# Thursday Afternoon, October 23, 2008

**Electronic Materials and Processing**
**Room: 210 - Session EM-ThA**

**Organic Electronics**
**Moderator:** R.L. Opila, University of Delaware

**2:00pm EM-ThA1 Dependence of Contact Resistance and Field-Effect Mobility on Morphology in Poly(3-hexylthiophene based Field-Effect Transistors**, *K.A. Singh, G. Sauvé, R. Zhang, T. Kowalewski, R.D. McCullough, L.M. Porter*, Carnegie Mellon University

The field-effect mobility and the contact resistance (Rc) of field effect transistors (FETs) based on regioregular poly(3-hexylthiophene) (P3HT) were investigated as a function of the molecular weight (Mw). Bottom-contact FETs were fabricated having Pt or Au contacts with the channel lengths varying from 3 to 40 μm. Our electrical measurements show an initial increase (decrease) of the mobility (contact resistance) with Mw followed by a saturation of the values. For example, at a gate voltage of -80V and for Mw between 5.5 and 11 kDa in FETs with Pt contacts, the mobility increased from 0.05 to 0.16 $cm^2V^{-1}s^{-1}$, whereas the contact resistance decreased from 1.7 to 0.5 MΩ. However, above 11 kDa, the values remained relatively constant. Devices with Au contacts displayed a similar trend, although the mobilities were lower and the contact resistances were higher, as expected due to the lower work function of Au. The inverse relationship between mobility and Rc is attributed to the dependence of Rc on bulk transport through a depletion region associated with defects near the contacts.[1] Atomic force microscopy (AFM) images indicate that P3HT self assembles in a nanofibrilar morphology.[2] It is also evident that an increase in Mw leads to an increase in the width of the self-assembled nanofibrils and, at the highest molecular weights, to a simultaneous disruption arising from folding of the polymer chains. An associated loss in conjugation within the polymer chains, along with a possible disruption in the π-π stacking that occurs concurrently with the increase in nanofibril size, would account for the saturation of the mobility and the contact resistance at higher molecular weights. In summary, our results show that mobility and contact resistance in P3HT-based FETs depend strongly on the polymer nanomorphology and display an inverse relationship with each other, supporting the theory that the contact resistance is affected by the bulk transport properties of P3HT. Future experiments including X-ray scattering studies are planned to further quantify the structure within the P3HT films.

[1] L. Bürgi, T. J. Richards, R. H. Friend, and H. Sirringhaus, J. Appl. Phys. 94[9], 6129(2003).
[2] R. Zhang, B. Li, M.C. Iovu, M. Jeffries-EL, G. Sauvé, 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).

**2:20pm EM-ThA2 In-Situ Characterization of the Thermal Transformations of High Performance Polymer Semiconductors**, *L.J. Richter, A.J. Moad, D.M. DeLongchamp, R.J. Kline, D.A. Fischer, D.J. Gundlach, B.H. Hamadani,* National Institute of Science and Technology, *M. Heeney, I. McCulloch*, Imperial College London, UK

Polymer semiconductors are inexpensive solution processable alternatives to amorphous silicon for applications in flexible large area electronics. Recently, thin films of spun-cast poly(2,5-bis(3-alkylthiophen-2yl)thieno[3,2-b]thiophene) (pBTTT) have been demonstrated to exhibit exceptional hole mobilities in thin film transistors (TFTs) after heating into a low temperature (~ 150 °C) mesophase. This mild thermal cycle results in high level of crystalline order in the annealed film with a morphology exhibiting single molecular layer terraces. Recently we have discovered that heating into a second, higher temperature (~240°C) phase results in a distinct ribbon morphology. The ribbon phase can be oriented over large (cm$^2$) areas by a simple flow coating process. We have applied polarized optical spectroscopies: spectroscopic ellipsometry and FTIR, along with x-ray diffraction and NEXAFS to the in-situ study of the structural evolution in the two high temperature phases. The first mesophase is a well ordered liquid crystal characterized by melted side chains, but excellent vertical lamella order. The second, high temperature phase appears to be an isotropic melt. The behavior of pBTTT is contrasted with that of poly(dialkylthieno[3,2-b]thiophene-2,5-bithiophene) (pTTBT), a newly synthesized isomer of pBTTT with side chains attached to the thienothiophene rather than the bithiophene unit. This subtle structural change results in distinct thermal behavior. The structural transitions of the isomers are generally similar; however, the side chain melting transition Tm occurs about 50°C lower in pTTBT than in pBTTT. The significant drop in Tm appears to correlate with a subtle decrease in main chain packing interactions. Both materials exhibit high hole mobility, even in their respective liquid crystal mesophases. The slight overall higher order in pBTTT is reflected in the annealed device performance.

**2:40pm EM-ThA3 Advances in Plexcore™ Active Layer Technology Systems for Organic Solar Cells**, *S.P. Williams, D.W. Laird, S. Li, J. Bernkopf, S. Jia*, Plextronics, Inc.

Abstract: Plextronics designs and develops active layer technology for printed electronics devices - OLED displays and lighting, polymer solar cells and plastic circuitry. Active layer technology is the printed semiconductors and conductors that drive device performance. Plextronics has robust control of polymer design and ink formulation, as well as an intimate understanding of device physics and its impact on device performance. This knowledge is applied to the creation of Plexcore™ technology. Plexcore technology is designed to maximize the efficiency, lifetime and stability of printed electronic devices. This talk will emphasize advances to our Plexcore™ PV technology system for Organic Solar Cells. This active layer system includes the hole-transport layer (HTL), and the p-type and n-type semiconductors. To date, Plexcore™ PV has achieved world-class NREL certified efficiency for an all-organic solar cell at 5.4%. In addition, we will discuss both advances in both materials and device properties/performance, OPV cell lifetime measurement and performance, and our trajectory toward commercialization.

