

Wednesday Morning, November 11, 2009

Electronic Materials and Processing

Room: B1 - Session EM-WeM

Organic & Molecular Electronics

Moderator: L.M. Porter, Carnegie Mellon University

8:00am **EM-WeM1 Nanoscale Guided Molecular Engineering of Organic Electro-Optical Materials**, *D.B. Knorr, X. Zhou, Z. Shi, J. Luo, S. Jang, A.K.-Y. Jen, R.M. Overney*, University of Washington

Increasing complexity in bottom-up molecular designs of amorphous structures with multiple relaxation modes demand an integrated and cognitive design approach, where chemical synthesis is guided by both analytical tools and theoretical simulations. This is true of organic second-order nonlinear optical (NLO) materials, which are being actively pursued for applications in photonic devices. For practical applications, NLO materials must have both high macroscopic EO activity and thermal stability. High EO activity can be achieved by acentrically ordering a system containing a high density of high dipole chromophores via electric field poling at elevated temperatures. Thermal stability requires the system to have internal constraints to prevent collapse of the acentric order at operating temperatures. Recent efforts for achieving both requirements have focused on dendrons capable of self-assembly through arene-perfluoroarene ($\text{Ar}^{\text{H}}\text{-Ar}^{\text{F}}$) quadrupolar interactions within self-assembled glassy chromophore systems, which provided excellent EO activity above 300pm/V and good thermal stability.

In this study, nanoscale scanning probe based thermo-mechanical analyses, intrinsic friction microscopy (IFM) and shear-modulation force microscopy yield direct insight into the molecular enthalpic and entropic relaxation modes of these materials. $\text{Ar}^{\text{H}}\text{-Ar}^{\text{F}}$ interactions of dendritic moieties for coarse self assembly are found to impose three phase relaxation regimes with two transition temperatures, T_1 and T_2 . Energetic analyses based on IFM identify increasing temporal stability with increasing arene size for the low temperature regime. Electric field poling efficiency is found to be inversely proportional to entropic cooperative contributions. Based on a molecular dynamic simulation, activation energies are tied primarily to interactions between chromophore (dipole), dendritic (quadrupole) moieties and combinations thereof below the incipient glass transition temperature. Above T_1 , molecular mobility becomes increasingly cooperative. Sufficient mobility exists in the region of $T_1 < T < T_2$ to allow for chromophore acentric electric field alignment, as non-covalent interactions associated with stabilization of the system below T_1 are in competition with melt-like effects. Further, cooperativity increases with increasing arene size, and accounts for approximately 80% of the observed apparent activation energy above T_2 . Although beneficial to temporal stability with increased operating temperatures, cooperativity was found to lower the poling efficiency. Future synthesis efforts therefore must balance cooperativity to obtain satisfactory results in both stability and efficiency.

8:20am **EM-WeM2 Perpendicular Interaction between Donor and Acceptor Molecules on Au(111) Surface**, *U.G.E. Perera*, Ohio University, *R. Mishima*, Osaka University, Japan, *S.-W. Hla*, Ohio University

When two types of molecules having opposite tendency to donate and accept electrons are put together, charge transfer between the molecules can take place. Charge transfer alters the frontier molecular orbitals, and thus it can be used to engineer materials having a wide range of properties. Investigation of the charge transfer processes at a molecular level is a new avenue of exciting research. Here, we present a low temperature scanning tunneling microscopy (STM) and spectroscopy study of single molecule level charge transfer process between decamethylmanganocene ($\text{Mn}(\text{C}_5\text{Me}_5)_2$) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) on a Au(111) surface at 4.6K. Both molecules are deposited onto an atomically clean Au(111) surface at an ultrahigh vacuum environment. On Au(111), the TCNQ molecules form well ordered two dimensional self-assembled clusters while the $\text{Mn}(\text{C}_5\text{Me}_5)_2$ molecules adsorb either on TCNQ layer or on the bare surface areas. The STM images show that $\text{Mn}(\text{C}_5\text{Me}_5)_2$ molecules position on the surface with tilted cyclopentacene rings. A comparative tunneling spectroscopy between the $\text{Mn}(\text{C}_5\text{Me}_5)_2$ /Au(111) and $\text{Mn}(\text{C}_5\text{Me}_5)_2$ /TCNQ/Au(111) assemblies clearly reveals the shift of frontier molecular orbitals and thus the detailed charge transfer mechanism induced by deposition of $\text{Mn}(\text{C}_5\text{Me}_5)_2$ has been able to explain. This research is supported by the United States Department of Energy BES grant number DE-FG02-02ER46012.

