

## Electronic Materials and Processing

Room: 612 - Session EM-MoM

## Organic Materials and Devices

**Moderator:** D.J. Gundlach, National Institute of Standards and Technology

8:00am **EM-MoM1 An Organic Interlayer for Organic Thin Film Transistor.** *H.H. Lee, S.Y. Park, K.H. Kim, T. Kwon*, Seoul National University, Korea

An organic interlayer between source/drain metal and semiconductor is introduced for the purpose of improving the performance of pentacene-based organic thin film transistor (OTFT). The formation and patterning of both the interlayer and the source/drain electrode is accomplished by a one-step bilayer transfer with 'rigiflex' lithography. The interlayer organic material should be chosen in such a way that the HOMO level of the organic lies between the metal work function and the HOMO level of the organic semiconductor. It is shown that the use of the interlayer of m-MTDATA for the cop-contact OTFT results in a more than one order of magnitude improvement in the effective mobility and also in the on-off current ratio. The main reason for the improvement can be attributed to a reduction in resistance.

8:20am **EM-MoM2 Changing Band Offsets in Copper-Phthalocyanine to Copolymer Poly(Vinylidene Fluoride with Trifluoroethylene) Heterojunctions.** *J. Xiao, A. Sokolov, P.A. Dowben*, University of Nebraska-Lincoln

Copper phthalocyanine (CuPc) is an organic semiconductor with a small instantaneous dipole, while poly(vinylidene fluoride with trifluoroethylene), P(VDF-TrFE), is a ferroelectric polymer with a strong intrinsic (reversible) dipole. We explored the band offsets of CuPc deposited on crystalline P(VDF-TrFE) copolymers through combined photoemission and inverse photoemission studies at different temperatures. We also fabricated a thin film CuPc to crystalline ferroelectric copolymer P(VDF-TrFE) heterojunction diode. The formation of a diode is expected from the band offsets between the two molecular systems. Dipole interactions are implicated at the interface between CuPc and P(VDF-TrFE), and affect the band offsets and resultant diode properties: the diode current is adjusted by application of an electric field, which in turn may be affected by the dipole orientation.

8:40am **EM-MoM3 Control of the Molecular Orientation of Thin Films of a Solution Processable Organic Semiconductor.** *L.J. Richter, A.J. Moad, B.H. Hamadani, O.D. Jurchescu, D.J. Gundlach*, National Institute of Standards and Technology, *S. Subramanian, J.E. Anthony*, University of Kentucky

Considerable interest has developed in the potential of macro-electronics enabled by low-cost manufacturing techniques such as roll-to-roll printing. Solution-processable small molecule based semiconductor films are emerging as a viable candidate for the active layer in thin film transistors (TFTs). The performance of TFTs fabricated from fluorinated 5,11-Bis(triethylsilyl)ethynylanthradithiophene (diF-TESADT) are strongly dependent on processing conditions and the chemical treatment of the contacts. High performance devices can be fabricated with Au contacts treated with perfluorinated-benzenethiol PFBT. We report on the structure of thin films of diF-TESADT, formed on both Au and SiO<sub>2</sub> substrates, as a function of substrate treatment and film thickness. Both spectroscopic ellipsometry and infrared absorption are used to assess the molecular orientation in the films. In films formed on PFBT treated Au, the orientation is found to be consistent with the bulk crystal structure, with a near optimal orientation of the pi-stacked conjugated cores in the channel of the transistor, consistent with the observed good device performance.

9:00am **EM-MoM4 Interfacial Influences and Electron-Injection Mechanisms of Tris-(8-Hydroxyquinoline)-Aluminum Doped with Cesium-Derivatives In Organic Light Emitting Devices.** *M.-H. Chen, C.-I. Wu, Y.-J. Lu, C.-C. Wu*, National Taiwan University

The cesium-derivatives (Cs<sub>2</sub>CO<sub>3</sub>, CsF and CsNO<sub>3</sub>) have been investigated as a dopant in tris-(8-hydroxyquinoline)-aluminum (Alq<sub>3</sub>) or a thin electron injection layer in organic light emitting devices. Unlike low work function metal which would be evaporated from a complex deposition process, the cesium-derivatives have a very simple deposition process and are easy to

handle. By using ultraviolet and x-ray photoemission spectroscopy, the properties of electronic structures and the interface chemistry are studied. The paper presents the investigation of interfacial interactions and electron-injection between cesium-derivatives and Alq<sub>3</sub>. According to our results, the Fermi level of Alq<sub>3</sub> after doped with cesium-derivatives shifts inside the gap toward the lowest unoccupied molecular orbital (LUMO) as a result of the charge transfer from cesium atom to Alq<sub>3</sub>, showing that electron-injection ability would be improved as a result of strong n-type doping effect. It is noteworthy to emphasize that through the ultraviolet and x-ray photoemission spectroscopy measurement, Cs<sub>2</sub>CO<sub>3</sub> does not decompose during evaporation with various evaporation rates and pressures. The relatively abrupt decreasing in vacuum level is found via UPS, which can be explained by charge exchanges and a strong dipole field at the interface with deposition of cesium-derivatives. Moreover, doping cesium-derivatives into Alq<sub>3</sub> not only reduces the electron-injection barrier height, but also increases the carrier concentration for current conduction. We also demonstrate that the interfacial chemical reaction leads to the excellent electron injection efficiency.