**3:00pm EM-ThA4 Isolation of Aging Components in Organic Transistors**, *J.E. Royer, J. Park, C.N. Colesniuc, F. Bohrer, A. Sharoni, I.K. Schuller, W.C. Trogler, A.C. Kummel*, University of California, San Diego

A systematic approach to isolating the cause of device degradation ("aging") in copper phthalocyanine (CuPc) organic thin film transistors (OTFTs) is presented. Aging is one of the primary impediments to the widespread deployments of OTFTs in gas sensors and as drivers for OLEDs. Exposure of 1000ML thick CuPc OTFTs to a sequence of environments including ambient air, clean dry air (20% $O_2/N_2$), water vapor and $N_2$ isolated the causes of device degradation in thick CuPc OTFTs. Initial exposure to ambient air increases conductivity of the CuPc film but also causes rapid device aging characterized by increased threshold voltage and loss of saturation behavior consistent with a loss of control of the channel conductivity by the gate. Exposure of the thick CuPc OTFTs to clean dry air, $H_2O/N_2$ mixture, or clean air/$H_2O$ mixture not only prevents aging but can counter the aging effect of ambient air. This suggests that $O_2$, $H_2O$ and $O_2/H_2O$ products are not responsible for the aging process in ambient air. The data is consistent with trace strong oxidants in ambient air (e.g. $O_3$ and $NO_x$) being responsible for OTFT aging via formation of fixed charge. The aging effect is only present in thick films and is attributed to strong oxidants dissociative chemisorbing in grain boundaries to form fixed charges which degrade the control of the OTFT conductivity by the gate.

**3:20pm EM-ThA5 Modification of Transport Levels of Organic Single Crystals Functionalized with Self Assembled Monolayers**, *A.S. Wan, S. Rangan, D.D.T. Mastrogiovanni, E. Bersch, B. Lee, S. Katalinic, M. Connors, E. Garfunkel, R.A. Bartynski, V. Podzorov*, Rutgers University

We present the first detailed study of energy level modification of single crystal organic semiconductors by functionalization with self-assembled monolayers (SAMs) deposited from the vapor phase by combined photoemission and inverse photoemission spectroscopy (PES-IPES). Large changes in conductivity in organic crystal transistors are observed between pristine and functionalized surfaces. For example, in the case of rubrene functionalized with fluorinated trichlorosilane (FTS) SAMs the conductivity increases almost 6 orders of magnitude at full coverage.[1] Preliminary evidence suggests that the presence of electron-withdrawing SAM on the organic crystals acts to p-type dope the surface, which could lead to the observed energy level and conductivity changes. X-ray photoemission (XPS) results examining both the band bending in the bulk of the organic crystals as well as interface chemistry, as well as scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) will also be discussed.

[1] M. F. Calhoun, J. Sanchez, D. Olaya, M. E. Gershenson, and V. Podzorov. Nat. Materials 7, 84 (2008).

**4:00pm EM-ThA7 Ion Scattering Studies of Self-Assembled Monolayers Grown on Organic Molecular Single Crystals and Polymers**, *L.S. Wielunski, S. Katalinic, B. Lee, V. Podzorov, E. Garfunkel, L.C. Feldman*, Rutgers University

It has been recently observed that electrical conductivity of small-molecule organic semiconductors (such as Rubrene) can be strongly enhanced in the presence of fluorinated silane SAM at the surface.[1] In order to understand the microscopic origin of this large electronic effect and to resolve the exact SAM composition, we have performed Rutherford Backscattering Spectrometry (RBS) of SAM-rubrene and SAM-polymer systems using 2

MeV He ions. RBS allows a determination of the fluorine and silicon concentrations in a monolayer-thick film formed at the surface of organic crystals and polymers. Preliminary results indicate a modified SAM composition upon adsorption, possibly due to new interfacial chemistry or possibly due to beam induced effects. The analytical results will be compared with electrical measurements of SAM-induced conductivity in organic semiconductors.

[1] M. F. Calhoun, J. Sanchez, D. Olaya, M. E. Gershenson and V. Podzorov, Nature Mat. 7, 84 (2008).

4:20pm **EM-ThA8 Soft X-Ray Spectroscopic Studies of the Electronic Structure of Cu(tfacac)$_2$en (TFAC)**, *A. DeMasi, L.F.J. Piper, R. Allenbaugh, L. Doerrer, K.E. Smith*, Boston University

The valence and core level electronic structure of the organic molecule Cu(tfacac)$_2$en, or TFAC, has been measured using synchrotron radiation-excited resonant x-ray emission spectroscopy (RXES) and x-ray photoelectron spectroscopy (XPS). Samples were in the form of thin films, grown in-situ in an organic molecular beam deposition chamber attached to the spectrometer system. The thin films were characterized with scanning electron microscopy (SEM) after growth, and ordering is observed that is consistent with expectations for molecular beam deposition. The films were found to be sensitive to photon induced beam damage, but this problem could be alleviated by continuous translation of the films during measurement. Our measurements indicate that TFAC potentially has semiconducting properties, and may compare favorably with copper phthalocyanine as an organic semiconductor. Work supported in part by the AFOSR.

# Authors Index

**Bold page numbers indicate the presenter**