8:40am **EM-WeM3 An Ultra-Thin Molecular Superconductor**, *K. Clark*, Ohio University, *A. Hassani*, Nanotechnology Research Institute, Japan, *K.-F. Braun*, Physikalisch Technische Bundesanstalt, Germany, *H. Tanaka*, Nanotechnology Research Institute, Japan, *S.-W. Hla*, Ohio University

Almost a century after its discovery by H. Kamerlingh Onnes, superconductivity continues to be an inspirational subject for many physicists because of its rich physical phenomena. Among a variety of superconducting materials, the organic superconductors are regarded as "unconventional superconductors" based on the different nature of their superconducting states as compared to the conventional BCS superconductors. A class of Bechgaard type-5 charge transfer salts having a D_2A arrangement, where D and A are the donor and acceptor respectively, exhibit superconductivity in the bulk. Here, we form an ultra-thin Bechgaard salt with the smallest possible molecular-unit thickness composed of just a sheet of molecular layer having individual GaCl_4 molecules sandwiched between the chains of a double domino stacked BETS on a Ag(111) surface. Remarkably, scanning tunneling spectroscopy of this ultra-thin Bechgaard layer at 5.4K reveals a clear superconducting gap exhibiting d-wave pairing symmetry. Real space spectroscopic images with a molecular resolution provide an experimental paradigm: The stacked BETS chains in the layer act as the superconducting sites. In stark contrast to the high T_c superconductors, the spectroscopic maps clearly display nanoscale electronic order indicating a robust superconductivity down to an extreme spatial limit.

9:00am **EM-WeM4 Correlating Structure and Electronic Properties in Oligothiophene Monolayers, an AFM Study**, *F. Martin, B. Hendriksen, A.J. Katan*, Lawrence Berkeley National Laboratory, *C. Mauldin*, University of California, Berkeley, *J.M.J. Frechet, M. Salmeron*, Lawrence Berkeley National Laboratory

Organic compounds are currently considered as the main building block of electronic devices that could lead to new commercial applications which include flexible electronics as well as organic photovoltaics. Correlating structural and electrical properties is a key requirement to understand charge transport in organic thin films.

We investigated the effect of crystallinity and grain boundaries on the conductivity of Langmuir-Blodgett oligothiophene monolayers using Current-Sensing Atomic Force Microscopy (CS-AFM).

We used the AFM tip as a tool to inject charges and manipulate the crystalline monolayer. We found that passing electrical current locally from the conductive AFM tip led to reversible charging of the native SiO_2 layer supporting the film as far as microns away from the charge injection point. This effect, due to charge spreading through the crystalline monolayer, was used to image conduction pathways and study the effect of grain boundaries on the resistivity of the monolayer.

In addition, we found that scanning manipulation at loads in the order of 100nN lead to a 5 fold decrease of the monolayer conductivity in CS-AFM. Subsequent molecular resolution AFM revealed that the degree of crystalline order in manipulated regions of the monolayer had strongly decreased, offering a direct proof of the correlation between order and conductivity in organic monolayers.

9:20am **EM-WeM5 Transport through a Single Octanethiol Molecule Adsorbed on a Pt-modified Ge(001) Surface**, *D. Kockmann, H.J.W. Zandvliet, B. Poelsema*, University of Twente, Netherlands

We have studied (single) octanethiol molecules adsorbed on a Pt-modified Ge(001) surface, using scanning tunneling microscopy/spectroscopy.

On a clean Ge(001) surface we deposited a submonolayer amount of platinum by evaporation. Patches of dimerized atomic chains form via self-organization on the surface during the subsequent annealing-step. We have decorated the Pt-modified Ge(001) surface with octanethiol molecules. STM at 77 K revealed that at low coverage the molecules selectively adsorb on the Pt chains and not on the underlying terrace. The molecules lay down on the Pt chains, in contrast to SAM's, where they stand upwards.

In order to distinguish between the octane-tail and the thiol-head of the molecule, we have performed STS above the different regions of the molecule, again at 77 K. We observed that the $I(V)$ spectra recorded above the thiol-head were conspicuously different from the spectra recorded above the octane-tail. From that we could determine the molecular orientation of the adsorbent.

In addition, we have measured current-time traces on the adsorbed octanethiol molecules. Throughout these experiments we turned off the feedback-loop of the STM. Then each measurable rearrangement or

conformational change of the molecule is reflected in the $I(t)$ traces. During these measurements we occasionally found a sudden dramatic increase in current from 1 nA (set point current) to values between 10-15 nA. The residence times at this high current varied between 10-40 seconds. In most cases the current jumps back to its original set point value of 1 nA within the open-loop measurements, which typically last for 50-100 seconds. STM images recorded after the open-loop experiments revealed that the octanethiol molecules remained at their original position.

From these observations we concluded that during the $I(t)$ measurements the molecule wagged its tail upward, thereby making contact with the tip of the STM. Hence, we measured electron transport through the molecule instead of electron tunneling from tip to molecule. The derived single molecule resistance, 100-150 M Ω , is in accordance with literature.