9:20am **EM-MoM5 Ultraviolet-Enhanced Device Properties in Pentacene-Based Thin-Film Transistors.** *J.M. Choi, D.K. Hwang, J.H. Kim, S. Im*, Yonsei University, Republic of Korea

Pentacene thin-film transistors (TFTs) have attracted much attention due to their unique potentials. Nevertheless, there are still several issues to be considered before the TFTs are launched into real applications. Among these issues, the ultraviolet (UV)-induced degradation of pentacene is probably the most immediate and serious. However, in the present study we unexpectedly found that a lower energy UV radiation could rather be advantageous. Since this finding is quite surprising and may be applicable to the improvement of the performance of pentacene TFTs, we report on the contrasting effects of deep and shallow UV on the device performance of pentacene-based TFTs. Furthermore, we also fabricated the low-voltage high-gain pentacene-based inverter using a thin polymer/high-k dielectric through UV treatments. A substrate of 200 nm-thick SiO<sub>2</sub> or 450 nm-thick poly-4-vinylphenol (PVP) on p<sup>+</sup>-Si (-0.01 Ωcm) was adopted for the gate dielectric and gate electrode in the present TFTs. The pentacene channel layers of 50 nm thickness were then patterned on the substrate by the thermal evaporation at RT. Subsequently, Au was evaporated onto the pentacene channels through a source/drain mask at RT (top-contact mode). Under the illumination of 254 nm-UV the TFTs showed degraded mobility and lowered saturation current. It is because the high energy UV degraded the crystalline quality of the pentacene channel as confirmed by optical absorption technique. However, under 352 nm UV the pentacene devices rather exhibited the enhancement of saturation current and also a positive shift of the threshold voltage (V<sub>T</sub>), maintaining their mobilities. We also found that these UV-induced advantages were more clearly obtainable from the TFTs with polymer dielectric where extra negative charges are generated to exist as permanent form at the pentacene/polymer interface while those charges are not necessarily fixed at the pentacene/SiO<sub>2</sub> interface. Through inverters fabricated by illuminating 352nm-UV onto the load-TFT to selectively adjust its V<sub>T</sub>, we also could achieve a stable high-gain low-voltage inverting within the input voltage (V<sub>in</sub>) range of 0 ~ -6 V. We thus conclude that illuminating a low energy UV on the TFT with pentacene/polymer dielectric interface is a simple promising way of enhancing the general performance of pentacene TFTs and controlling their V<sub>T</sub> that enables to achieve stable pentacene-based inverters as well.

9:40am **EM-MoM6 High Efficient Organic Light-Emitting Device with MoO<sub>3</sub>.** *C.-T. Lin, G.-R. Lee, C.-I. Wu, T.-Y. Cho, C.-C. Wu*, National Taiwan University, *T.-W. Pi*, National Synchrotron Radiation Research Center, Taiwan

Two high efficient devices will be discussed in this paper. The first is ITO/MoO<sub>3</sub>/N,N-diphenyl-N,N-bis(1-naphthyl)-1,1-biphenyl-4,4-diamine (NPB) based organic light emitting diodes (OLEDs). Current-voltage characteristics (I-V) and quantum-efficiency (η-J) measurements show the improvement of device performance with insertion of thin MoO<sub>3</sub> between ITO and NPB. Ultraviolet photoemission spectra (UPS) and core-level x-ray photoemission spectra (XPS) data show that MoO<sub>3</sub> would catch electrons from NPB and results in p-type doping in NPB. In addition, there is a significant structure transition from insulating MoO<sub>3</sub> to metallic MoO<sub>2</sub>. As a result of high work function MoO<sub>2</sub> in anode structure and p-type doping NPB, holes can easily be injected from ITO to NPB. The second efficient devices relate to MoO<sub>3</sub>/metal structures in tandem OLEDs. Non-stoichiometric MoO<sub>3</sub> films consist of defect states due to O defects which pins the Fermi level in the forbidden gap. I-V characteristics show that with the MoO<sub>3</sub> hole injection layer between anode and NPB, the current efficiency is almost identical, regardless the choice of anodes. We further

investigation the interaction between low work function metals and MoO<sub>3</sub>. According to UPS and XPS results, low work function metals would easily get O atoms from MoO<sub>3</sub>, resulting in the transition to MoO<sub>2</sub> and the increase in conductivity at the same time. The high work function of MoO<sub>3</sub> can be tuned to relatively low work function of MoO<sub>3</sub>/Al, Mg anode. These results show that MoO<sub>3</sub> can act as a effective hole injection layer in OLEDs, a charge generation layer in tandem OLEDs, and a high ohmic contact of metal/MoO<sub>3</sub> in top-emitting OLEDs.

