetic texture, which results in higher magnetic losses. The fibers were used in thin fabric structures, effective as shielding materials for millimeter and centimeter wavelength ranges. Anisotropy effects of conductivity were investigated in heterogeneous systems of different dimensionality, 1D composites (continuous conducting fibers), 2D composites (multilayered structures of conducting fibers), 3D composites (short conducting fibers). Effect of processing conditions on orientation of conducting species and resulting anisotropy of conductivity is investigated. Methods of controlling anisotropy in different directions are proposed and discussed in connection with particular structure of the composite material.

#### **P4.20** EFFICIENT LIGHT EMITTING DEVICES UTILIZING QUANTUM DOTS IN ORGANIC HOST MATRICES. Wing Woo, MIT

Department of Chemistry, Cambridge, MA; Seth Coe, Department of Electrical Engineering and Computer Science, Cambridge, MA; Professor Mounji Bawendi, MIT Department of Chemistry, Cambridge, MA; Professor Vladimir Bulovic, Department of Electrical Engineering and Computer Science, Cambridge, MA.

We demonstrate efficient electroluminescence from core-shell CdSe(ZnS) quantum dots (QDs) dispersed in an organic thin film structure. The QDs are doped in various concentrations into a N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) solution, which is spin-cast onto a clean, ITO coated glass substrate. Tris-(8-hydroxyquinoline) aluminum (Alq<sub>3</sub>) is then thermally evaporated onto the TPD:QD layer, followed by a Mg:Ag/Ag cathode. The devices are manipulated in a controlled nitrogen environment, with moisture and oxygen content of <1 ppm. These devices have external quantum efficiencies as high as 0.5% at 10mA/cm<sup>2</sup>. At 125mA/cm<sup>2</sup>, the LED luminance is 1500cd/m<sup>2</sup> at a peak wavelength of 570nm, which corresponds to a luminescence efficiency of 1.25 cd/A. This is a 20 fold improvement over the best previously reported result [1]. Yields over the hundreds of devices that we have made are greater than 90%, indicating a robust material system. Superposition of the small molecular organic Alq<sub>3</sub> and the QD emission spectra reproduces the electroluminescence signature of the device. The QD peak emission wavelength may be tuned from

500nm to 650nm without modifying the device structure. By varying QD concentrations in the doped film, the ratio of QD to Alq<sub>3</sub> emission intensity is tunable from zero to five. QD deep trap emission is observed at the LED turn-on, but quickly saturates at low current densities. This allows for the creation of high brightness, high color purity QD-LEDs. Our analysis indicates that excitons are created on the QD sites by charge trapping. The exciton dynamics are confirmed by the time resolved photoluminescence measurements on these hybrid structures, indicating a small probability of exciton energy transfer between molecular organics and QDs.

1. M.C. Schlamp, X. Peng, A.P. Alivisatos. J. Appl. Phys. 82, 11 (1997).

#### **P4.21** TWO-PHOTON ABSORPTION AND FLUORESCENCE OF EFFICIENT CONFORMATIONALLY TUNED CHROMOPHORES. Lixin Zheng, Takafumi Sassa, Alex K-Y. Jen, University of Washington, Dept. of MS&E, Seattle, WA.

A new series of symmetric two-photon absorbing chromophores with donor- $\pi$  bridge-donor (D- $\pi$ -D) motif were synthesized. Their two-photon absorption (TPA) properties were characterized by two-photon induced fluorescence technique using femtosecond pulse excitation. These chromophores exhibited both high fluorescence quantum efficiencies (> 0.7) and high TPA cross-section (>1000 GM). The study on the structure/property relationships showed that high TPA cross-sections could be achieved in the chromophores with twist  $\pi$ -bridges. The relationships between TPA properties with transition dipole moment and state ordering are also discussed. Moreover, strong spectrally narrowed emission was observed for the chromophores with naphthyl and binaphthyl moieties. This spectral narrowing feature is proved to be via a superradiant lasing mechanism.

#### **P4.22** NON-LITHOGRAPHIC FABRICATION OF POLYMERIC ELECTRONIC DEVICES USING INKJET PRINTING.

Michael L. Chabinc, William S. Wong, Kateri Paul, Raj B. Apte, Robert A. Street, Xerox Palo Alto Research Center, Palo Alto, CA; Ping Liu, Yiliang Wu, Beng S. Ong, Xerox Research Center of Canada, Mississauga, ON, CANADA.

Organic semiconductors are an attractive alternative to inorganic semiconductors because of the potential for a lower processing cost and their superior mechanical properties. We are developing non-lithographic methods to fabricate polymeric transistors using inkjet printing, a non-contact patterning technique that can produce micron scale features. We will report our results on the development of chemical deposition conditions for thin film transistors (TFTs) containing multiple layers of polymers. Control over feature sizes of polymeric layers can be achieved using surface treatments that modify the surface energies of both glass and polymeric substrates. For example, we have found that thin films (< 5nm) of poly(ethyleneimine) improve the wetting of aqueous solutions of PEDOT/PSS, an organic conductor, on both glass and polymeric substrates. The performance of regio-regular polythiophene-based TFTs fabricated using these procedures will be presented.

#### **P4.23** TOWARDS DESIGN OF AIR-STABLE POLYTHIOPHENES FOR THIN FILM TRANSISTORS. Beng Ong, Ping Liu, Yiliang Wu, Lu Jiang, Krish Murti, Sandra Gardner, Xerox Research Centre of Canada, Mississauga, Ontario, CANADA; Raj Apte, Robert Street, Xerox Palo Alto Research Center, Palo Alto, CA.

Polymeric semiconductors such as polythiophenes have attracted growing interest for their potential in fabricating low cost large-area and flexible electronic components. While regioregular poly(3-alkylthiophenes) have exhibited high mobility of up to about 0.2 cm<sup>2</sup>/Vs, they are nevertheless not air-stable, and over time they lose their field-effect transfer properties due to oxidative doping. We present here the design and synthesis of several classes of solution-processable polythiophenes which exhibit reasonably good field-effect transfer properties and air-stability. Bottom-gate thin film transistors with these polymers fabricated under ambient conditions have provided mobility up to about 0.02 cm<sup>2</sup>/Vs and current on-off ratio up to about  $5 \times 10^6$ . More importantly, these devices have shown enhanced resistance to oxidative doping in the presence of atmospheric oxygen.

SESSION P5/G3: JOINT SESSION  
ORGANIC DISPLAYS AND DEVICES  
Chairs: Sue Anne Carter and Paul S. Drzaic  
Wednesday Morning, April 3, 2002  
Franciscan II/III (Argent)

### 8:00 AM \*P5.1/G3.1

HYDROSTATIC PRESSURE DEPENDENCE OF THE ELECTRICAL PROPERTIES OF PENTACENE AND TETRACENE. Zhenlin Rang, P. Paul Ruden, and Marshall I. Nathan, University of Minnesota, Department of Electrical and Computer Engineering, Minneapolis, MN; Reid J. Chesterfield and C. Daniel Frisbie, University of Minnesota, Department of Chemical Engineering and Materials Science, Minneapolis, MN; Paul F. Baude and Dawn Muires, 3M Company, St. Paul, MN.

Pentacene and tetracene exhibit unusually high mobilities for organic semiconductors. However, the transport mechanisms that give rise to these mobilities is not understood. Moreover, the achievable values of the mobilities are not known. Therefore, a study of mobility as a function of molecular separation or pressure appears to be useful. Pentacene and tetracene show readily observable photoconductivity when illuminated with light in the blue part of the visible spectrum. We measured the change of photoconductivity with hydrostatic pressure in single crystal samples of both materials. Possible mechanisms for the observed increase in photoconductivity with pressure are discussed. We conclude that a carrier mobility increase under pressure is most likely to cause the increase in photoconductivity in the case of pentacene. For tetracene, changes in the absorption spectrum in the range of the excitation wavelengths may also be significant. We observe a phase transition near 0.3GPa in tetracene, in agreement with previous results. We have also studied the effect of pressure on the electrical characteristics of organic (pentacene) field effect transistors (OFETs). From the OFET measurements we obtain field effect mobility. The results from the photoconductivity measurements and the OFET measurements will be compared.

### 8:30 AM P5.2/G3.2

PENTACENE THIN FILM TRANSISTORS AND CIRCUITS: INFLUENCE OF PROCESSING AND DEVICE DESIGN. Dietmar Knipp, Robert A. Street, Brent Krusor, Jackson Ho, Xerox Palo Alto Research Center, Palo Alto, CA.

The electronic transport of thermal evaporated pentacene TFTs and circuits on neutral substrates will be presented. Since organic TFTs fabricated on thermal oxide are not of particular interest for large area and/or low cost applications, alternative dielectrics and processing methods consistent with thin film technology have been investigated. The influence of the dielectrics on the structural and electronic properties of pentacene films and TFTs will be discussed. For all applied dielectrics, we observed a strong correlation between morphology and structural properties of the pentacene films and the mobility of the TFTs. In the case of inorganic dielectrics like plasma enhanced chemical vapor deposited (PECVD) silicon nitride and silicon oxide the growth of pentacene is mainly determined by the roughness of the dielectric. The roughness inhibits the ordering of pentacene molecules on the surface. However, by optimizing the fabrication process of the dielectrics, we have achieved similar pentacene mobilities on PECVD dielectrics and thermal oxide ( $0.4 \text{ cm}^2/\text{Vs}$ ), without employing self-assembled monolayers like octadecyltrichlorosilane (OTS). With an OTS treatment of oxide based dielectrics the mobility increases by a factor of 2-3 up to  $>1 \text{ cm}^2/\text{Vs}$  for thermal oxide. Despite the high mobility for inorganic dielectrics, organic dielectrics are more attractive because the dielectric can be spin coated or inkjet printed. We have studied the growth of pentacene on poly-vinyl phenol (PVP) and bisbenzocyclobutene (BCB). The films on organic dielectrics are highly ordered, which is confirmed by structural and transport measurements. For pentacene films on inorganic and organic dielectrics we find similar mobilities of  $0.3\text{-}0.5 \text{ cm}^2/\text{Vs}$  and high on/off ratios between  $10^6$  and  $10^8$ . Different device designs will be discussed towards all-organic circuits on flexible substrates.

### 8:45 AM \*P5.3/G3.3

POLYMER LED DISPLAYS BUILT ON PLASTIC SUBSTRATES. Marie O'Regan, Mark Sellars, Blanca Lopez, Michel Dubeau, Napatat Juanko, Ralph Martinez and Alan Heeger, UNIAX Corporation, Santa Barbara, CA.

Emissive displays built on plastic substrates provide some major advantages to the display industry over glass-based displays, specifically in terms of weight, ruggedness, profile and form factor. Polymer LED (PLED) displays are being developed at UNIAX/DuPont; we have successfully built and demonstrated prototype displays on plastic substrates. Progress in the development of flexible PLED displays will be summarized. This talk will focus on some of the remaining challenges, including barrier properties and substrate patterning.

### 9:15 AM P5.4/G3.4

A NOVEL APPROACH FOR ADDRESSING PRINTED,

### ALL-POLYMER ELECTROCHROMIC DISPLAY CELLS.

Thomas Kugler, Linköping University, Dept. of Science and Technology, and Acreo AB, Norrköping, SWEDEN; Tommi Remonen, Anna Malmström, Jessica Hall, Björn Knuthammar, Lars-Olov Hennerdal, Acreo AB, Norrköping, SWEDEN; Magnus Berggren, Linköping University, Dept. of Science and Technology, and Acreo AB, Norrköping, SWEDEN.

We report on a completely novel approach for addressing the electrochemically active elements in conducting polymer-based devices. The principle is illustrated with our latest results on printed, all-polymer electrochromic displays realized on flexible substrates such as paper or plastic foil. The displays are based on lateral patterns of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrene sulfonic acid) (PSS), which is used both as conducting and electrochromic material. The key feature in our displays is the fact that the electrochromic material is not in direct contact with a conducting electrode. Instead, at least two, remote electrodes are used to apply an electric field across a slab of electrolyte interfacing an electrochromic element consisting of PEDOT-PSS. Based on the fact that PEDOT-PSS is conducting in the oxidized, optically transparent state, the presence of the electric field results in a polarization of the electrochromic element and the onset of electrochemistry: the edge adjacent to the (remote) cathode is oxidized further, whereas the edge adjacent to the (remote) anode is reduced to deep blue, neutral PEDOT. The concomitant reduction in conductivity results in a deep blue coloration front advancing from the negatively polarized edge towards the center of the electrochromic element. By modifying the ionic conductivity within the electrolyte along the electrochromic element, both dynamic and bi-stable switching can be realized. The displays operate at low voltages in the range 1-5 V, depending on geometrical parameters and the ionic conductivity of the electrolyte. Both gelled water-based and solid electrolytes have been tested. We will present different basic device architectures for realizing printed electrochromic display cells together with the factors determining the switching speed, coloration intensity, and lifetime of these devices.

### 9:30 AM P5.5/G3.5

POLYMER LIGHT-EMITTING DIODE DISPLAYS DRIVEN BY INTEGRATED NANOBLOCK IC DRIVERS. Jan Bernkopf, Yijian Shi, Diane Choquette, Alien Technology Corporation, Morgan Hill, CA.

Polymer light-emitting diode (PLED) displays can be operated in either passive matrix or active matrix mode. Passively-addressed displays, while suitable for many applications, are limited in pixel count and in size. Active matrix displays can achieve higher pixel densities, but require high quality and expensive polysilicon circuitry. Here, we describe an alternative addressing approach for PLEDs, using high quality, inexpensive CMOS circuitry. The single crystal silicon circuitry is built onto a wafer using standard CMOS foundries, and then converted to numerous small, square (360 microns on one side) NanoBlock ICs. These NanoBlock ICs are assembled onto glass sheets using Alien Technology Fluidic Self Assembly process. In this approach, the tiny NanoBlock IC drivers are uniformly distributed (and embedded) into the display backplane. Each driver is driving the nearest eight pixels locally (each pixel receives a maximum of  $180 \mu\text{A}$  of current). In this paper, we will demonstrate the successful synergy of NanoBlock IC/FSA process with light emitting polymers as basis for high-performance emissive displays. Material compatibility between the NanoBlock IC process and the PLED fabrication process is demonstrated. NanoBlock ICs can be deployed into many types of substrates, including plastic, showing a path for high quality silicon to drive future PLED displays on plastic.

### 10:15 AM \*P5.6/G3.6

ORGANIC BISTABLE DEVICE AND MEMORY CELLS. Liping Ma, Jerry Liu, Seungmoon Pyo, Faye Xu, Yang Yang, Univ of California-Los Angeles, Los Angeles, CA.

Electrical bistability is a phenomenon in which a device exhibits two states of different conductivities, at the same applied voltage. In this presentation, we report a novel organic electrical bistable device (OBD) comprising of a thin metal layer embedded within the organic material, as the active medium. The performance of this new device makes it attractive for memory cell type of applications. The two states of the OBD differ in their conductivity by about 107 and show remarkable stability, i.e. once the device reaches either state, it tends to remain in that state for a prolonged period of time. More importantly, the high and low conductivity states of an OBD can be precisely controlled by the application of a positive voltage pulse (to write) or a negative voltage pulse (to erase), respectively. One million writing-erasing cycles for the OBD have been achieved in ambient conditions without significant device degradation. These discoveries pave the way for newer applications, such as low-cost, large-area, flexible, high-density, electrically addressable data storage devices.

**10:45 AM \*P5.7/G3.7**

PLASTIC ORGANIC LIGHT EMITTING DISPLAYS. P.E. Burrows, W.D. Bennett, C.C. Bonham, G.L. Graff, M.E. Gross, M.G. Hall, E.S. Mast, P.M. Martin, D.W. Matson and M.R. Zumhoff, Pacific Northwest National Laboratory, Richland, WA; M.S. Weaver, J.A. Silvernail, A.B. Chwang, R.H. Hewitt, S.Y. Mao, L.A. Michalski, T. Ngo, M.R. Nugent, K. Rajan, M.A. Rothman, and J.J. Brown, Universal Display Corporation, Ewing, NJ.

Rapid degradation of organic light emitting devices (OLEDs) is observed in the presence of even low concentrations of moisture. In most conventional OLED displays described to date, this problem is addressed by encapsulating devices grown on glass or silicon using a glass or metal lid sealed to the substrate by means of an adhesive, typically a UV-curable epoxy product. Desiccant is often added to the package to absorb both residual moisture from the fabrication process and moisture diffusing through the epoxy seal. Pixels with > 10,000 hours of operating lifetime at video brightness have thereby been demonstrated. If we are to utilize the advantages of plastic substrates, however, this type of encapsulation approach is flawed due to the high moisture permeability of the substrate itself. In this paper, we describe a process to deposit transparent, flexible, organic-inorganic multilayer thin film barriers onto commercially available polymers by a hybrid process of cryo-condensation and polymerization of an organic precursor from a flash evaporation source followed by vapor deposition of a nanoscale barrier layer. The multilayer hybrid barrier restricts moisture and oxygen permeation rates to levels not measurable by conventional technology while retaining a high degree of flexibility and transparency. Residual permeation is dominated by pinholes rather than bulk diffusion, rendering large area permeation measurement techniques such as MOCON difficult to interpret. We will present further results of work to quantify a spatially resolved permeability of ultrabARRIER plastic substrates by observing the degradation of thin films of reactive metals. Furthermore, we will present operating lifetime results from various high efficiency electrophosphorescent small molecule OLEDs grown on moisture barrier substrates and show that better than 3,000 hours of operation is achievable at display brightnesses. Based on our results, we project that video-brightness plastic displays with better than 10,000 hours of operating lifetime are achievable.

**11:15 AM P5.8/G3.8**

POLYMER LIGHT EMITTING DISPLAYS AND PHOTO-VOLTAICS ON FLEXIBLE SUBSTRATES. H. Tillmann, H.-H. Hoerhold, University of Jena, Institute for Organic and Macromolecular Chemistry, Jena, GERMANY; S. Tuttle, Add-Vision Inc., Scotts Valley, CA; M.A. Kreger, T. Omabegho, S.A. Carter, University of California Santa Cruz, Dept of Physics, Santa Cruz, CA.

Polymer light-emitting diodes, light-emitting electrochemical cells and photovoltaics on flexible substrates have been fabricated and their electrical and optical properties have been characterized. Various device structures are discussed with reference to cost effective construction, optimum performance and display stability. Electrical properties and electroluminescence spectra have been measured for poly phenylene vinylene (PPV) and polyfluorene (PF)-based materials on several different flexible substrates, including PET and flexible glass, and compared with similar devices on thick glass. Stability of polymer light emitting devices has been monitored in both a dry nitrogen atmosphere and on encapsulated devices in air atmosphere. Aging-dependent Current-Voltage-Radiance measurements, complimented by atomic force and fluorescent microscopy images, allow us to determine the primary device degradation mechanisms, which may include electrode delamination, irreversible chemical reactions, air/water migration at impurities and defects, and polymer chain breakage. We also will present our work on the performance of photovoltaics consisting of conjugated PPV-based polymers cast on TiO<sub>x</sub> sol gel and nanoparticle layers on flexible substrates. The stability of the polymer layer to photobleaching under solar condition and the effect of the TiO<sub>x</sub> morphology on polymer stability and performance will also be addressed. We will conclude by discussing the optimization of polymer-based optoelectronic devices for manufacturing inexpensive printable large-area displays and detectors on flexible substrates.

**11:30 AM \*P5.9/G3.9**

CHARGE INJECTION AT THE METAL-ORGANIC INTERFACE. J. Campbell Scott, Luisa. D. Bozano and Amelia R. Span, IBM Almaden Research Center, San Jose, CA.

The performance of virtually every type of organic electronic device depends on the efficiency of charge injection from metallic electrodes into the semiconducting organic material. In the cases where there is no chemical reaction between the metal and the organic, it has been shown that the injected current is proportional to charge carrier

mobility in the organic layer, with a field dependence that is dominated by Schottky barrier lowering. The net injected current can be described theoretically as the difference between the injection current (metal to semiconductor) and the surface recombination current (semiconductor to metal). The charge density on the interface layer of organic molecules is given by a thermal occupation probability, provided that the net current flow is low compared to the surface recombination term. We describe additional experimental tests of this description using chemical modification of the metal surface to alter the nature of the interface states.

SESSION P6/G4: JOINT SESSION  
ORGANIC TRANSISTORS

Chairs: Paul S. Drzica and Sue Anne Carter  
Wednesday Afternoon, April 3, 2002  
Franciscan II/III (Argent)

**1:30 PM \*P6.1/G4.1**

DIRECT PRINTING OF POLYMER TRANSISTOR CIRCUITS. Henning Sirringhaus, University of Cambridge, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

Polymer transistor circuits offer new opportunities for the controlled manufacturing of active electronic circuits by a combination of solution processing and direct printing. Control over the morphology of the polymer semiconductor is obtained by making use of self-organisation mechanisms, such as liquid-crystalline phase behaviour. Accurate definition of the transistor channel and other circuit components is achieved by high resolution printing techniques such as surface energy-assisted inkjet printing. Here we will discuss recent progress towards new architectures and the controlled definition of high performance polymer transistors.

**2:00 PM P6.2/G4.2**

JET PRINTING FOR THE FABRICATION OF ORGANIC-BASED THIN FILM TRANSISTORS. Kateri E. Paul, William S. Wong, Steve Ready, Michael L. Chabynyc, Raj B. Apte, Xerox Palo Alto Research Center, Palo Alto, CA; Beng S. Ong, Ping Liu, Yiliang Wu, Xerox Research Centre of Canada, Mississauga, Ontario, CANADA.

The expense and difficulty of fabricating large-area thin-film transistor (TFT) arrays for applications such as flat panel displays or imager arrays has led to the development of alternative fabrication methods including direct-write methods such as jet printing. The spatial control of jet printing makes it an ideal technology for direct writing of materials. We fabricated a-Si:H TFTs using printed wax masks in place of conventional lithography. Bottom-gate TFTs with source-drain contacts overlapping the channel were created using a printed three-mask process. These TFTs have I-V characteristics comparable to photolithographically patterned devices, with mobility of 0.6-0.9 cm<sup>2</sup>/Vs, threshold voltage of 2-3 V, and on/off ratios exceeding 10<sup>7</sup>, for devices with channel lengths below 50 μm. We are exploring the efficacy of jet printed organic semiconductors. Using conventional semiconductor processing techniques we have fabricated TFT devices using regioregular polythiophenes as the semiconductor; preliminary device characteristics show mobility on the order of 10<sup>-3</sup> cm<sup>2</sup>/Vs. We will describe a method for fabricating organic semiconductor-based TFTs by jet printing, discuss the critical parameters in the printing process that affect feature size and resolution, and compare the organic TFTs fabricated by jet printing with devices fabricated by other methods.

**2:15 PM P6.3/G4.3**

THE INVESTIGATION OF USING CONTACT AND NON-CONTACT PRINTING TECHNOLOGIES FOR ORGANIC TRANSISTOR FABRICATION. Jie Zhang, Paul Brazis, Abhijit Roy Chowdhuri, John Szczech, Dan Gamota, Motorola, Schaumburg, IL.

Low-cost and high-volume manufacturing processes are envisioned for solution processable organic semiconductor integrated circuits fabrication. The organic IC may be the low-cost solution for driving communication devices, i.e., smart cards, RFID tags, flexible displays, and personal-area and body-area networks. This study is investigating the use of commercially-available contact and non-contact printing technologies to fabricate organic transistors in a non-clean room manufacturing environment without the use of vacuum processing. The contact printing technologies investigated were pad printing and screen printing; the non-contact printing technologies were ink jetting and micro dispensing. The material system selection for transistor structures and layers was based on printing technology requirements and commercial availability. The materials were polymer thick film conductors and insulators, conductive nanoparticle suspensions, and organic polymer systems. A series of material property characterization and printing process development were conducted. As a result, several OFET designs were fabricated and the all-printed organic

transistors were repeatedly shown to be functional. The electrical performance was evaluated and will be discussed.

### 2:30 PM P6.4/G4.4

EFFECT OF DIELECTRIC SURFACE ON CARRIER MOBILITY IN POLYMER SEMICONDUCTORS. A. Salleo, M.L. Chabinyk, W.S. Wong, K.E. Paul, R.B. Apte, and R.A. Street, Xerox Palo Alto Research Center, Palo Alto, CA; B.S. Ong, P. Liu, Y. Wu, L. Jiang, Xerox Research Centre of Canada, Mississauga, Ontario, CANADA.

The use of semiconducting polymer films in transistor devices has become increasingly interesting as their carrier mobilities approach  $1 \text{ cm}^2/\text{Vs}$ . In general, mobility in polymers is found to increase with interchain ordering. Because they can be solution-processed, polymers are appealing for large-area applications. Deposition methods include spin-coating, dip-coating and jet-printing. However, since none of these operations is carried in vacuum, the processing history of the dielectric surface prior to the deposition of the semiconductor has a large effect on carrier mobility in the polymer. In this study we characterize promising semiconducting polymers (e.g. polyfluorene and regio-regular polythiophene). Both inorganic and organic dielectrics are tested. When possible, the dielectric/semiconductor interface is modified by adsorption of functionalized monolayers. The flexibility of this approach allows to control surface energy and can be used to promote specific chemical interactions with the semiconductor. For instance alkylation of the oxide surface leads to an increase in carrier mobility in F8T2 from  $3.10\text{-}4 \text{ cm}^2/\text{Vs}$  to approximately,  $6\text{-}8.10\text{-}3 \text{ cm}^2/\text{Vs}$ , higher than the reported mobility of isotropic F8T2 [ $3\text{-}5.10\text{-}3 \text{ cm}^2/\text{Vs}$ ]. As most samples show bias stress effects a pulsed bias technique is used to measure transistor characteristics. The deposition process is expected to play a role in the ordering of the polymer as well. Therefore, the interplay of surface preparation and deposition technique in optimizing carrier mobility for FET devices will be explored.

### 2:45 PM P6.5/G4.5

CRITICAL CONSIDERATIONS IN POLYMER TFT DIELECTRICS. Munira Raja, Giles Lloyd, Naser Sedghi, Bill Eccleston, Department of Electrical Engineering and Electronics, University of Liverpool, Liverpool, UNITED KINGDOM; Raffaella Di Lucrezia, Simon Higgins, Department of Chemistry, University of Liverpool, Liverpool, UNITED KINGDOM.

Gate dielectrics form a critical part in the design of TFTs for integration into displays and other circuits. Obviously the use of thermally grown  $\text{SiO}_2$  is impractical in real devices, as is used for the majority of test devices. It remains, however, the standard to which most dielectrics are compared. There is an increasing demand, as TFT properties improve, to find a more suitable dielectric for large-scale integration of polymer TFTs. Such a dielectric needs to be compatible with fabrication procedures and not prone to high leakage, as  $\text{SiO}_2$  is known to be in polymeric devices. We propose the use of anodised aluminium as the gate dielectric. Anodisation as opposed to gaseous deposition allows for complicated growth procedures such as oxide growth on a vertical wall. This is essential for production of ultra-fast vertical channel TFTs. Presented is a comparison of aqueous and plasma anodisation techniques of aluminium and their performance in electronic devices compared with that of  $\text{SiO}_2$ . Particular emphasis is placed on the I-V and C-V analysis of the oxides. Oxide leakage current is observed to increase by up to 4 orders of magnitude with deposition of the polymer onto the oxide. This is also observed in  $\text{SiO}_2$  dielectrics with polymer as the semiconductor. Leakage currents are also observed to increase when the polymer is doped with DDQ. C-V analysis shows good oxide formation giving reasonable quality MOS structures in all cases. A frequency dependence of the accumulation layer is observed for all oxides. It has been suggested that this is a relaxation effect of charge carriers in the polymer. These relaxation effects are believed to be associated with charge carrier dynamics and analysis enables charge carrier mobility to be determined.

### 3:15 PM P6.6/G4.6

MODELING OF I-V CHARACTERISTICS IN ORGANIC TFTS. A.R. Völkel, R.A. Street, D. Knipp, Xerox Palo Alto Research Center, Palo Alto, CA.

Recent interest in organic electronics has led to the development of a wealth of organic semiconducting materials suitable for making thin film transistors (TFT). While experimental methods can reveal many valuable insights into the properties of these transistors, it is often hard to extract definite answers on the distribution of potential barriers and/or trap states without the knowledge of an appropriate physical model. We have developed a computer model that allows us to study the impact of various trap state distributions on the transport properties of thin film MOS structures. Though this model describes only some aspects of a complete transistor structure, it allows us to explicitly study the correlation of threshold and onset

voltages, as well as the shape of I-V curves, on concentration and distribution of inter-band states. In particular, we compare our results to experiments performed on poly-crystalline pentacene TFT's which were thermally evaporated onto a bottom gate structure with a CVD grown dielectric. Our calculations show that we can describe many of the experimentally observed I-V curves very well with two different sets of low-lying inter-band states: (1) a narrow (0.1 eV) exponential distribution of donors and (2) a broader (0.5 eV) Gaussian distribution of acceptors. The donor states account for the shift of the threshold voltage and are most likely due to some residual disorder in the pentacene film. The acceptor states account for the current onset at positive gate voltages and the model also suggests that these states are localized near the dielectric interface. The model is used to analyze the changes in the pentacene TFT characteristics that are induced by illumination and bias-stress effects. The analysis of data from transistors based on polymeric organic materials will also be discussed.

### 3:30 PM \*P6.7/G4.7

ORGANIC MATERIALS FOR MULTIFUNCTIONAL TRANSISTOR-BASED DEVICES. H.E. Katz, T. Someya, B. Crone, X.M. Hong, A. Dodabalapur, A. Gelperin, Bell Laboratories-Lucent Technologies, Murray Hill, NJ.

For many applications of organic transistor-based electronics, properties other than semiconductor mobility may be more important than mobility itself. In this work, we consider four applications: an electrophoretic pixel switch, a complementary inverter, a simple nonvolatile memory element, and a chemical sensor array, and discuss the particular device and material properties that need to be optimized for each one. The pixel switch requires minimal off current, the inverter depends on an ambipolar transistor pair, the memory depends on a dielectric-semiconductor pairing in which both charge storage and threshold voltage adjustment occur, and the sensor is based on reversible and selective chemical interaction between an analyte and the semiconductor. Achievements reported here include a dynamic range  $>10$  for the inverter and memory element, and sensory discrimination between organic functional groups such as alcohols and ketones. Deposition of semiconductors including thiophene/phenylene co-oligomers and NTCIDs from solution and device operation in the presence of air and solvents are emphasized.

### 4:00 PM P6.8/G4.8

STRATEGIES FOR ORGANIC INTEGRATED CIRCUITS - NOVEL SURFACE MODIFICATIONS FOR HIGH PERFORMANCE DEVICES. Tommie W. Kelley, Dawn Muyres, Dennis Vogel, Kim Vogel, Paul Baude, Mark Pellerite, Tim Dunbar, Larry Boardman, Todd Jones, Terry P. Smith, 3M Company, Science Research Center, St. Paul, MN.

We show novel and selective means to modify the dielectric surfaces in organic TFTs. Modification schemes include alkyl phosphonic acid monolayers which have a strong affinity for alumina surfaces. Monolayers form robust, extremely uniform thin films and are deposited through simple washing with a dilute solution of the monolayer precursor in solvent. Adding monolayers to organic TFTs has resulted in polycrystalline devices with mobilities nearly equal to single crystal values, while maintaining other device parameters (for example, threshold voltage, on/off ratio and subthreshold slope) required for fully functional integrated circuits.

### SESSION P7: PHOTOVOLTAICS

Chair: Niyazi Serdar Sariciftci  
Thursday Morning, April 4, 2002  
Franciscan II/III (Argent)

### 8:00 AM \*P7.1

EFFICIENT ORGANIC PHOTODETECTORS AND PHOTOVOLTAICS. Stephen Forrest, Peter Peuman, Aharon Yakimov, Princeton Univ, Dept of Electrical Engr, Princeton, NJ.