10:20am **EM-MoM8 Electronic Transport Processes in Polymer Transistors**, R.A. Street, M.L. Chabynyc, J.E. Northrup, Palo Alto Research Center **INVITED**

Solution deposited polymer thin film transistors have mobility reaching of order 1 cm<sup>2</sup>/Vsec making them interesting for applications such as flat panel displays. The increase in mobility is a result of new materials synthesis and an understanding of how the surface energy of the deposition surface controls the structural order of the film. A polymer such as polythiophene is highly anisotropic and conduction occurs essentially in a single 2-dimensional sheet of polymer next to the dielectric interface. Band conduction, coupled with a simple density of states model to account for disorder effects, are able to explain the main features of the electronic transport, based on theoretical calculations of the electronic structure. The upper limits on the mobility, of about 10 cm<sup>2</sup>/Vs can also be estimated from calculations. Although polymer semiconductors cannot be doped by conventional atomic substitution, doping is possible by the incorporation of molecular impurities, and allows further test of transport models. We describe a particular case of acceptor doping with ozone and show that the transport models are able to explain the results and that acceptor binding energies can be deduced. In common with other disordered semiconductors, polymer TFTs exhibit electrical bias stress effects, which induce a change in the threshold voltage due to trapping in states that communicate weakly with the conduction holes. Electrical stress measurements in polythiophene TFTs show properties with a wide range of time constants. The threshold voltage shift increases as a power law in time and in gate voltage. However, after a few days of stress, the threshold voltage shift stabilizes because there is a thermally activated recovery mechanism. The physical mechanisms of the bias stress effects, and whether they are intrinsic to the polymer semiconductor, will be discussed.

11:00am **EM-MoM10 Relationship between the Morphology, Contact Resistance and Field-Effect Mobility in Poly(3-hexylthiophene) based Field-Effect Transistors**, K.A. Singh, G. Sauve, R. Zhang, R.D. McCullough, L.M. Porter, Carnegie Mellon University

In this study we report on the interdependence of morphology, mobility, and contact resistance in field effect-transistors (FETs) based on poly(3-hexyl thiophene) (P3HT) as the active layer. Bottom-contact FETs with Pt electrodes were fabricated with channel lengths varying from 3 to 40µm. The P3HT films were deposited using a solvent-assisted drop casting technique. Atomic force microscopy images indicate that P3HT self assembles into a lamellar structure consisting of nanorods, which contribute to high field-effect mobilities. Our AFM images, along with prior X-ray data,<sup>1</sup> show that an increase in the molecular weight of the polymer leads to an increase in the size of the self-assembled nanorods, leading to higher crystallinity of the polymer. Our results show that both the mobility and the contact resistance depend strongly on the molecular weight, or morphology, of the polymer. For example, at a gate voltage of -80V, the mobility increased from 0.03 to 0.16cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> and the contact resistance decreased from 2.2 to 0.4MΩ when the molecular weight was increased from 5.5 to 11Kg mol<sup>-1</sup>. These mobility values were obtained after correcting for the contact resistance. The results also show a dependence of the mobility and the contact resistance on the gate voltage: The contact resistance decreased from 1.2 to 0.4MΩ with an increase in gate voltage from -20 to -80V; the mobility correspondingly increased by a factor of 8. The dependence of the mobility on the gate voltage is attributed to the presence of traps that limit the charge transport. The effect of mobility on contact resistance can be explained by a diffusion-limited charge injection theory.<sup>2</sup> In summary, our results expand on prior individual studies, primarily on Au/P3HT, that indicate a correlation between mobility and either the contact resistance<sup>3</sup> or molecular weight<sup>1</sup>, to a systematic study on Pt/P3HT transistors. Future experiments with higher molecular-weight P3HT are also planned for comparison.

<sup>1</sup> R. Zhang, B. Li, M.C. Iovu, M. Jeffries-EL, G. Sauve, J. Cooper, S. Jia, S. Tristram-Nagle, D.M. Smilgies, D.N. Lambeth, R.D. McCullough, and T. Kowalewski, J. Am. Chem. Soc. 128[11], 3480(2006)

<sup>2</sup> V. I. Arkhipov, E. V. Emelianova, Y. H. Tak, and H. Bassler, J. Appl. Phys. 84[2], 848(1998)

<sup>3</sup> B. H. Hamadani and D. Natelson, Appl. Phys. Lett. 84[3], 443(2004).