We have found that multiple heterojunctions can be used in photodetectors to obtain high efficiency organic photodetectors and photovoltaic cells, as well as very high bandwidth operation. In a double heterojunction photovoltaic cell, photogenerated excitons are confined by the appropriate choice of boundary layers within the zone containing the donor-acceptor interface[1]. The exciton dissociates at the interface, thereby producing the required electron and hole pair which are detected in the external circuit. Using a double heterostructure employing a BCP exciton blocking layer adjacent to a CuPc/C60 D-A interface, we demonstrate a high efficiency organic photovoltaic cell with an external power efficiency of 3.6% at AM1.5G solar radiation of  $150 \text{ mW}/\text{cm}^2$  intensity[2]. To our knowledge this is nearly a factor of two higher efficiency than any previous

demonstrations for organic photovoltaics. Using light trapping geometries, we anticipate nearly a doubling of this efficiency. Furthermore, increasing the diffusion length of excitons in the cell by growing organic thin films with increased order should also lead to an enhancement in efficiency, perhaps eventually approaching that of inorganic semiconductor cells. We have also found that stacking multiple heterojunctions separated by "exciton recombination zones", high open circuit voltages equal to the product of that of a single junction cell by the number of cells in a stack can also lead to high efficiency solar energy conversion. Finally, we discuss a high efficiency (~80%), high bandwidth (~450MHz) organic photodetector consisting of multiple very thin ( $\approx$  each) alternating D-A interface layers[3]. By such a layering scheme, excitons are always photogenerated very near to a dissociating interface. This reduces the diffusion time needed for transport the excited state to that interface, and hence significantly reduces the opportunity for nonradiative recombination while increasing the device operational bandwidth.

[1] P. Peumans, V. Bulovic and S.R. Forrest, *Appl. Phys. Lett.*, 76, 2650 (2000).

[2] P. Peumans and S.R. Forrest, *Appl. Phys. Lett.*, 79, 126 (2001).

[3] P. Peumans, V. Bulovic and S.R. Forrest, *Appl. Phys. Lett.*, 76, 3855 (2000).

### 8:30 AM \*P7.2

PHOTOINDUCED ENERGY AND ELECTRON TRANSFER IN CONJUGATED DONOR-ACCEPTOR ARRAYS: MOLECULES AND MATERIALS FOR PHOTOVOLTAICS. René A.J. Janssen, Stefan C.J. Meskers, Alicia Marcos Ramos, Edda E. Neuteboom, Edwin H.A. Beckers, Paul A. van Hal, Jeroen K.J. van Duren, Eindhoven University of Technology, THE NETHERLANDS; Joop Knol, Minze T. Rispens, Jan C. Hummelen, University of Groningen, THE NETHERLANDS.

Of particular importance to polymer solar cells is the mechanism of charge separation and recombination. We have studied molecular and polymeric systems in which p-conjugated fragments as a donor are connected to fullerenes or perylenes as an acceptor via covalent or hydrogen bonds. Photovoltaic devices of these covalent and supramolecular systems have been characterized. Various spectroscopic techniques, including ultrafast femtosecond pump-probe spectroscopy, have been used to study the formation and recombination of the charge-separated state in these systems. Studies on oligomer-fullerene dyads as model compounds for polymer/fullerene blends revealed that in solution the electron transfer occurs in a two-step mechanism. Subsequent to a sub-picosecond singlet-energy transfer, electron transfer occurs on a 10 ps timescale, resulting in a charge-separated state with a lifetime of 50 ps. In thin solid films of these dyads, a much longer-lived charge-separated state is formed after photoexcitation. Surprisingly, charge-separation in thin films occurs in one step and energy transfer is not observed. The long lifetime in the film is attributed to the migration of charges to different molecules. The increase in lifetime could be modeled using a triad prepared using a fullerene and two donor segments connected in series. Results on other donor-acceptor systems reveal that the different behavior of molecules and molecular materials is a general phenomenon and that electron and energy transfer processes are competing on short time scales in general, the actual process and its rate depends strongly on the mutual orientation of the two segments in space.

### 9:00 AM P7.3

A NANOCOMPOSITE GEL ELECTROLYTE MADE BY THE SOL-GEL ROUTE FOR A SOLID-STATE DYE-SENSITIZED PHOTOELECTROCHEMICAL CELL. Urška Lavrenčič Štangar, Angela Šurca Vuk, Boris Orel, National Inst of Chemistry, Ljubljana, SLOVENIA; Panagiotis Lianos, Univ of Patras, Engineering Science Dept, Patras, GREECE; Philippe Colomban, LADIR, CNRS and Paris VI Univ, Thiais, FRANCE.

Graetzel's discovery that ruthenium bipyridyl derivatives can efficiently sensitize titanium dioxide nanocrystalline films with visible light and the subsequent construction of a Dye-Sensitized Photoelectrochemical Cell (DSPEC) has instigated a great deal of research in several laboratories. A standard configuration of DSPEC encompasses  $\text{TiO}_2$  sensitized with a ruthenium bipyridyl complex and a thin semitransparent Pt electrode. The gap between the electrodes is filled with a liquid electrolyte containing a redox couple, usually  $\text{I}_3^-/\text{I}^-$  in an aprotic solvent. Because the liquid electrolyte creates serious sealing problems, efforts were done to substitute a liquid electrolyte with a thin solid film conductors. This work describes the construction and the performance of a DSPEC made of solid components in a thin sandwich configuration. Its main component is a gel electrolyte made through the sol-gel route by gelation of a poly(propylene glycol) modified alkoxy silane precursor (ICS-PPG) with acetic acid in the absence of water. The structure and interactions of the organic-inorganic hybrid with  $\text{I}_2$ , KI and  $\text{KI}+\text{I}_2$  were studied using infrared ATR measurements. Temporal ATR

spectra were employed to follow the sol-gel transitions of ICS-PPG revealing the two-step reaction mechanism of the alkoxy groups with the acetic acid. Using the micro Raman technique we recorded the resonance Raman spectra of the hybrid conductor that was encapsulated in a DSPEC. The intensity variations of the  $\text{I}_3^-$  and  $\text{I}_2$  resonance Raman bands served as a probe to follow changes of the redox components during the operation of the DSPEC under open-circuit and short-circuit conditions. I/U characteristics of the DSPEC with ICS-PPG/KI+ $\text{I}_2$  were measured revealing that the cell efficiency was of about 4%. The utilization of the thin film sol-gel hybrid conductor with incorporated  $\text{I}_3^-/\text{I}^-$  redox couple for the construction of an electrochromic device was demonstrated on  $\text{WO}_3/(\text{I}_3^-/\text{I}^-)$  conductor/ Pt electrochromic cell.

### 9:15 AM P7.4

TUNING TO THE SOLAR SPECTRUM WITH ORGANIC AND INORGANIC HYBRID SOLAR CELLS. Wendy U. Huynh, Janke J. Dittmer, A. Paul Alivisatos, University of California at Berkeley, Dept of Chemistry, Berkeley, CA.

Semiconductor nanorod and conjugated polymer blend photovoltaic devices join both the processing advantages of polymers and the stability and efficient charge transport of inorganic materials. The combined advantages of these organic and inorganic materials were realized in the fabrication and design of a novel series of highly efficient photovoltaic devices with tunable absorption. We constructed a set of devices from CdSe and CdTe nanorods and poly-3(hexylthiophene) in which the absorption onset was tailored from 600 nm to 820 nm. Since these nanorods exhibit quantum confinement effects, the band gap can be adjusted by just altering the radius of the particles. Devices were fabricated with power conversion efficiencies of up to 2% under AM 1.5 Global conditions. This work demonstrates that it is possible to construct tandem solar cells with a series of band gaps using simple processing conditions.

### 9:30 AM P7.5

TRANSIENT TERAHERTZ EMISSION FROM CONJUGATED POLYMER PHOTOCONDUCTIVE ANTENNA. Daniel Moses and Cesare Soci Institute for Polymers and Organic Solids University of California, Santa Barbara, CA.

We report on Terahertz (THz) emission from conjugated polymer (poly (phenylene vinylene), PPV) generated by means of ultrafast transient photocurrent. The THz antenna was in the form of an Auston switch made of a stretched-oriented PPV film that was photoexcited by femtosecond laser pulses. The THz spectroscopy was measured using autocorrelation technique in which the time integrated THz intensity was measured by a bolometer as a function of the time lag between two coherent laser pulses generated by a Michelson interferometer. The observed THz emission gives insight into the underlying carrier generation and dynamics promptly following the carrier photoexcitation. Our results demonstrate that the carriers are generated at time shorter than our temporal resolution <100fs. Moreover, comparing the results obtained from the PPV samples to those from single crystal GaAs indicates that the carrier mobility promptly following excitation (i.e. at  $t \sim 100$  fs) is many orders of magnitude larger than the one typically measured at longer time scales.

### 9:45 AM P7.6

IMPROVED EFFICIENCIES IN POLYMER - PERYLENE DIIMIDE BILAYER PHOTOVOLTAICS. Alison Breeze, Ashley Salomon, David Ginley, and Brian Gregg, National Renewable Energy Laboratory, Golden, CO; H.-H. Horhold, Friedrich-Schiller-Universitat, Jena, GERMANY.

We have explored the use of small molecule organic / polymer composites in the form of a perylene diimide / polymer bilayer in order to combine the advantageous properties of both materials. Using the electron transporting perylene benzimidazole (PBI) and the hole conducting polymer poly[2,5-dimethoxy-1,4-phenylene-1,2-ethynylene-2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-1,2-ethynylene (M3EH-PPV), we have achieved increased power conversion efficiencies for a planar device of up to 1.4% under one sun. By varying the order of the photoactive layers and the values of the electrode workfunctions, we have probed the mechanisms creating the photovoltage. We have found that the photovoltage is not determined by the difference in electrode workfunctions alone. The interfacial chemical potential gradient, caused by exciton dissociation at the perylene diimide / polymer interface, and the formation of a p-n heterojunction are both possible mechanisms which appear to more strongly influence the photovoltage than the internal field caused by the electrodes in these devices. We also discuss why, contrary to some expectations, the perylene diimide / polymer devices are more efficient than the analogous pure small molecule perylene diimide / phthalocyanine cells.

**10:00 AM P7.7**

PHOTOVOLTAIC CELLS MADE FROM SEMICONDUCTING POLYMERS IN SELF-ASSEMBLED MESOPOROUS TITANIA FILMS. Kevin Coakley, Yu-Xiang Liu, Michael Preiner, Michael McGehee, Stanford University, Dept. of Materials Science, Palo Alto, CA; Karen Frindell, Galen Stucky, University of California Santa Barbara, Dept. of Chemistry, Santa Barbara, CA.

Previous studies have shown that efficient photovoltaic cells can be made by filling films made of titania nanocrystals with conjugated polymers. When light is shone on these devices, the polymer absorbs light and then donates its photoexcited electron to the titania. This charge separation helps prevent geminate recombination, which is what limits the efficiency of single component organic photovoltaic cells. After the charge transfer, electrons are carried by the titania to one electrode and holes are carried by the polymer to the other electrode. One of the limiting factors on the performance of these polymer/titania devices is that the titania and polymer networks are both disordered. Consequently, charge carriers have to travel over unnecessarily large distances and can be trapped at dead ends. In addition, because of the relatively low porosity of these films, the films must be made quite thick (1 - 10  $\mu\text{m}$ ) in order to absorb a significant fraction of the incoming light. We have used block copolymers as structure directing agents to make well-ordered nanoporous titania films via sol-gel chemistry. These films are much more porous than those that are made with titania nanocrystals and can therefore absorb a lot more polymer. This makes it possible to make much thinner photovoltaic cells. The ordered films also provide straighter channels for charge transport. We have incorporated polymers into the nanopores by diffusion from melts, diffusion from solution and polymerization of monomers directly in the pores. X-ray photoelectron spectroscopy (XPS) depth profiling was used to show that the polymers penetrate all the way into the nanoporous titania films. Preliminary measurements show that photovoltaic cells made with these films have significantly higher energy conversion efficiency than control devices that were made in our lab with solid titania instead of the nanoporous titania. We are in the process of optimizing these devices.

**10:30 AM \*P7.8**

OPEN-CIRCUIT VOLTAGE CHARACTERISTICS OF POLYMER HETEROJUNCTION SOLAR CELLS. C.M. Ramsdale, A.C. Arias, J.D. MacKenzie, R.H. Friend and N.C. Greenham, University of Cambridge, Department of Physics, Cambridge, UNITED KINGDOM.

The open-circuit voltage of photovoltaic devices is important in determining the power efficiency. In polymer photovoltaic devices it is often assumed to arise from the difference in workfunction of the two electrodes. However, in some device structures open-circuit voltages are found to exceed the predicted value. This implies the presence of additional sources of electric field within the device, either in the bulk or due to dipole formation at the polymer/metal interfaces. In the field of polymer semiconductors, blends and bi-layers of electron and hole acceptors are used to achieve the most efficient devices. Hence in this work the origin of the open-circuit voltage is studied in bi-layer devices based on polyfluorenes. The devices were fabricated using a lamination technique, which avoids the problems that usually arise when making well-defined bi-layers from soluble polymers. ITO/PFB/F8BT/Al devices, for example, exhibited an open-circuit voltage of 1.5V despite the workfunction difference between the electrodes being only 0.5V. This 1V difference is also observed when copper, chromium or gold is used as the cathode. We conclude that this additional open-circuit voltage is largely a result of a photo-induced dipole at the donor-acceptor interface. This dipole is formed by charges that are separated as a result of exciton dissociation when the device is illuminated. Devices where the order of the polymer layers was reversed showed very different open-circuit voltages, close to the difference between the workfunctions of the electrodes. This confirms that the open-circuit voltage is heavily dependent on the structure of the active layer in the device. The effects of temperature and excitation intensity on open-circuit voltage will also be discussed.

**11:00 AM P7.9**

FABRICATION AND CHARACTERIZATION OF POLYMER-BASED PHOTOVOLTAIC DEVICES INCORPORATING RIGID-ROD MACROMOLECULES. Michael F. Durstock, Jeff Franklin, Marc Mecoli, Air Force Research Lab, AFRL/MLBP, Wright-Patterson Air Force Base, OH; Barney E. Taylor, University of Dayton Research Institute, Dayton, OH.

Photovoltaic devices based on donor/acceptor complexes of organic materials are fast becoming recognized as a potentially viable, low-cost alternative to the more traditional devices based on inorganic materials. We have been examining the fabrication of these devices using alternative materials based on rigid-rod, electron accepting macromolecules. These have included BBL (a benzimidazole-benzo-

phenanthroline ladder polymer), PBZT (poly(benzobisthiazole)), and carbon nanotubes. A variety of device architectures have been examined to determine the suitability of these materials as components in photovoltaic devices. These have included simple two-layer test structures, to the more complex, blended structures for improved device performance. PBZT is believed to be an n-dopable polymer and as such exhibits a large electron affinity and has been used as the electron accepting species in devices. Similarly, BBL has a very large electron affinity and attempts have been made to create a blended structure between it and PPV, the electron donating species for improved performance. Carbon nanotubes have also been examined by incorporating them into the electron accepting layer. As such, they appear to act as three-dimensional extensions of the top electrode into the uppermost layer of which they are a part.

**11:15 AM P7.10**

ELECTRONIC PROPERTIES OF POLYMER-FULLERENE SOLAR CELLS STUDIED WITH LIGHT-INDUCED ELECTRON SPIN RESONANCE AND ADMITTANCE SPECTROSCOPY. V. Dyakonov, I. Riedel, C. Deibel, J. Parisi, Univ of Oldenburg, GERMANY; J.C. Hummelen, Stratingh Institute and MSC, Univ of Groningen, THE NETHERLANDS; J. De Ceuster, E. Goovaerts, Univ of Antwerp, BELGIUM.

Within recent years, the development of polymer-fullerene plastic solar cells has made significant progress. In such devices, an efficient charge generation takes place via photoinduced charge transfer between the photoexcited conjugated polymer and acceptor-type fullerene molecules. Due to the paramagnetic nature of the radical species, the photoinduced charge transfer can be studied by means of light induced electron spin resonance (LESR) techniques. We carried out W-band (95 GHz) LESR at high magnetic field strengths. Two well separated line groups with a strong anisotropic structure were detected for the composite MDMO-PPV:PCBM. From the analysis of the line shape, we obtained an environmental axial symmetry for the positive polaron P+ and a lower, rhomboedric symmetry for the fullerene anion. The signals were found to be independent of each other with different spin-lattice relaxation times. In order to study the bulk transport properties, we carried out admittance spectroscopy on the ITO/PEDOT:PSS/MDMO-PPV:PCBM/Al device. Two frequency-dependent contributions to the device capacitance with the activation energies 10 meV and 180 meV were found. For the very shallow trap state, we assume a bulk impurity, whereas the latter one is assigned to an interfacial defect state, located at the composite-aluminium interface.

**11:30 AM \*P7.11**

THE INFLUENCE OF THE MICROSTRUCTURE UPON THE PHOTOVOLTAIC PERFORMANCE OF MDMO-PPV:PCBM BULK HETERO-JUNCTION ORGANIC SOLAR CELLS. T. Martens, T. Munters, Z. Beelen, D. Vanderzande, L. De Schepper, Instituut voor Materiaal Onderzoek (IMO), Limburgs Universitair Centrum (LUC), Diepenbeek, BELGIUM; J. D'Haen, L. Goris, J. Manca, M. D'Oleslaeger, D. Vanderzande, L. De Schepper, IMEC, Division IMOMEC, Diepenbeek, BELGIUM; R. Andriessen, Agfa-Gevaert NV, Mortsel, BELGIUM.

Particular interest in the recent wave of breakthroughs in the development of plastic electronics goes out to the field of bulk donor-acceptor hetero-junction solar cells. In these solar cells, the active layer consists of a blend of a donor and an acceptor material. Most recent devices have a power conversion efficiency of 2.9% under AM1.5 using MDMO-PPV and PCBM, a soluble C60 derivative. Key issues in these devices with good performance are to have a good charge separation, good transport to the opposite electrodes and to prohibit recombination, all in which morphology can play an important role. Using Atomic Force Microscopy (AFM), the surface morphology and phase separation behaviour of MDMO-PPV:PCBM blends, as used in bulk hetero-junction solar cells, can be studied. For the first time, a clear view on the inner microstructure of these blends was obtained by means of Transmission Electron Microscopy (TEM). Planar view and cross-sectional view TEM studies result in 3-dimensional information on phase-separated regions, formed during casting. Particle statistics illustrate quantitatively that a.o. drying conditions and the choice of casting solvent dramatically influence the blend structure. It will be proven that control over the morphology of these blends leads to control over photovoltaic performance. The information achieved by TEM in addition to AFM, makes this an excellent tool for understanding and upgrading today's organic solar cells and for screening new sets of materials and blends.

SESSION P8: DEVICES—PHYSICS AND  
ENGINEERING

Chair: Alex K-Y. Jen

Thursday Afternoon, April 4, 2002

Franciscan II/III (Argent)

**1:30 PM P8.1**

CHARGE MOTION AND TRAPPING IN MOLECULAR DOPED HOLE TRANSPORTERS. H.H. Fong, K.C. Lun, and S.K. So, Dept of Physics, Hong Kong Baptist Univ, Hong Kong, CHINA.

The charge transporting properties of of N',N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD), TPD doped with rubrene, TPD doped with DCM1, and other organic charge transporters were examined by time-of-flight (TOF) technique, and by current-voltage measurements between 180-300K. At room temperature, the hole mobility for pristine TPD was in the range of  $2 \times 10^{-3}$  cm<sup>2</sup>/Vs. Doping TPD with rubrene reduced the hole mobility to about 1/3 of the original values; doping TPD with DCM1 reduced the hole mobility substantially to about 5% of the original values. The TOF time transients remain non-dispersive for both kind of doped samples. The dependence of the mobility on electric field and temperature for undoped and doped TPD was investigated. Undoped TPD exhibited a weak field dependence while the DCM1-doped TPD exhibited a much stronger field and temperature dependence. It is proposed that DCM1 molecules act as deep hole traps in TPD while rubrene molecules in TPD behave as shallow traps. The Gaussian Disorder Model (GDM) is applicable to describe transport in both pristine TPD and rubrene-doped TPD. For DCM1-doped TPD, GDM appears not to be valid. The results indicate that DCM1 dopant introduced deep traps that substantially influence the energy distribution of TPD.

**1:45 PM P8.2**

SPIN-DEPENDENT RECOMBINATION IN PPV AND POLYFLUORENE LEDs. Anoop Dhoot, Neil Greenham, University of Cambridge, Cavendish Laboratory, Cambridge, UNITED KINGDOM.

In a polymer light-emitting diode, the fraction of excitons formed as singlets is of crucial importance in determining the quantum efficiency. We have shown that it is possible to measure excited state absorptions due to triplet excitons and polarons in working polymer LEDs, and we are able to quantify the triplet generation rate by measuring the strength of the triplet absorption. Here, we show that by careful study of singlet emission and triplet absorption in an LED based on a poly(it p-phenylenevinylene) derivative it is possible to obtain an accurate value of  $83 \pm 7\%$  for the singlet formation probability, significantly higher than the value of 25% predicted by simple spin statistics. We extend these measurements to devices based on poly(dioctyl-fluorene), where we find similarly high values for the singlet formation probability. In devices using the polyfluorene copolymer F8BT, we find that the triplet absorption is extremely small, consistent with even higher singlet formation probabilities. We also present temperature-dependent current-voltage measurements on these devices which allow the temperature dependence of the electron mobility to be determined in F8BT.

**2:00 PM P8.3**

ORGANIC LIGHT EMITTING DIODE WITH 'BLACK' CATHODE. Zugang Liu, Oleg Salata Department of Materials, University of Oxford, Oxford, UNITED KINGDOM.

An efficient organic light emitting diode with improved contrast has been fabricated by introducing an absorbing and conducting carbon film between electron injecting layer and the aluminium cathode. Different vacuum deposition techniques such as resistive thermal evaporation, electron beam evaporation and glow discharge were evaluated for the purpose of carbon film deposition in OLED. Further, we found that application of a magnetic field and substrate cooling can protect the underlying organic layer from the damage caused by the heat and irradiation with secondary electrons. The measurements of the absorption and the reflectivity of films, and the electro-luminescent performance of the devices have revealed that the electron injecting layer not only protects the organic layers, but also contribute to the contrast enhancement.

**2:15 PM \*P8.4**

USE OF ADJUSTABLE ANODES IN ORGANIC SEMI-CONDUCTOR DEVICES. Klaus Meerholz, Univ of Munich, GERMANY.

Spincasted PEDOT is often used as a hole conducting layer in polymeric semiconductor devices. The use of these layers has several advantages, but these films also suffer from a illdefined electronic work function. Our approach adjusts PEDOT electrochemically to a wide range of work functions. Evidence for the direct correlation between the doping level (electrochemical potential) and the resulting work function will be presented. The method offers a powerful new tool for optimization of different devices such as organic solar cells and OLEDs.

**2:45 PM P8.5**

DYNAMICS OF EXCITON DIFFUSION IN AMORPHOUS

ORGANIC THIN FILMS. Conor Madigan, Vladimir Bulovic, MIT, Dept. of EECS, Cambridge, MA.

We observe time-dependant red shifts in the spectra of Alq<sub>3</sub>:DCM2 and Zr<sub>q4</sub>:DCM2 thin films upon excitation by  $\lambda = 400$  nm, 1 ps laser pulses. For DCM2 concentrations between 0.5% and 10%, we observe shifts in the peak emission energy of between 0.08 eV and 0.12 eV during the 4 ns window following excitation. In this report, we show that these shifts can be attributed to the diffusion of excitons throughout the film by means of Förster energy transfer between inhomogeneously distributed DCM2 molecules. We present a theoretical model detailing this mechanism, and demonstrate that simulation results are consistent with our experimental data. The diffusion mechanism we propose assumes the presence of significant variations in the peak energy of the individual DCM2 molecular spectra within the film, and we present spectroscopic data supporting this assumption. Based on our theory, the observed spectral shifts are found to be an effective probe of the density of exciton energy levels for DCM2 molecules in both polar (Alq<sub>3</sub>) and non-polar (Zr<sub>q4</sub>) hosts.

**3:15 PM \*P8.6**

PERFORMANCE OF INJECTION-LIMITED POLYMER LIGHT-EMITTING DIODES. Paul W.M. Blom, Teunis van Woudenberg, Materials Science Centre and DPI, University of Groningen, THE NETHERLANDS; Hans Huiberts, Philips Research Laboratories, Eindhoven, THE NETHERLANDS.

Injection-limited hole currents from Ag into poly(p-phenylene vinylene) exhibit a strongly reduced temperature dependence. This is explained by an injection model which is based on hopping from the electrode into the localized states of PPV. The device characteristics of PPV based light-emitting diodes with an injection limited hole contact have been studied. It is demonstrated that the generated current and light-output strongly exceed the predictions based on the limited hole injection. This performance enhancement is explained by interface traps which increase the electric field and resulting injection efficiency at the injection limited hole contact.

**3:45 PM \*P8.7**

ANOMALOUS EXCIPLEX STATES FORMED BY NONBONDED N-ORBITALS IN ELECTRONIC POLYMER BLENDS AND BILAYERS. Arthur J. Epstein, Frank C. Delucia, Jr., Erica M. Kylo, Terry L. Gustafson and Daïke K. Wang, Ohio State University, Columbus, OH.

Photoexcited bound exciplexes generated at interfaces in bilayers and blends of hole and electron transporting polymers are unusual and differ from excitons formed by photoexcitations of bulk polymers. Exciplex emission conventionally is expected to be red-shifted from the emission of both polymers forming the interface. We present the first time resolved temperature and wavelength dependent studies of the photoluminescence decay of exciplex states that form at the interface of polyvinylcarbazole and pyridine containing polymers and compare these results to the emission from single layers of conducting polymers. Surprisingly the exciplex emission is intermediate in wavelength as compared to the emission of the two polymers comprising the interface. Further, the exciplex emission has little temperature dependence or spectral shift with decay time. These data demonstrate that the photophysics of the exciplex differ from that of excimers and aggregates. We propose that the exciplex is a highly localized state based on the highest occupied molecular orbitals of each of the two polymers and the non-bonded orbital of the nitrogen in pyridine interacting with the carbazole moieties. We compare the dynamics of emission of exciplex states confined at the interface of two polymers to the dynamics of emission of excitons confined in short conjugated chromophores of segmented block co-copolymers, for which near-unity temperature independent quantum efficiencies are obtained.

Supported in part by Office of Naval Research.

SESSION P9: POSTER SESSION  
ORGANIC BASED MATERIALS AND DEVICES II

Chair: Junji Kido  
Thursday Evening, April 4, 2002  
8:00 PM  
Metropolitan Ballroom (Argent)

**P9.1**

MECHANISMS FOR NEAR-IR EMISSION FROM PHTHALOCYANINE- AND NAPHTHALOCYANINE-DOPED SINGLE LAYER OLEDs: ENERGY TRANSFER VS. CHARGE TRAPPING FOLLOWED BY "CROSS-REACTIONS". Ware Flora, Neal Armstrong, University of Arizona, Department of Chemistry, Tucson, AZ.

Understanding the mechanism of doping in organic light-emitting diodes, and extending the emission of these devices into the near-IR spectral region has led us to incorporate both phthalocyanine and naphthalocyanine dyes into single layer devices, based on either Al(q)3/PVK, or a higher electron affinity derivative, Al(q)3/PVK. The spectral overlap of these host quinolates with the guest dyes is weak, thereby providing for an opportunity to study the effects of charge trapping by the guest dye on the EL process. EL efficiencies appear to track with excess free energies for the radical cation/radical anion (PVK(+)/Guest(-)) cross-reactions, as determined from solution electrochemical studies, consistent with our previous studies of quinacridone doping of OLEDs.

#### **P9.2**

**NOVEL MATERIALS FOR SECOND HARMONIC GENERATION - SALTS OF L-VALINE AND SELENIC ACID.** Ivan Nemeč, Robert Gyepes, Zdenek Micka, Charles University of Prague, Faculty of Science, Dept of Inorganic Chemistry, Prague, CZECH REPUBLIC; Frantisek Trojanek, Charles University of Prague, Faculty of Mathematics and Physics, Prague, CZECH REPUBLIC.

In recent years, materials possessing non-linear optical properties, especially those exhibiting second harmonic generation (SHG) have received considerable attention due to their wide-ranging technical applications. A novel class of SHG active compounds based on hydrogen-bonded salts of inorganic oxyacids and polarizable organic cations seems to be very promising because of the higher SHG efficiency and better chemical and/or physical properties compared to the traditional classes of SHG active materials (i.e. inorganic salts or oxides and organic molecules). Di-L-valine selenate monohydrate (DVSe) was synthesized and intensively studied within the frame of searching for new SHG active salts. The methods of X-ray structural analysis and vibrational spectroscopy were used to explain bonding conditions in the crystals of the compound prepared. The crystal structure of DVSe, FTIR and FT Raman spectra of polycrystalline samples (in the range of 50-4000 cm<sup>-1</sup>) are reported and discussed. The results are compared to previously described tri-L-valine selenate (TVSe) [1]. Quantitative SHG measurements of DVSe and TVSe, relative to a powdered standard of urea, were carried on powdered samples of uniform thickness and particle size. The results are discussed with respect to crystal structures of both compounds.

References:

[1] I. Nemeč, Z. Micka: *J. Mol. Struct.* 563-564, 289 (2001).

#### **P9.3**

**ELECTRICAL CONDUCTIVITY BEHAVIOR OF HIGH IMPACT POLYSTYRENE/LIQUID CRYSTALLINE POLYMER/CARBON BLACK TERNARY SYSTEMS.** Roza Tchoudakov, Moshe Narkis, Technion, Dept of Chemical Engineering, Haifa, ISRAEL; Arnon Siegmann, Technion, Dept of Material Engineering, Haifa, ISRAEL.

Electrically conductive carbon-black (CB) particles tend to distribute non-uniformly in one of the phases, at the interface or both in immiscible polymer blends, depending on the components properties and on the melt processing parameters. The CB networks thus obtained lead to high conductivity levels at low CB contents. A liquid crystalline polymer (LCP) was selected as the dispersed phase in a binary polymer blend due to its polarity, unique rheological behavior, high orientability and fibrillation, and long relaxation times. High impact polystyrene (HIPS) was selected as the matrix polymer owing to its low surface energy and easy processability. The tendency of CB to locate upon LCP, which undergoes fibrillation, leads to the generation of co-continuous structures, with enhanced conductivity. The effects of blending temperature and the blends' composition on the resulting morphology were analyzed in light of the blends' rheological behavior and the resulting conductivity. Blends with 2 phr CB become conductive when a blend contains at least 10 wt.% LCP and it is processed at a relatively high temperature. The rheological behavior of the blends varies with composition in a complex manner. The level of shear rate used to produce extruded filaments affects their morphology and conductivity. At 20wt.% or higher LCP contents, at 2 phr CB, an almost constant conductivity throughout the whole studied shear rate range is observed. SEM studies show that the LCP domains are deformed and fibrillated, and the CB particles are located upon the LCP fibrils. This structuring, induced by the melt flow processing, results in the stable resistivity behavior of the HIPS/LCP/CB blends. The filaments of the studied ternary systems show an interesting resistivity behavior in contact with different chemicals, and may thus have a sensing capability of chemicals.

#### **P9.4**

**SELECTIVE ASSEMBLY OF SUPERMOLECULAR AGGREGATES FOR MOLECULAR DEVICES.** Shiyoshi Yokoyama, Takashi Yokoyama, Toshiya Kamikado, Yoshishige Okuno, Shinro Mashiko, Communications Research Laboratory, Kobe, JAPAN and National Institute for Materials Science, Nagoya, JAPAN.

Making patterns from molecular building blocks may ultimately lead to molecule-based devices. We show a new way to coax specially designed planner molecules to assembled into simple, controllable patterns on a surface [T. Yokoyama et al, *Nature*, 413, 619 (2001)]. Porphyrin building blocks are functionalized with 3,5-di-tert-butyl-phenyl groups and either one or two cyanophenyl groups. These molecules are deposited on a clean gold surface under ultra-high vacuum condition and then observed by a low-temperature scanning tunneling microscope (STM). STM images reveal that size and aggregation pattern are rationally controlled by tuning the non-covalent interactions between individual adsorbed molecules. The porphyrin molecules adsorbed on gold surface form monomers, trimers, tetramers, or extended wire-like structures. Finally molecular wires can be more than 100 nm long. We attributed these aggregation properties to their dipole nature of cyano groups, where porphyrins can undergo long-range dipole-dipole interactions, as well as hydrogen-bonding interactions. We demonstrate that these molecular systems are capable of extending useful electronic and optoelectronic functions.

#### **P9.5**

**HIGH OPEN CIRCUIT VOLTAGE PHOTOVOLTAIC DEVICES FROM CARBON NANOTUBE POLYMER COMPOSITES.** Emmanouil Kymakis, Gehan A.J. Amaratunga, Cambridge Univ, Engineering Dept, Cambridge, UNITED KINGDOM.