11:20am **EM-MoM11 Potential Profile Evolution in Static and Dynamic Junction Light-Emitting Electrochemical Cells**, L.S.C. Pingree, D.B. Rodovsky, G.P. Bartholomew, D.S. Ginger, University of Washington

Recently, there has been a renewed interest in light-emitting electrochemical cells (LECs) as methods for improving upon their transient performance and lifetimes have emerged. Such devices promise one-step junction deposition and very little dependence upon the electrode materials due to ionic-assisted injection. However, with this renewed interest in LECs, the debate over the appropriate model for their ionic concentration profiles and the underlying charge transport mechanisms has become more important. Three models for device operation have been independently developed,<sup>1,2,3</sup> however, direct evidence of the accuracy of these models through potential profiling has yet to be reported in the literature. In this talk, we present experimental data using Scanning Kelvin Probe Microscopy (SKPM) to directly image the potential profile in planar (gap width ~15 µm) operating LECs. We examine both dynamic junction LECs and chemically-fixed LECs, and find that in the dynamic junction LECs, > 90% of the potential drops near the cathode. This profile develops within 10's of seconds of applying a potential across the planer devices, and evolves very little with time. In the chemically fixed LEC's we find that the potential is initially dropped at the contacts and that the potential profile evolves over minutes to hours in time, dependent upon the ion concentration. Once steady-state is achieved, the majority of the potential is dropped in a similar manner to the dynamic junction LEC. We deduce that the low ionic conductivity of the counter-ions in the chemically-fixed system retards this evolution. Furthermore, we show direct evidence for the accuracy of a primarily p-type model with the emitting junction near the cathode and relatively small electric fields across the bulk of the device.<sup>3</sup>

<sup>1</sup> Pei et al. Science (1995)

<sup>2</sup> deMello et al. Phys. Rev. B (1999)

<sup>3</sup> Leger et al. J. Appl. Phys. (2005).

11:40am **EM-MoM12 Rubrene Polycrystalline Transistor Channel Achieved through In-Situ Vacuum Annealing**, S.W. Park, S.H. Jung, J.M. Choi, J.M. Whang, J.H. Kim, S. Im, Yonsei University, Republic of Korea

Semiconducting organic materials have attracted much attention during the last and even this decade, because of their potentials toward low temperature-, low cost-, and flexible substrate-based electronics. The most popular organic semiconductor is pentacene which has a high field effect mobility exceeding 1 cm<sup>2</sup>/Vs in the form of a channel of a thin-film transistor (TFT). Among the promising candidate materials, rubrene is also attracting recent interests because in single crystal form it shows a very large field-effect mobility (up to 20 cm<sup>2</sup>/Vs). For practical applications, several groups have also studied crystalline thin film phase. But it has been found not easy to get a good crystalline rubrene thin film unlike the case of pentacene, although other group could obtain a good crystalline phase film through a solution-process-involving technique.<sup>1-3</sup> We have studied the crystalline thin film fabrication by thermal evaporation, that may be more compatible with device patterning. In the previous work,<sup>4</sup> we have obtained a rubrene thin film which has an amorphous-crystalline mixed phase on SiO<sub>2</sub> substrate. The film thus contained crystal domains of few hundred diameters embedded in amorphous matrix. In the present work, based on our new findings, we report on how to increase the crystal domain size so that the mobility of a rubrene-TFT may be maximized on SiO<sub>2</sub> dielectric. Initially, amorphous rubrene thin film was obtained on 200 nm-thick SiO<sub>2</sub>/Si substrate at 40 °C in a vacuum chamber by thermal evaporation but in-situ long time post-annealing at the elevated temperatures of 60 ~ 80 °C transformed the amorphous phase into crystalline. Based on an optimum condition to cover whole channel area with polycrystalline film, we have fabricated a rubrene-TFT with a relatively high field effect mobility of 0.002 cm<sup>2</sup>/Vs, on/off ratio of ~ 10<sup>4</sup> and a low threshold voltage of -10V.

<sup>1</sup> D. Käfer and G. Witte, Phys. Chem. Chem. Phys. 7, 2850 (2005).

<sup>2</sup> S. Seo, B. Park, and P. G. Evans, Appl. Phys. Lett. 88, 232114 (2006).

<sup>3</sup> N. Stingelin-Stutzmann, E. Smits, H. Wondergem, C. Tanase, P. Blom, P. Smith and D. Deleuw, Nature. Mater. 4, 601 (2005).

<sup>4</sup> S. Park, J. Whang, J. Choi, D. Whang, M. Oh, J. Kim, S. Im, Appl. Phys. Lett. 90, 153512 (2007).

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