Recently, we demonstrated that the photovoltaic effect of a conjugated polymer, poly(3-octylthiophene) (P3OT), solar cell can be significantly improved upon the introduction of single-wall carbon nanotubes (SWNTs), as the electron acceptors into the polymer [1]. It is proposed that the enhancement in the photovoltaic properties is due to the introduction of internal polymer/nanotube junctions within the polymer matrix. The bulk-heterojunction solar cells show unusually high open-circuit voltage (Voc) values, which cannot be explained by the metal-insulator mode. In order to investigate the origin of Voc, we have prepared P3OT-SWNT based devices varying both the metal negative electrode and the nanotube dispersion. The Voc turns out to be substantially intensive to the work function of the metal. These results suggest that the photovoltaic characteristics being measured are mainly those of a positive electrode/ polymer/ nanotube MIM diode, with the metal negative electrode forming ohmic contacts to the nanotube percolation paths. Following the MIM model, the Voc of the cell would then be determined by the ITO-SWNT work function difference rather than that between the two electrodes. Similar investigation have also taken place for polymer-fullerene based solar cells [2]. The results support the view that a Fermi level pinning between the negative electrode and the nanotube, similar to that which occurs in the fullerene case, could be the origin of the ohmic-like behaviour of the nanotube-negative electrode contact. It is of great interest to study the correlation between this model and the experimental data from polymer-carbon nanotube solar cells.

[1] E. Kymakis, G.A.J. Amaratunga, *Applied Physics Letters* (24 Dec 2001 issue).

[2] C.J. Brabec, A. Cravino, D. Meissner, N.S. Sariciftci, T. Fromherz, M.T. Rispen, L. Sanchez, J.C. Hummelen, *Adv. Funct. Mater.* 2001, 11, No. 5, 374-380.

#### **P9.6**

**STUDIES TOWARDS THE DEVELOPMENT OF MOLECULES WITH SWITCHABLE HELICITY.** Homar S. Barcena, James W. Canary, New York University, Dept of Chemistry, New York, NY; Biao Liu, Michael V. Mirkin, Queens College-CUNY, Dept of Chemistry and Biochemistry, Flushing, NY.

Molecular switches are gaining recognition as possible building blocks for applications such as molecular electronics, optical displays, and nanomechanical devices. We have previously introduced the utility of chiroptical recognition on electronically switchable molecules, and are actively pursuing the potential for practical applications. This necessitates studying physical properties such as the rate of switching and complex stability in order to assess the development and applicability of our molecules.

We have shown that certain metal ion complexes of tripodal ligands exhibiting conformational enantiomerism can be biased to adopt single enantiomer, propeller-like structures when a chiral center is incorporated into the ligand scaffold. Since the ligand conformation is fluxional and dependent upon metal ion coordination, circular dichroism spectra of the ligand are highly dependent upon the identity and oxidation state of the metal ion, as well as on the coordination of counter ions of varied size and shape.

This presentation will focus on redox-induced inversion of helicity in Cu(I) and Cu(II) complexes of derivatives of amino acids and amino alcohols with two N-atom appended chromophores. Upon one-electron oxidation/reduction, the complexes display mirror image circular dichroism spectra. The unique chiroptical properties arise from an inversion of the orientation of the appended chromophores. The change in oxidation state induces an intramolecular ligand exchange



event that, in turn, inverts the propeller-like orientation of the three coordinated ligand arms through a gearing mechanism. Thus, an electrochemical event induces an inversion of an element of helical chirality in the molecule. This paper describes detailed examination of electrochemical switching of the compounds. The mechanism of this electrochemical event is related to a square-scheme type, and is studied using cyclic voltammetry and scanning electrochemical microscopy. The complexity of this system prompts other studies such as conductometric and circular dichroic titrations to further elucidate the behavior of these compounds in solution.

#### **P9.7** SEMICONDUCTOR NANOCRYSTAL-ORGANIC COMPLEXES: SOLUBLE BUILDING BLOCKS FOR PHOTOVOLTAICS.

Delia J. Milliron, Claire Pitois, Janke J. Dittmer, Wendy U. Huynh, Jean M.J. Frechet, A. Paul Alivisatos, University of California, Dept of Chemistry, and Lawrence Berkeley National Lab, Materials Science Division, Berkeley, CA.

Solar cells with an organic-inorganic composite active layer have been demonstrated using soluble semiconductor nanocrystals and a conjugated polymer. Inorganic nanocrystals can be ideal chromophores, exhibiting size tunable absorption covering the whole solar spectrum. Integrating nanocrystals with organic semiconductors creates a very large interface for charge transfer and facilitates solution processing. Such hybrid devices can combine the optical advantages of inorganic semiconductors with the flexibility and processibility of polymers. However, the extent to which these properties can be exploited depends critically on control of the interface between these dissimilar materials. Direct binding of thoughtfully designed organic molecules to the nanocrystals provides low level control. The resulting inorganic-organic complexes are the building blocks to assemble an optimal hybrid solar cell. Here we demonstrate the direct attachment of oligothiophenes to semiconductor nanocrystals. The resulting composite material absorbs a broad range of the solar spectrum and yields efficient charge transfer between the organic and inorganic components. These complexes can then be incorporated into solar cells to take advantage of this charge transfer to generate current.

#### **P9.8** CONTROLLED GROWTH OF HYBRID NANOMATERIALS.

Fatma Vatansever, Richard Vaia, Wright Patterson AFB, AFRL/MLBP, Dayton, OH.

Quantum dots (QDs) have attracted substantial interest due to their novel size dependent electronic and optical properties. Fine tuning of these properties as well as providing efficient processing and assembly methods are the key to success in various aerospace applications. This work examines surface modification of CdSe/ZnS and ZnSe/ZnS core-shell QDs. The core of the QDs is prepared by injecting the core components in a hot coordinating solvent (TOPO), precipitating and washing with MeOH. Subsequently, they are re-introduced into TOPO stabilized at 600C and the shell component, ZnS, is injected in small portions. Precipitation and washing with MeOH is the final work-up. The so-formed core/shell nanocrystals are ligated by a TOPO monolayer ensuring solubility and chemical processibility. Since the surfactant-QD bonding is relatively weak the surfactant can be exchanged from the QD surface due to mass action displacement with another surfactant. Mercaptoacetic acid is used to exchange the TOPO monolayer, which is further modified to render sites for ruthenium alkylidene catalyst attachment. The presence of the catalyst tethered directly to the QD surface is then used to grow an organic corona of organic nonlinear optical macromolecules. Since Ring Opening Metathesis Polymerization (ROMP) takes place at the strained-ring attached to the active chromophore monomer the later remains unchanged in the course of the polymerization reaction. FT-IR, NMR, TEM, and nonlinear transmission experiments, are used to characterize the materials at different synthetic steps.

#### **P9.9** TRIPLET-TRIPLET ENERGY TRANSFER IN PHOTO- CROSSLINKABLE DENDRIMERS. Seichi Furumi, Akira Otomo, Shiyoshi Yokoyama and Shinro Mashiko, Kansai Advanced Research Center, Communications Research Laboratory, Kobe, JAPAN.

Electronic energy transfers are categorized into two classes; Forster and Dexter ones. Current efforts have been focused on developing the Dexter (triplet-triplet) energy transfer induced by electron exchange in order to improve emitting efficiency of organic electroluminescences. This energy transfer process requires collision between donor and acceptor at each triplet excited state, and therefore occurs in a short range of 1.0 nm. Dendrimers, consisting of nanometric confined macromolecules with three-dimensional symmetry, is one of candidates to examine triplet-triplet energy transfer process in nanometer scale. We describe herein the synthesis of photocrosslinkable dendrimers with peripheral cinnamide residues, exhibiting

photoisomerization as well as photodimerization, and their photochemical and photophysical properties in solutions and polymer matrices. Photoirradiation with 313 nm gave rise to monotonous decrease in absorbance of trans-cinnamide at 270 nm as a result of both photoisomerization and photodimerization. The spectral analysis revealed the changes in photoproduct distribution of trans-, cis-isomerized and dimerized cinnamide groups as a function of the irradiation exposure energy. In the dilute solutions, the first-generation dendrimer displayed preferential formation of cis-isomer of the cinnamide while the photodimerization took place more favorably for the third- and fifth-generation dendrimers. The photochemical behavior was strongly depended on the dendrimer generation rather than the concentration, probably due to the extent of steric crowding among the cinnamide residues at terminal positions. Taking account of the fact that photodimerization of cinnamoyl derivatives occurs at a distance of ca. 4.0 angstrom between the neighboring molecules, the third- and fifth-generation dendrimers display intramacromolecular photocycloaddition even in fluid media. Furthermore, the third- and fifth-generation dendrimers show capturability of a benzophenone derivative into the macromolecules and triplet-triplet energy transfer in the photocrosslinkable dendrimers. This procedure of triplet-triplet energy transfer in dendritic molecules opens up way to design novel optical and electrical molecular devices.

#### **P9.10** TEMPERATURE DEPENDENT STUDY ON M3EH-PPV POLYMER PHOTOVOLTAIC DEVICES. Yuko K. Nakazawa, Sue A. Carter, Univ. of California-Santa Cruz, Dept. of Physics, Santa Cruz, CA; H. Tillmann, H.-H. Hörhold, Friedrich-Schiller-Univ Jena, Inst für Organische Chemie und Makromolekulare Chemie, GERMANY.

We will present our results on the temperature dependent I-V characteristics of poly[2,5-dimethoxy-1,4-phenylene-1,2-ethynylene-2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-1,2-ethynylene] (M3EH-PPV) based photovoltaic devices. The polymer photovoltaic devices consist of patterned ITO, a spun cast and sintered TiO<sub>x</sub> sol-gel layer, a spun cast M3EH-PPV polymer layer, and an evaporated Au electrode. The M3EH-PPV/TiO<sub>x</sub> interface serves as the electronic dissociating surface. The current-voltage curves are measured in a temperature controlled OXFORD cryostat in the range 200 - 400K, under illumination with InGaN (with peak emission at 505nm) light emitting diodes. The short circuit current, fill factor, and open circuit voltage (~1mA/cm<sup>2</sup>, ~50%, ~0.75V at 300K, respectively) are extracted from the data. We also measure the temperature-dependent hole-mobility through fits to space charge limited current at negative biases. These measurements will be analyzed to determine how changes in the carrier mobility affect device performance. An analytical model will be proposed for describing the effect of charge transport on polymer-based photovoltaics.

#### **P9.11** INVERTED TRANSPARENT OLEDs WITH DOPED CARRIER INJECTION AND TRANSPORT LAYERS. X. Zhou, M. Pfeiffer, J.S. Huang, J. Blochwitz, A. Werner, K. Leo, Institut für Angewandte Photophysik, Technische Universität Dresden, Dresden, GERMANY.

Conventional OLEDs having doped carrier injection layers with high conductivity exhibit extremely low driving voltages, which is due to the formation of radical anions and cations and ohmic contacts at the electrode interfaces [1,2]. For display drivers employing n-channel field effect transistors, it is desirable that the bottom contact of the OLEDs is the cathode. We report here AIQ-based inverted transparent OLEDs with ITO cathode as bottom contact. In order to reduce the driving voltage, both doped electron and hole injection layers were used. For improving efficiency and blocking dopant migration, both electron and hole blocking layers were inserted. The device structure is ITO / Li (1 nm) / Li doped BPhen (15 nm) / BPhen (5 nm) / AIQ (20 nm) / TPD (5 nm) / F<sub>4</sub>-TCNQ doped m-MTDATA (100 nm) / Au (10 nm). The OLEDs are about 50% transparent in the AIQ emission region and emit light from both sides with total external efficiency of above 1.5 cd/A when turned on. The operating conditions for first devices are (from the ITO side) 5.6 V operating voltage and 9.8 mA/cm<sup>2</sup> for a brightness of 100 cd/m<sup>2</sup>, and 7.8 V @ 72.8 mA/cm<sup>2</sup> @ 1000 cd/m<sup>2</sup>, respectively. Currently, we are optimizing the device parameters. [1] X. Zhou, M. Pfeiffer, J. Blochwitz, A. Werner, A. Nollau, T. Fritz, and K. Leo, Appl. Phys. Lett. 78, 410(2001). [2] J.S. Huang, M. Pfeiffer, A. Werner, J. Blochwitz, K. Leo and S.Y. Liu, Appl. Phys. Lett. (in press).

#### **P9.12** IN SITU STUDY ON THE RE-ORIENTATION PROCESS OF CONJUGATED POLYMER CHAINS UNDER ELECTRICAL BIAS IN POLYMER LIGHT-EMITTING DIODES. Tzung-Fang Guo, Yang Yang, University of California at Los Angeles, Department of MS&E, Los Angeles, CA.

A reflection-absorption Fourier transform infrared spectroscopy (RA-FTIR) experiment has been designed to in situ monitor poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene vinylene) (MEH-PPV) based polymer light-emitting diodes under stress test. The experimental results indicate that the plane of the conjugated pi-electron cloud in MEH-PPV tends to align parallel to the substrate. This rearrangement enhances the pi-pi electron coupling and lowers the device operating voltage under high current densities. To the best of our knowledge this is the first in situ study on the co-relation between device performance and the conformational transformation of a conjugated polymer. Correspondence should be addressed to yangy@ucla.edu.

#### **P9.13**

**THE SYNTHESIS OF HIGH SOLUBLE 1,4-DIALKOXY DERIVATIVES OF POLY(p-PHENYLENEVINYLENE).** Mikhail Belov, Igor Yakushchenko, Mikhail Kaplunov, Oleg Efimov, Inst of Problems of Chemical Physics, Chernogolovka, RUSSIAN FEDERATION.

The known procedure for the preparation of PPV dialkoxy derivatives [1] reveals a number of shortcomings which strongly restrict the application of such polymers in electroluminescent devices. This procedure requires large amounts of solvents (low concentrations of reagents) and does not allow molecular mass to be controlled. The polymer solutions are prepared by the ultrasonic method and even the resulting solutions are thixotropic, thus preventing the formation of thin films by spin coating. Additionally, the resulting polymers contain a noticeable amount of active chlorine, which lowers the performance of the devices. We found that polymerization of the same monomers under soluble bases in weak-polar media yields polymers fully soluble in organic solvents, and the addition of a small amount of tertiary alcohol provides molecular mass to be controlled from tens of thousands to hundreds of thousands units. Besides, the resulting polymers do not contain chlorine and their solutions are stable in time. We have fabricated an electroluminescent device based on MEH-PPV synthesized by us, which exhibits a lower ignition threshold and a higher quantum yield.

1. F.Wudl, et al. US Pat. 5189136.

#### **P9.14**

**TRIPHENYLENE BASED PPES- EXCITED STATE LIFETIME EXTENSION FOR ENHANCEMENT OF ENERGY MIGRATION.** Aimee Rose, Claus G. Lugmair, Timothy M. Swager, Massachusetts Institute of Technology, Cambridge, MA.

Triphenylene exhibits a long excited state lifetime due to a symmetrically forbidden ground state transition. Triphenylene chromophores were incorporated into a poly(phenyleneethylene) (PPE) backbone. This universally extended the lifetime of these polymers over their phenyl-based analogues. Energy migration in these materials was investigated through polarization spectroscopy. Greater depolarization ratios in triphenylene-based PPEs (TPPEs) indicate their extended lifetimes engender more extensive energy migration. Because we exploit energy migration mechanisms to amplify fluorescence quenching in response to trinitrotoluene (TNT), advancements achieved in photophysical properties in TPPEs have led to systems capable of rapid detection of this analyte at sub part-per-trillion levels. This approach has been extended to other systems in our laboratory, indicating a novel paradigm for modulating photophysical behavior of conjugated polymers.

#### **P9.15**

**ELECTROLUMINESCENCE- AND ELECTRICALLY-DETECTED MAGNETIC RESONANCE STUDY OF ELECTRO-PHOSPHORESCENT ORGANIC LIGHT EMITTING DEVICES (OLED'S).** G. Li and J. Shinar, Ames Laboratory - USDOE\* and Department of Physics and Astronomy, Iowa State University, Ames, IA; G. Jabbour, Optical Sciences Center & Department of MS&E, University of Arizona, Tucson, AZ.

The electroluminescence- and electrically-detected magnetic resonance (ELDMR and EDMR, respectively) of 2,3,7,8,12,13,17,18-octaethylporphine Pt (PtOEP)-based electrophosphorescent OLED's is described. At room temperature the measurements yield a negative (EL-quenching) spin 1/2 resonance similar to those exhibited by fluorescence-based OLED's. This resonance was concluded to result from magnetic resonance enhancement of the formation of negative bipolarons at the organic-cathode interface, which enhances the nonradiative quenching of singlet excitons (SE's) [1]. It is therefore suspected that similar quenching of SE's by charges at the organic/cathode interface may compete significantly with the transfer of the SE energy to TE's in the electrophosphorescent devices as well. Ames Laboratory is operated by Iowa State University for the USDOE under Contract W-7405-Eng-82.

[1] G. Li and J. Shinar, submitted.

#### **P9.16**

**STUDIES OF SELF-ASSEMBLED MONOLAYERS OF CONJUGATED MONO- AND DI-THIOL COMPOUNDS.** David Abusch-Magder, Zhenan Bao, Hong Meng, J. Hendrik Schön, Bell Labs, Lucent Technologies, Murray Hill, NJ; Weirong Jiang, Alexei Ermakov, Eric Garfunkel, Chemistry Department, Rutgers University, Piscataway, NJ.

We have deposited self assembled monolayers (SAMs) of a variety of conjugated mono and di-thiol compounds on gold surfaces. These materials have been used to fabricate a self-assembled monolayer field effect transistor, SAMFET (Schön, *et. al.*, *Nature*, **413**, 713 (2001)). We have studied the surface morphology, and electron transport properties of these SAMs using both scanning tunneling microscopy (STM) and atomic force microscopy (AFM). In addition we have also studied SAMs consisting of conjugated thiols diluted in an alkanethiol matrix. We report on our findings and comment on how they help us understand the SAMFET structure.

#### **P9.17**

**STRUCTURAL AND MORPHOLOGICAL DIFFERENCES OF THIN FILMS OBTAINED BY PLASMA POLYMERIZATION OF PYRROL (Ppy) AND THIOPHENE (Pth).** M. Paz Diago, Salvador Borros, Material Science Lab, Department of Physical Chemistry, IQS, Universitat Ramon LLull Barcelona, SPAIN; Joan Esteve, Applied Physics Department, Universitat de Barcelona, Barcelona, SPAIN.

Plasma polymerization has been described as a technique of developing new types of materials with properties completely different from those obtained by conventional polymerization methods. In this work, thin films (thickness  $\sim 0.5$  mm) were obtained by plasma polymerization of pyrrol (Ppy) and thiophene (Pth) at 25-30 W and 0.1-0.2 mbar of pressure. Further doping with iodine was carried out to some of the Ppy and Pth films (Ppy/I2, Pth/I2) in order to enhance their electrical conductivity properties. Structural and morphological characterization of both Ppy and Pth as well as of Ppy/I2 and Pth/I2 was performed using Infrared Spectroscopy (IR), X-ray Photoelectron Spectroscopy (XPS) and Atomic Force Microscopy (AFM). IR revealed a structure of an hydrocarbon backbone containing functional groups with O atoms and some monomer units for both polymeric films. The presence of bands at wavenumbers around 2950  $\text{cm}^{-1}$  corresponding to methyl and methylene groups are seen as a result of the monomer fragmentation occurred during the polymerization process. XPS analysis performed before and after a sputtering treatment for all four types of films outlined two important and unknown features: fragmentation occurs in a higher rate for pyrrol rings than for thiophene ones, which is related to the higher quantity of iodine incorporated to the polymeric structure of Pth exhibited in the XPS spectra, in contrast to the almost unnoticeable amount of iodine of Ppy/I2 films. Observation of both undoped and I2 doped films by AFM provided spectacular micrographs (600-600 nm; 2-2mm). Unlike undoped films, which exhibited an extremely flat surface (rms  $\leq 1$  nm) for both Ppy and Pth, I2 doped films showed strong morphological differences between Ppy/I2 and Pth/I2. Whereas Ppy/I2 topography was flat with isolated "mountains" (diameter  $\sim 50$  nm), Pth/I2 showed plenty of symmetrically ordered "mountains" (diameter  $\sim 60$  nm, height  $\sim 12.5$  nm). The presence of such "mountains" is related to the incorporation of iodine to the PTH structure which leads to the formation of these "Iodine clusters". In the light of the information given by IR, XPS and AFM techniques, exhaustive and accurate description of both undoped and I2/doped Ppy and Pth films obtained by Plasma Polymerization is attained.

#### **P9.18**

**INVESTIGATION OF THERMAL STABILITY AND PHOTOREACTIVITY OF HIGHLY SWITCHABLE SAMS ON GOLD.** T.X. Wei, K. Tamada, H. Akiyama, K. Yase, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, JAPAN; S.A. Kim, Organic Thin Films Lab, Hanyang University, Sungdong-gu, Seoul, KOREA.

We have developed highly photoreactive azobenzene SAMs by using molecular design with unsymmetrical disulfides and methyl group attached to azobenzene. In this paper we focus on the characterization of thermal stability of the SAM structure by PM-IRRAS and AFM, and thermal endurance of the photoreactivities of these functional SAMs by SPR. The SPR data revealed that the thermal endurance of photoreactivity is improved for C6Az(Me)SSC12 SAM, compared with that of C6AzSSC12 SAM. We investigated the AFM images of these SAMs before and after annealing at 100 degrees centigrade in oven for 3 h. Both disulfides' SAMs exhibited clear phase segregations after annealing. The difference between their segregations was considered to be the influence of methyl group. The polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) data indicate that c-o-benzene vibration at 1259  $\text{cm}^{-1}$  of C6Az(Me)SSC12 SAM decreases after annealing much more than the corresponding vibration

at 1252 cm<sup>-1</sup> of C6AzSSC12 SAM. This suggests that azobenzene groups in C6Az(Me)SSC12 SAM lean at larger angle than that in C6AzSSC12 SAM after annealing. Our results show that high thermal endurance of photoreactivity does not have to accompany with the improved structural stability of the SAMs.

#### **P9.19**

**HIGH EFFICIENCY ORGANIC PHOTOVOLTAICS FROM SOLUBLE DISCOTIC LIQUID CRYSTALLINE MATERIALS.** L. Schmidt-Mende, J.D. MacKenzie, Univ of Cambridge, Dept of Physics, Cambridge, UNITED KINGDOM; A. Fechtenkötter, K. Müllen, Max-Planck-Institut für Polymerforschung, Mainz, GERMANY; D.M. Russell, C. Silva, R.H. Friend, Univ of Cambridge, Dept of Physics, Cambridge, UNITED KINGDOM.

High efficiency organic solar cells have been created by spin-coating thin films from a blend solution of the liquid crystalline discotic peri-hexabenzocoronene (HBC-PhC<sub>12</sub>) and a perylene derivative. Self-organization of phase separation leads to segregated structures optimized for charge separation and transport in photovoltaic devices. Atomic force microscopy and device characteristics suggest that the driving forces for phase separation and surface energy effects during spin coating result in a spontaneous vertical segregation of the hexabenzocoronene and the perylene normal to the plane of the spun film. The existence of a nearly ideal, self-organized structure in which vertical segregation of charge transport layers exists, with a high interfacial area between the two charge transfer components, is supported by electron microscopy and photocurrent action spectra comparisons. Maximum external quantum efficiencies up to 34% near 490nm have been achieved. The high efficiencies result from efficient charge transfer between the hexabenzocoronene and the perylene as well as effective transport of electrons and holes to the cathode and anode through segregated perylene and discotic hexabenzocoronene  $\pi$ -systems. To further explore the properties of this tailored thin film structure, the dynamics of charge separation have been investigated by femtosecond transient absorption spectroscopy. The charge recombination kinetics have been interrogated by cw photoinduced absorption spectroscopy. In conjunction, the consequence of geminate and non-geminate carrier recombination is discussed.

#### **P9.20**

**MOLECULAR ALIGNMENT OF EMBOSSED POLYFLUORENE STRUCTURES.** Michael Banach, Richard Friend, Henning Sirringhaus, Cavendish Laboratory, University of Cambridge, Cambridge, UNITED KINGDOM.

Molecular alignment of conjugated polymer films are of technical interest for backlighting of flat panel displays and to realize higher mobilities for polymer transistors. Recently, many researchers have obtained highly oriented films of the polyfluorene polymers by either thermal processing on a rubbed surface or directly rubbing the polymer while in the thermotropic nematic phase. However, the nematic phase of many of these polymers occurs at relatively high temperatures (at least >180°) which limits device structures to high temperature materials. Also, for some moderately high molecular weights (>100K) good orientation cannot be achieved because of the high viscosity of the polymer film limits the molecular mobility even in the nematic phase. We used a soft lithographic patterning technique to create polyfluorene grating structures directly from solution. The gratings are formed due to capillary flow of the polymer solution in the PDMS channels as the solvent evaporates. Polymer alignment was achieved by the capillary flow. The molecular orientation can be tuned by changing the stamp dimensions which dictate the capillary flow forces. Polarized PL spectra showed that flow-aligned poly(9,9-dioctylfluorene) (PFO) exhibited an polarization ratio of up to 7. This technique is advantageous because it does not require a high temperature anneal and is not limited to templating surfaces.

#### **P9.21**

**THEORETICAL STUDY ON THE LUMINESCENCE OF CONJUGATED COPOLYMERS.** Dae-Yup Shin, Soo-Jin Park, Dong Hyun Jung, Ji-Hoon Lee, Corporate R&D Center, Samsung SDI Co. Ltd., Suwon, KOREA; Jung In Seo, Sung Soo Park, Maeng Eun Lee, Seeyarl Sung, Computer Aided Molecular Design Research Center, SoongSil University, Seoul, KOREA.

Organic conjugated polymers have been thoroughly investigated to achieve proper chromaticity and sufficiently high luminous efficiency for polymer light emitting devices. In recent years, the theoretical methods of quantum-chemistry have provided significant insight into the electronic and optical properties of conjugated polymers. We carried out quantum chemical calculations for light emitting polyfluorene and PPV-based copolymers. Relationship between the molecular structure and optical properties were investigated by semiempirical calculation methods such as AM1 and INDO/S for the geometry optimization and for the information of electronic transition, respectively. Comparing the result of these calculations

with experimental observations, we evaluated the chain length effect on the optical properties of conjugated copolymers. Based on the calculated optical properties, quantitative structure property relationship (QSPR) study on the photoluminescence was carried out using multiple linear regression (MLR) analysis and genetic algorithm (GA). It was found that the characteristics of molecular volume and intermolecular interactions strongly correlate with photoluminescent properties. Our calculations could also predict the position of emission maxima of conjugated copolymers successfully.

#### **P9.22**

**THE OPTIMIZATION OF THE TiO<sub>x</sub> LAYER IN POLYMER PHOTOVOLTAIC DEVICES.** Tosan Omabegho, Melissa Kreger, UCSC, Physics Dept., Santa Cruz, CA; H. Horhold, H. Tillmann, Univ. of Jena, GERMANY; S.A. Carter, UCSC, Physics Dept., Santa Cruz, CA.

Organic photovoltaics offer possible alternatives to silicon based solar technology currently in use. Many organic-based photovoltaics use a TiO<sub>x</sub> layer to enable charge dissociation and separation at the interface between the TiO<sub>x</sub> and the photoconductive polymer. The morphology and processing conditions of the titanium oxide layer have been shown to substantially affect device performance. We will present a systematic study on the TiO<sub>x</sub> layer in polymer-based photovoltaics consisting of a M3EH-PPV photoactive polymer layer. These devices have been shown to have quantum efficiencies of 10% with short circuit currents up to 1 mA/cm<sup>2</sup> under solar illumination, open circuit voltages of 0.8 V, and fill factors of 50% using smooth sol-gel TiO<sub>x</sub> layers. We will discuss how the properties of these devices are affected by the processing conditions, such as thickness, temperature, annealing time and doping, of the TiO<sub>x</sub> sol-gel layer. To address the role of surface morphology on the excitation dissociation, we also have studied a variety of TiO<sub>x</sub> nano-particle layers with varying surfactant, particle size, solution concentration and film porosity. AFM pictures of the titanium oxide layer will be presented along with speculation of how the surface morphology affects device performance.

#### **P9.23**

**BEHAVIOR COMPARISON OF PMMA-PTEGDMA COPOLYMERS POLYMERIZED BY TWO DIFFERENT METHODS.** R. Velazquez, J. Reyes and V.M. Castaño. Instituto de Física, UNAM, Querétaro, Qro. MEXICO.

An acrylic system, consisting of a Casting Syrup (polymethyl methacrylate dissolved in methyl methacrylate monomer) and triethylene glycol dimethacrylate monomer, was polymerized using two different types of reaction initiation. One of them, used the thermal decomposition of benzoin peroxide (conventional method) and the other one, employed the promoted decomposition of benzoin peroxide by dimethyl p-toluidine (phase separation method). The Casting Syrups had three different concentration of 10%, 20% and 30% by weight of the polymer and each syrup was mixed with different proportions of triethylene glycol dimethacrylate (TEGDMA) from 0% to 100% by wt. When the polymerization reaction was carried out using the conventional method, single phase polymers were obtained and, when the phase separation method was employed, the system underwent a phase separation and microdomains were formed. Volume variation as a function of the reaction time were determined by dilatometry, in the two types of polymers, and using Scanning Electron Microscopy, their corresponding morphologies were observed. Differential Scanning Calorimetric (DSC) and Thermal Gravimetric Analysis (TGA) studied the thermal behavior of all the polymer. The microstructure of polymers obtained by phase separation method was analyzed by micro-Raman with the propose of identify the chemical composition of the different phases. the behavior of each type of polymer is very different and this is a consequence of the polymerization method employed.

#### **P9.24**

**THICKNESS DEPENDANT CHANGES IN THE OPTICAL AND ELECTRICAL PROPERTIES OF RED-EMITTING PPV AND BLUE-EMITTING PF POLYMER LIGHT EMITTING DIODES.** J.M. Leger, S.A. Carter, Dept of Physics, University of California, Santa Cruz, CA; H. Tillmann, H.-H Hoerhold, University of Jena, GERMANY; Heinz-Georg Nothofer, Ullrich Scherf, Max Planck Institute for Polymer Research, GERMANY.

We explore the optical and electronic properties of single layer PLEDs as a function of emissive layer thickness. Devices are constructed on glass substrates with a patterned ITO/ PEDOT-PSS anode and Ca/Al cathode, and polymer films are spin cast at varying speeds to achieve a range of film thicknesses. Devices are made both with Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylene-ethynylene-2,5-dioctyloxy-1,4-phenylene-ethynylene] (MEH-DOO-PPV) and with Poly(2,7-(9,9-bis(2-ethylhexyl)fluorene)-2,7-bis(4-methylphenyl)phenylamine (PFO with 2% endcap). In addition to single layer MEH-DOO-PPV devices, we construct devices with a thin (9 nm)

layer of silver between the transparent anode and the polymer layer to explore microcavity effects. The PLED devices reached a luminosity of 100 cd/m<sup>2</sup> below 3 V and 10,000 cd/m<sup>2</sup> below 5 V. Quantum efficiencies up to 1% are typical for the most efficient devices. With MEH-DOO-PPV, we observe a significant EL redshift and decrease in quantum efficiency with increasing polymer thickness for both device architectures; however, the red shift observed for microcavity devices is substantially different than for non microcavity structure. With PFO, we first observe a blue shift due to changes in the relative weights of the vibronic peaks followed by a redshift with increasing polymer thickness. We will discuss the relative roles that self absorption, surface morphology (i.e. aggregation), charge carrier mobility, and microcavity effects have on the thickness dependant changes observed in PLEDs.

#### **P9.25**

##### **NEW HOST-GUEST POLYMERIC SYSTEM FOR THERMAL STABILITY ENHANCEMENT OF ELECTRO OPTIC EFFECT.**

Seung Koo Park, Jung Yun Do, Jung-Jin Ju, Sunkak Park, Myung-Hyun Lee, ETRI, Polymeric Photonics Devices Team, Taejon, S KOREA.

A new host-guest electric optic (EO) polymer, in which a chromophore can be reacted with the polymer main chain during poling to give the corresponding side-chain EO polymer, has been prepared. The polyisoimide (PII), synthesized from 2, 2-bis (4-aminophenyl) hexafluoropropane and oxydiphthalic anhydride, with number and weight-average molecular weights of 6,500 and 13,000, respectively, and Disperse Red 1 (DR1), one of common electro optic chromophore, are used as a host and guest, respectively. Infrared spectra showed that the reaction between the hydroxyl groups in DR1 and the isoimide groups in PII occurred at 120-140°C. The isoimide-imide rearrangement temperature was decreased from 295 to 150°C with increasing chromophore concentration from 0 to 50 wt. %. The glass transition temperatures of the resulted EO polyimide film with 0, 10, and 30 wt. % of chromophore concentration after the rearrangement reaction were 275, 218, and 140°C, respectively. The EO coefficient obtained at a wavelength of 1.55 μm was 10.5 pm/V from the polyimide film with 30 wt. % DR1 and poled at 140°C and annealed at 165°C under applied electric field. The EO signals exhibited only a slight decay at 100°C due to the chemical reaction between the host and guest during poling. Now, we are trying to find the best process condition in our system for high electro optic effect.

#### SESSION P10: ORGANIC-BASED TRANSISTORS

Chair: Yang Yang  
Friday Morning, April 5, 2002  
Franciscan II/III (Argent)

#### **8:00 AM \*P10.1**

**MOLECULAR-SCALE ORGANIC TRANSISTORS BASED ON SELF-ASSEMBLED MONOLAYERS.** Zhenan Bao, Bell Labs, Lucent Technologies, Murray Hill, NJ.

In this talk, we report organic transistors using self-assembled monolayers as the active components, such as dielectric and semiconducting layers. Transistors with drain and source electrodes separated by 1-2 nm can be realized using a self-assembled semiconducting dithiol monolayer. Performance similar to Si devices can be achieved. A number of dithiol molecules were synthesized to study structure property relationships and their performance will be discussed. Finally performance of nano-scale transistors based on vacuum evaporated organic semiconductors will be presented.

#### **8:30 AM P10.2**

**TWO-DIMENSIONAL MODELING OF PENTACENE FIELD EFFECT TRANSISTORS.** T. Li, P.P. Ruden, ECE Dept, University of Minnesota, Minneapolis, MN; I.H. Campbell, D.L. Smith, Los Alamos National Laboratory, Los Alamos, NM.

We present device simulations for p-channel organic field effect transistors (OFETs). The charge carrier conservation equation and Poisson's equation are solved self-consistently in two dimensions. We model transistor structures consisting of a gate electrode, a silicon dioxide gate insulator, and a pentacene layer, with source and drain contacts either on top of the organic layer (top contact structure) or between the gate insulator and the organic layer (bottom contact structure). The electric field dependence of the mobility extracted from recent experimental data on single crystal pentacene [1] is taken into consideration. Of particular interest is the formation of the channel due to charge carrier injection from the source contact under non-equilibrium conditions. We show that this process is affected by charges on the surface of the device, an effect that may enable the OFET to operate as a chemical sensor. We also examine the effects associated with differences in charge carrier injection for different

source and drain contact materials. Results of the device model calculations are used to identify critical OFET design parameters. [1] J.H. Schon, Ch. Kloc, and B. Batlogg, Phys. Rev. B 63, 245201 (2001).

#### **8:45 AM \*P10.3**

**ORGANIC LIGHT-EMITTING DEVICES WITH SINGLE CRYSTALLINE TFTs ON GLASS.** L.S. Hung, Center of Super-Diamond and Advance Films (COSDAF) and Department of Physics & Materials Science, City University of Hong Kong, Hong Kong, CHINA; S.S. Lau, Department of Electrical and Computer Engineering, University of California, San Diego, La Jolla, CA

Active-matrix OLEDs are commonly fabricated using a polysilicon-on-glass technology. Considering the low electron mobility in polysilicon and process complexity to achieve high-quality large-grain polysilicon, it is highly desirable to fabricate OLEDs on single crystalline Si. With a Si substrate, surface-emitting OLED structures are currently used with a transparent top electrode consisting of a thin buffer layer and a thicker overlying ITO film. However, the use of sputtering deposition of ITO for OLEDs is fraught with difficulties because of the susceptibility of organic molecules to radiation damage. In this presentation our progress in ITO-free surface-emitting OLEDs will be briefly addressed. Then particular attention is paid to the integration of OLEDs with single crystalline Si thin film transistors, TFTs, on glass. The single crystalline Si films on glass, about 100-150 nm thick, are prepared by ion cutting and wafer bonding, and provide sufficiently high electron mobilities, thus allowing for small channel areas for high pixel densities. With single crystalline Si on glass, light generated in OLEDs is emitted from the transmissive substrate, and thus conventional OLED structures (bottom emitting) and processing sequence in manufacturing could be fully utilized.

#### **9:15 AM P10.4**

**TEMPERATURE EVOLUTION OF PENTACENE CRYSTAL STRUCTURE AND PHONON DYNAMICS.** Matteo Masino, Alberto Girlando, Parma Univ, Dip. Chimica G.I.A.F., Parma, ITALY; Raffaele G. Della Valle, Elisabetta Venuti, Aldo Brillante, Bologna Univ, Dip. Chimica Fisica ed Inorganica, Bologna, ITALY.

Pentacene is among the most promising organic semiconductors for microelectronics. Recent improvements in the crystal growth/purification has yielded crystals exhibiting even more interesting properties, such as huge low-temperature carrier mobilities or charge-injected superconductivity. However, it is not yet clear how the conditions under which the molecules assemble to form the solid determine these outstanding physical properties. In this communication we address the above problem by calculating the pentacene crystal structures by the Quasi Harmonic Lattice Dynamics (QHLD) method. We are able to show that two distinct bulk crystalline phases of pentacene exists, with very subtle structural differences but clearly different phonon spectra. The method of crystal growth (from solution or vapor) is not the determining factor for obtaining either structure. We then compute the temperature dependence of both crystal structures, together with the corresponding changes in the intermolecular hopping integrals between pairs of pentacene molecules. It appears that these integrals (and hence the bare band structure) change very little by lowering the temperature. Therefore the observed huge increase in the carrier mobilities cannot be ascribed to a simple bare bandwidth increase: other factors, such as the coupling to phonons, are probably able to strongly affect the *effective* bandwidth. The relevance of these factors is checked by calculating the temperature evolution of the phonon spectra and of the coupling strength of intermolecular phonons with electrons and holes.

#### **9:30 AM P10.5**

**TRANSPORT MECHANISMS AND TRAPPING STATES IN PENTACENE TFTS.** R.A. Street, D. Knipp, A.R. Volkel, Xerox PARC, Palo Alto, CA.

The interest in organic thin film transistors (TFT) makes it important to understand the hole transport mechanisms. Electrostatic potential barriers, potential wells, or a distribution of traps have each been proposed for polycrystalline pentacene and other organics. We use a pulsed gate and drain bias to overcome bias-stress effects and obtain more accurate pentacene characteristics. We show that the Levinson plot previously used to identify potential barriers is not a good fit to our data, and the standard MOS model does better. Above threshold, the hole mobility does not depend significantly on either the gate or drain field, and hence is not compatible with potential barriers. Furthermore, the observed variations in the TFT turn-on voltage and the threshold voltage also cannot be explained by potential barriers, but instead clearly indicate acceptor-like trap states. The trapping states are studied further through measurements of the transient response of the TFT as the gate is turned off. The drain current decay

extends to 0.1-1 msec, initially following approximately a 1/time dependence but eventually becoming steeper. This transient response is interpreted in terms of the thermal emission time of holes from shallow states, and provides further evidence for the presence of localized trap states near the valence band edge. The transients provide an estimate of the trap depth, distribution and concentration. Numerical TFT modeling studies tie these results together. We find that the sub-threshold characteristics of pentacene TFTs are modeled by a broad band of acceptors near the dielectric interface, extending about 0.5 eV into the band gap. The transient drain current decay is consistent with this distribution of acceptor states. The concentration of these acceptors varies substantially between samples, and their possible origin will be discussed.

#### 9:45 AM P10.6

**BTQBT THIN FILMS; A NOVEL ORGANIC SEMICONDUCTING MATERIALS FOR ORGANIC TRANSISTORS.** Masaki Takada, The Graduate Univ for Advanced Studies, Dept of Functional Molecular Science, Okazaki, JAPAN; Harald Graaf, Inst for Molecular Science, Okazaki, JAPAN; Yoshiro Yamashita, Tokyo Inst of Technology, Dept of Electronic Science and Technology, Yokohama, JAPAN; Hirokazu Tada, Inst for Molecular Science, Okazaki, JAPAN.

Field effect transistors (FETs) using organic semiconductor thin films as active layers have been studied intensively because they have great potential of applications to low cost electronic devices and their circuits. Most organic compounds examined so far showed rather low field effect mobilities in the range of  $10^{-5}$  -  $10^{-3}$   $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ . Thin films of pentacene and polythiophene are known to exhibit high mobilities and received a considerable attention. We have prepared and characterized thin films of bis-(1, 2, 5-thiadiazolo)-p-quinobis(1, 3-dithiole) (BTQBT) as active semiconducting layers of FETs. Preparation and characterization of the films were carried out under ultrahigh vacuum condition. BTQBT films deposited at room temperature showed p-type semiconducting behaviors with mobility of  $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ . The on/off drain current ratio was  $10^7$ . The mobility and on/off ratio reached to  $0.2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  and  $10^8$ , respectively, by optimizing the film growth conditions. These performances are almost comparable to those of pentacene and polythiophene thin films, indicated that BTQBT molecule is a prominent semiconducting material as a high mobility thin film. Influence of gas adsorption and crystal structures onto electrical properties will also be discussed in detail.

#### 10:00 AM P10.7

**FIELD EFFECT CONDUCTIVITY OF POLYMERS BETWEEN NANO-ELECTRODES.** David Abusch-Magder, Takao Someya, Zhenan Bao, Bell Labs, Lucent Technologies, Murray Hill, NJ; Ananth Dodabalapur, Bell Labs, Lucent Technologies and University of Texas, Austin, TX; Don M. Tennant, Agere Systems, Murray Hill, NJ.

We have measured the field effect conductivity of a variety of conjugated polymers between narrow metallic gaps. Our structures are fabricated using electron beam lithography and have gaps ranging from 10nm to  $> 1 \mu\text{m}$ . We have found that the conductivity is enhanced as the electrode separation is reduced and approaches the length of the polymer chain. In this talk we will describe work carried out on various poly-thiophene, and poly-phenylenevinylene compounds.

#### 10:30 AM P10.8

**HIGHLY CONDUCTING  $\text{C}_{60}$  THIN FILMS AND RELATED SPECIES.** Siobhán Phelan, Gordon Chambers, Hugh James Byrne, Facility for Optical Characterisation And Spectroscopy (FOCAS), School of Physics, Dublin Institute of Technology, Dublin, IRELAND.

Organic materials have, in recent decades, been shown to be insulators, semiconductors, or even metallic when doped and the prospect of cheap, easily fabricated devices has attracted much interest. Primitive devices have been demonstrated and yet potentially competitive performance has been limited to polymer light emitting diodes. The recent report that lattice expanded  $\text{C}_{60}$  single crystals can be made superconducting, with a transition temperature of 117K, by the injection of charge via a FET type geometry has once again highlighted the potential of  $\text{C}_{60}$  in the development of molecular electronic devices. In light of the aforementioned report it is thus essential that a true understanding the importance of inter- and intramolecular processes in terms of their contribution to the electronic transport be obtained. In this study current voltage characteristics of thin film  $\text{C}_{60}$  devices produced in a sandwich structure and in a FET type geometry are fabricated by vacuum deposition employing gold as the metal electrode. A strongly nonlinear behaviour is observed in both electrode geometries, with a sharp increase in the device conductance being observed at relatively low voltages. The high conductance state of the device is temperature independent from room temperature down to 20K, indicative of a metallic-like metastable state of the material. The effect is discussed

in terms of a solid state voltammetric process. In situ Raman measurements indicates that the behaviour originates from a solid state reduction of the fullerene. Moreover the evidence suggests that this species maybe similar in nature to a high intensity optically excited state species which has a Raman signature of  $1463\text{cm}^{-1}$ . It is further speculated that the species recently reported in the superconducting lattice expanded  $\text{C}_{60}$  single crystals may also be analogous to the conducting species observed here.

#### 10:45 AM P10.9

**CHARGE CARRIER MOBILITY IN ORGANIC FIELD-EFFECT TRANSISTORS.** C. Tanase, P.W.M. Blom, University of Groningen, Materials Science Center, Groningen, THE NETHERLANDS; E.J. Meijer, D.M. de Leeuw, Philips Research Laboratories, Eindhoven, THE NETHERLANDS.

The transport properties of the solution processed organic semiconductor poly(2,5-thienylene vinylene)(PTV) and poly(3-hexyl thiophene)(P3HT) have been investigated. The electrical characteristics of PTV and P3HT field-effect transistors operating in the accumulation regime have been measured as a function of temperature under controlled atmosphere. Typically, in field-effect transistors, the field-effect mobility is determined from the conventional equations, either from the saturation current, or from the transconductance at low drain voltages. However, for organic semiconductors, the apparent field-effect mobility is showing a strong dependence on the gate voltage. This is due to the dependence of mobility on the density of charge carriers. From numerical calculations it is demonstrated that the charge carrier distribution in the transistor channel is not uniform, but decreases from the semiconductor/insulator interface to the bulk. The characteristics of the FET have been modeled taking into account the distribution of charge carriers and mobility over the accumulation channel. The numerical calculations show that the charge carriers at the semiconductor/insulator interface have a higher mobility than the so-called field-effect mobility.

#### 11:00 AM \*P10.10

Joseph Salbeck, University of Kassel, GERMANY.

ABSTRACT NOT AVAILABLE

#### 11:30 AM P10.11

**ORGANIC CONDUCTING COMPOSITES FOR FIELD EMISSION APPLICATIONS.** Ioannis Kymissis, Aikintunde Ibitayo Akinwande, Massachusetts Institute of Technology, Microsystems Technology Laboratory, Cambridge, MA.

Field emission devices are cold cathodes which are used in a wide variety of applications including displays, lithographic systems, and space propulsion. Broad commercial success has been hampered by the high cost of processing materials traditionally used for this application, namely metals and crystalline semiconductors. High performing alternatives using diamond-like carbon, graphite, and nanotubes have been extensively studied as alternatives to traditional materials, but the processability of such systems is still limited. Only one paper in the literature has examined the use of organic conductors for this application (1). We have used conducting organic materials to create micron-sized formed field emission tips with simple processing technology. Tips with a radius of approximately 20nm at their sharpest points are fabricated at a tip density of approximately four million tips per square centimeter. Both solution processing on templates and nanoimprint techniques have been used to form these devices from a variety of doped conducting polymers dispersed in insulating matrices. A field factor of approximately 50 000 is observed at a cathode-anode spacing of 50 microns. We will present electrical and optical data demonstrating the use of these devices as electron sources exciting a phosphor screen. The effect of contaminant gases in the vacuum environment on the performance of these tips will also be discussed. This system also represents the first demonstration of field emission in a thermoplastic material, and the ramifications of this type of technology on both processing and operation will also be discussed.

(1) I. Musa et al. *Nature*, **395** 362 (1998).

#### 11:45 AM P10.12

**DEVELOPMENT OF A NANOSCALE METHOD FOR THE MEASUREMENT OF IMPEDANCE IN ORGANIC SYSTEMS.** Elizabeth F. Fabbroni, Matthew W. Such, Mark C. Hersam, Kenneth R. Shull, Northwestern University, Dept of MS&E, Evanston, IL; Mauro Castellani, Swiss Federal Institute of Technology, Dept of Matls Sci, Zurich, SWITZERLAND.

As organic devices approach the nanometer scale, spatial variations in their electronic properties become increasingly important. By probing device characteristics with nanometer spatial resolution, structure/property relationships indicated by the electronic response can be

elucidated. Our research focuses on the development of a new technique for measuring time dependent electronic signals at the nanoscale, in an effort to complement techniques that are currently available at the macroscale. In order to test this general charge transport characterization technique, a model organic system has been chosen that is composed of a poly(ethylene)-co-maleic anhydride matrix that is filled with carbon particles, at filler loadings that are well above the percolation threshold. Industrial applications of these materials include electrical circuit protection devices where the current must be limited at high temperatures. In order to develop our technique, studies have been conducted on both the macroscale and nanoscale in order to measure the response to both DC and AC applied voltages. The resulting measurements provide valuable information in determining the method of transport. While the macroscale measurements provide useful information about bulk responses, the nanoscale response reflects the measurement of individual agglomerates of carbon black at the surface. In the past, conductive measurements at the nanoscale have been limited to the DC measurements, which have typically been obtained by atomic force microscopy (AFM) using a conductive probe. Our approach furthers this technique by utilizing conductive AFM as a probe of local impedance variations as a function of frequency. In effect, we are combining conductive AFM potentiometry with impedance spectroscopy. We will address the capabilities and limitations of this technique and suggest other candidate organic technologies that may benefit from this type of nanoscale spatial impedance mapping.

#### SESSION P11: SPECTROSCOPY AND INTERFACES

Chair: J. Campbell Scott  
Friday Afternoon, April 5, 2002  
Franciscan II/III (Argent)

##### 1:30 PM **P11.1**

THE INFLUENCE OF POTENTIAL BARRIER MATERIALS ON DEVICE PERFORMANCE IN ORGANIC MULTIPLE LAYER LIGHT-EMITTING DIODES. Zhiyuan Xie, T.C Wong, F.L. Wong, M.K. Fung, Y.Q. Li, S.T. Lee, and L.S. Hung, Center of Super-Diamond and Advanced Films (COSDAF) & Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, PR CHINA.

Great progress has been made since the first organic thin-film light-emitting diode (LED) consisting of a hole-transporting layer and a light-emitting layer was reported by C.W. Tang in 1987. Rational device structures play an important role in improving light-emitting efficiency of organic LEDs. In this work a double-heterostructure of ITO/NPB/doped-Alq/BCP/Alq/MgAg was developed to form a narrow recombination zone where both charge carriers and excitons are confined, thus resulting in efficient electron-hole recombination and energy transfer. It was found that though current efficiency was enhanced, the low electron mobility of BCP resulted in higher driving voltages and limited the improvement of power efficiency. Therefore, we investigated the utilization of various materials as a hole-blocking layer, such as TPBI, DNA, etc. The carrier mobility in the hole blocking materials was determined by measuring transient electroluminescence, and the barrier to hole injection at the interface between the Alq light-emitting layer and the hole blocking layer was examined by ultraviolet photoelectron spectroscopy. Significant improvements on both quantum efficiency and power efficiency were achieved by using those hole-blocking layers, and well correlated with the effectiveness of hole blocking and the magnitude of the electron mobility.

##### 1:45 PM **P11.2**

SPECTROSCOPIC STUDY ON DEGRADATION OF OLEDs BASED ON TB(III) CHELATING POLYUREAS. Jeremiah Mwaura, Baocheng Yang, Martha Morton, Fotios Papadimitrakopoulos, Department of Chemistry, Naomaterials Optoelectronics Laboratory, Institute of Materials Science, University of Connecticut, Storrs, CT.

Terbium chelates of 2,6-aminopyridine based polyureas were utilized to fabricate single and multi layer organic light emitting diodes (OLEDs). Their PL and EL characteristics were found to be greatly dependent on the nature of chelating agent (i.e. polyurea), which upon prolonged exposure to UV, gradually shifts its emission to blue. Fluorescence, UV/Vis, and Nuclear Magnetic Resonance (NMR) spectroscopy were utilized to examine these photodegradation processes as a function of UV dose, O<sub>2</sub> and water. This involves the photocleavage of the urea compounds to form primary phenyl amines and subsequent release of CO<sub>2</sub>. The presence of water was found to accelerate the transformation but apparently O<sub>2</sub> plays no particular role. All the results have led us to suggest that the photo-cleavage of the urea happens via radical intermediates and the pyridinyl nitrogen plays an important role in the entire mechanism. These results and

potential applications of this type of ureas in the field of photolithography and optoelectronics will be discussed.

##### 2:00 PM **\*P11.3**

SINGLET EXCITON (SE) QUENCHING MECHANISMS IN  $\pi$ -CONJUGATED MATERIALS AND ORGANIC LIGHT-EMITTING DEVICES (OLED'S). J. Shinar, Ames Laboratory - USDOE\* and Department of Physics and Astronomy, Iowa State University, Ames, IA; E.J.W. List, Institut für Festkörperphysik, Technische Universität Graz, Graz, AUSTRIA; W. Graupner, Austria Microsystems "concerto", Unterpremstaetten, AUSTRIA; C.-H. Kim, A. Naik, and G. Li, Ames Laboratory - USDOE\* and Department of Physics and Astronomy, Iowa State University, Ames, IA; D.-W. Lee and J.-I. Jin, Center for Electro and Photo-Responsive Molecules and Department of Chemistry, Korea University, Seoul, KOREA; G. Jabbour, Optical Sciences Center & Department of MS&E, University of Arizona, Tucson, AZ.

Several significant SE quenching mechanisms are reviewed: (i) Quenching by polarons. Recent analysis of photoluminescence (PL)-detected magnetic resonance (PLDMR) measurements lead to the conclusion that the rate of this bulk mechanism becomes comparable to the SE radiative decay rate when the polaron density approaches  $10^{17} \text{ cm}^{-3}$ , a situation commonly reached in OLED's. (ii) Quenching by triplet excitons. Other PLDMR measurements, conducted on guest-host polymer blends, suggest that at high excitation densities this bulk mechanism is also significant. (iii) Quenching by charges, including negative bipolarons, at the organic/cathode interface. Electroluminescence (EL) and electrically-detected magnetic resonance (ELDMR and EDMR, respectively) measurements on small molecular OLED's yield negative (EL- and current-quenching) spin 1/2 resonances which are attributed to the spin-dependent formation of negative bipolarons at the organic/cathode interface. The results indicate that the charge density at this interface depends strongly on its nature, but is generally very high, and may account for the differences in the behavior of OLED's with different interfaces. (iv) Quenching by negative bipolarons in bulk polymer films, the formation of which is induced by holes which are trapped at, e.g., electron donating sidegroups. Triplet excitons (TE's), which are more localized, have a higher binding energy, and are less mobile than SE's, are expected to be largely impervious to these quenching mechanisms. However, recent ELDMR measurements on 2,3,7,8,12,13,17,18-octaethylporphine Pt (PtOEP)-based electrophosphorescent OLED's yield negative spin 1/2 quenching resonances similar to those exhibited by fluorescence-based OLED's. It is therefore suspected that quenching of SE's by charges at the organic/cathode interface may compete significantly with the transfer of the SE energy to TE's.

Ames Laboratory is operated by Iowa State University for the USDOE under Contract W-7405-Eng-82.

##### 2:30 PM **P11.4**

FERMI LEVEL EQUILIBRATION IN ORGANIC SEMI-CONDUCTOR INTERFACES. R. Schlaf, Department of Electrical Engineering, Center for Microelectronics Research, University of South Florida, Tampa, FL.

Photoemission spectroscopy measurements at small molecule/metal interfaces allow the determination of their electronic structure. In these experiments the organic semiconductor is usually grown on the metal in several steps starting at submonolayer coverages up to a few hundred ngstroms. During the growth sequence the sample surface is characterized by x-ray and ultraviolet photoemission spectroscopy (XPS, UPS) measurements. This yields a series of spectra showing the development of the electronic structure of the interface. During such experiments, peak shifts are encountered reminiscent of band bending phenomena in inorganic semiconductor/metal systems due to Fermi level equilibration. In organic systems the origin of such shifts is less clear since these materials are less conductive. Hence, charging effects or polarization energy shifts are likely candidates causing all or part of the shifts. Our experiments suggest that band bending like effects do occur, and that they likely are responsible for most of the observed shifts.

##### 2:45 PM **P11.5**

STRUCTURAL AND PHOTOPHYSICAL CHARACTERIZATION OF ALIGNED MESOMORPHIC SUPRAMOLECULES IN CONJUGATED ROD-LIKE POLYMERS. Matti Knaapila, Olli Ikkala, Helsinki University of Technology, Espoo, FINLAND; Mika Torkkeli, Kaija Jokela, Ritva Serimaa, University of Helsinki, Helsinki, FINLAND; Lars-Olof Palsson, Lockhart E. Horsburgh, Andrew P. Monkman, University of Durham, Durham, UNITED KINGDOM; Igor Dolbnya, Wim Bras, DUBBLE CRG/ESRF, Grenoble, FRANCE; Gerrit ten Brinke, University of Groningen, Groningen, THE NETHERLANDS.

The molecular level structure dealing with conjugated polymeric

material in lamellae microstructures is often studied in the case of the chains with the small intercalant species, or, on the other hand, in the case of covalently bonded hairy rods, such as poly(alkylthiophenes). Herein we report studies of self-organized comb-shaped supramolecules based on rod-like poly(2,5-pyridinediyl), and amphiphilic side chains being connected with the synergistic hydrogen bonds. Lamellar self organization arises from bonding and polar effects combined. We have performed X-ray diffraction measurements at small and wide angles both in bulk and thin films including grazing incidence studies. We also report measurements of the photophysical behaviour of complexes, including absolute photoluminescence quantum yield, solid and mesomorphic state photoluminescence properties. Mesomorphic structure is considered as a highly organized lamellar architecture in which polymer chains alternate with layers of dopants and amphiphiles. The structure is weakly crystalline revealing axial reflections (h00), (020), (040), and (004) and is assigned as orthorhombic unit cell. Along the layer normal it reveals triangular correlation function that damps out exponentially with large correlation length characteristic for well-defined layers and consistent with the appropriate model. The structures form in bulk or in thin film where the layers are aligned onto surface. Material can be straightforwardly aligned and reveal strong photoluminescence. Properties can be tailored by varying the side chain character.

### 3:15 PM P11.6

MONOMER DIFFUSION ASSISTED PREPARATION OF POLYMER GRATINGS, A NUCLEAR MICROPROBE STUDY. Christian Leewis, Arthur de Jong, Martien de Voigt, Accelerator Laboratory, Department of Applied Physics, Eindhoven University of Technology, THE NETHERLANDS; Dirk Broer, Eindhoven Polymer Laboratories, Eindhoven University of Technology, THE NETHERLANDS.

Polymers with an ordered molecular structure can be applied in optical systems for e.g. data transport, data storage and displays. Patterned UV photo-polymerization is used to prepare polymer gratings from a mixture of two acrylate monomers. A 3 MeV proton microprobe is used to study these gratings, prepared from two different monomers, each containing a different easily detectable label element, e.g. Cl, Si or F. During the preparation process, the difference in reactivity and mobility of these two monomers in combination with polymer-monomer interaction results in diffusion of monomers. Since this diffusion process takes place on length scales of micrometers, a scanning ion microprobe is a powerful tool for the quantitative analysis of the polymer films, obtained after complete polymerization. The microprobe is equipped with PIXE, PIGE (proton induced X-ray and gamma emission), and RBS (Rutherford backscattering spectrometry), to quantify both the label elements and C and O. This makes it possible to determine the concentration of monomer units as a function of position and thus to study the diffusion process. Combinations of different monomers are studied. In the case of a 0.5:1 mixture of a monofunctional and a difunctional monomer, both monomers migrate towards the illuminated areas and large thickness variations are observed. When a 1:1 mixture of two difunctional monomers is used, opposite migration of the two monomers is observed, while the film shows no variation in thickness. The lateral variations in composition and structure in these polymer films can be described with a theoretical model based on the Flory-Huggins theory.

### 3:30 PM P11.7

DETERMINATION OF TRAPS IN POLY(P-PHENYLENE VINYLENE) LIGHT EMITTING DIODES BY CHARGE-BASED DEEP LEVEL TRANSIENT SPECTROSCOPY. Olivier Gaudin, Richard B. Jackman, Electronic Engineering, Univ College London, UNITED KINGDOM; Thien-Phap Nguyen, Philippe Le Rendu, Lab de Physique Cristalline, Inst des Materiaux de Nante, FRANCE.

Charge-based deep level transient spectroscopy (Q-DLTS) has been used to study the defect states that exist within poly(p-phenylene vinylene) (PPV), a semiconducting polymer with a band gap of about 2.4eV for the first time. The technique allows the determination of activation energies, capture cross-sections and trap concentrations. In some circumstances, it is also possible to distinguish between minority and majority carrier traps. The structures investigated here consisted of ITO/PPV/MgAg light emitting diode (LED) devices. Two types of trapping centres were found. The first type has activation energies in the range 0.49 - 0.53eV and capture cross-sections of the order of  $10^{-16}$  -  $10^{-18}$  cm<sup>2</sup>. It shows a Poole-Frenkel, field assisted-emission process. This level has been identified as a bulk acceptor-like majority carrier (i. e. hole) trap. The second type has activation energies in the range 0.40 - 0.42eV and capture cross-sections of the order of  $10^{-19}$  cm<sup>2</sup>. This level has been identified as a minority carrier (i. e. electron) trap. This second trap type is therefore expected to limit minority carrier injection into the PPV layer within the LED, and hence reduce electroluminescence under forward bias conditions.

### 3:45 PM P11.8

ODD-EVEN UNITS DEPENDENCE OF ADSORPTION STATES IN SELF-ASSEMBLED MONOLAYERS OF THIOPHENE OLIGOMERS. Eisuke Ito, Jaeguen Noh, Fumio Nakamura, RIKEN, Frontier Research System, Wako, JAPAN; Tohru Araki, Saitama Univ., Faculty of Science, Saitama, JAPAN; Kotaro Kajikawa, Tokyo Institute of Technology, Interdisciplinary Graduate School of Science & Engineering, Yokohama, JAPAN; Hisao Ishii, Yukio Ouchi, Nagoya Univ, Graduate School of Science, Nagoya, JAPAN; Kazuhiko Seki, Nagoya Univ, Research Center for Materials Science, Nagoya, JAPAN; Masahiko Hara, RIKEN, Frontier Research System, Wako, JAPAN.

Self-assembled monolayers (SAMs) have been attracted wide attention because it is easy to obtain uniform and stable monolayer films on metal substrates. Recently, it is reported that thiophene molecules can form self-assembled monolayers on an Au substrate. In this paper, we studied adsorption states of thiophene oligomer (nT) SAMs on Au(111) with their unit numbers (n) from 1 to 4 by X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS). The S2p XPS and C K-edge NEXAFS spectra showed that thiophene monomer (1T) and terthiophene (3T) strongly interact with the Au surface, suggesting the formation of the chemisorbed monolayers. On the other hand, we found that bithiophene (2T) and quarterthiophene (4T) are physisorbed on the Au surface, because their XPS and NEXAFS spectra were very similar to those of polythiophene films reported previously. The amounts of adsorbed molecules estimated from the S2p peak intensities were different between the two kinds of adsorption states mentioned above, that is 2T and 4T molecules were adsorbed about 3 times more than 1T and 3T. These results show that the adsorption states of thiophene oligomers depend on odd or even unit numbers. Such odd-even dependence was investigated in the kinetics of film growth revealed with the surface plasmon resonance (SPR) measurements of 1T, 2T and 3T. The growth process of these SAMs will be discussed in more detail, combined with results of immersion time dependences of the XPS spectra.

### 4:00 PM P11.9

CORRELATING SURFACE MOLECULAR COMPOSITION TO NANOSCALE ELASTIC BEHAVIOR AND TOPOGRAPHY OF STRETCHED POLYURETHANE FILMS. Ella Amitay-Sadovskiy, Department of Mechanical Engineering, University of California, Berkeley, CA; Department of Chemistry, University of California, Berkeley, CA; Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA; Kyriakos Komvopoulos, Department of Mechanical Engineering, University of California, Berkeley, CA; Gabor A. Somorjai, Department of Chemistry, University of California, Berkeley, CA; Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, CA.

Correlation of the surface molecular composition with the nanoscale elastic behavior and topography of stretched polyurethane films was examined by surface specific sum frequency generation (SFG) vibrational spectroscopy and atomic force microscopy (AFM). Changes in the molecular composition due to stretching were elucidated by identifying the SFG spectral fingerprints of the soft and hard copolymer segments. The molecular composition is correlated with AFM results for the roughness and elastic modulus. In addition to molecular reorientation, upon stretching, randomly oriented hard segments migrate to the surface, leading to an increase of the hard to soft segment concentration and a decrease of the surface roughness. A continuous migration of hard segments to the surface occurred at constant strain.