9:40am **EM-WeM6 Modulation of Charge Injection and Transport in Poly(3-hexylthiophene)-Based Field-Effect Transistors by Self-Assembled Monolayers**, *K.A. Singh, T. Nelson, J. Belot, R.D. McCullough, T. Young, T. Kowalewski*, Carnegie Mellon University, *P. Nachimuthu, S. Thevathasan*, Pacific Northwest National Laboratory, *L.M. Porter*, Carnegie Mellon University

Charge injection and transport in bottom-contact poly(3-hexylthiophene) (P3HT) based field-effect transistors (FETs), wherein the Au source and drain contacts are modified by self-assembled monolayers (SAMs), is reported. Four SAMs of different chemical composition were selected to either enhance or reduce charge injection across the contacts. The rr-P3HT films were drop cast from a solution in chloroform in a saturated environment. Prior to P3HT deposition the FETs were treated with octyltrichlorosilane (OTS) solution in hexadecane for 2 hrs, dried and then immersed in a solution containing one of the SAMs in ethanol for another 2 hrs. The contact resistance (R_c) was measured using the transmission line method and the effective field-effect mobility (μ) was determined from the linear region of the transistor characteristics. Treatment of FETs with the first two SAMs resulted in an increase in μ and a decrease in R_c , whereas treatment with the other two SAMs resulted in a decrease in μ and an increase in R_c . For example, in one case, μ increased from 0.15 to 0.20 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and R_c decreased from 0.61 to 0.34 M Ω ; in the opposite case, μ decreased to 0.09 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ and R_c increased to 0.90 M Ω . The electrical properties of the transistors correlate with changes in the metal workfunction by up to 0.9 eV, as estimated using ultraviolet photoelectron spectroscopy. Besides using the SAMs for tuning the charge injection, the monolayer formed by OTS on SiO_2 at the insulator/ P3HT interface resulted in improved morphology of the P3HT film, as observed by atomic force microscopy, and an associated increase of μ from 0.03 to 0.15 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$. In summary, the charge carrier injection and transport in P3HT-based FETs were successfully modulated by treatment with SAMs. The use of OTS at the SiO_2 /P3HT interface also resulted in improved morphology and enhanced charge transport. Further details regarding the use of self-assembled monolayers will be presented along with the device and photoemission characteristics.

10:40am **EM-WeM9 Reliable and Selective Formation of Metallic Contacts to Organic Thin Films: Towards Molecular Electronics**, *P. Lu, Z. Shi, A.V. Walker*, Washington University in St. Louis

We have investigated the selective deposition of copper on alkanethiolate self-assembled monolayers (SAMs) using electroless deposition. This work has important applications in molecular and organic electronics, sensing, biotechnology, photonics and other technologies. We demonstrate that useful deposition rates can be obtained by "self-seeding" - the immersion of the SAM in a solution containing Cu^{2+} ions prior to addition of the reducing agent, formaldehyde. The selectivity of the deposition is achieved by increasing the bath temperature to 45 °C. At this temperature Cu deposition ceases on $-\text{CH}_3$ terminated SAMs but continues on $-\text{COOH}$ terminated SAMs. Finally, and perhaps most importantly, copper penetration through SAMs can be prevented by the addition of adenine to the bath. The addition of adenine also leads to smooth film morphologies. Each of these effects is explained by the formation of complexes with the SAM terminal group. Copper-terminal group complexes lead to useful deposition rates and control of the selectivity of the deposition. The formation of adenine-terminal group complexes prevents Cu penetration through the monolayer. Similarly, we observe that strongly adherent nickel films can be selectively deposited on functionalized SAMs through careful control of the bath conditions, especially temperature and pH.

11:00am **EM-WeM10 Quantum Dot Polymer Light Emitting Device With a Zinc Oxide Nanoparticle Film**, *L. Qian, Y. Zheng, J. Xue, P.H. Holloway*, University of Florida

A polymer light emitting device (PLED) with an active layer consisting of CdSe/ZnS or CdS/ZnS core/shell quantum dots (QDs), and an electron transport/passivation layer consisting of 5 nm ZnO nanoparticles has been

studied. The complete device consists of a glass substrate with the following layers: glass/ITO/PEDOT-PSS/poly-TPD/QDs/ZnO/Al-top-contact. The PEDOT-PSS, poly-TPD, QD, and ZnO layers were all deposited from solutions using spin casting, while the ITO layer was sputter deposited and the Al contact was deposited by thermal evaporation through a shadow mask. Thus the device is predominantly a solution-processed QD-LED with simple vacuum processing instead of thermal evaporation of multiple organic small molecule layers. The emitted color was tuned from blue (CdS/ZnS) to green or red (CdSe/ZnS) by adjusting the composition and size of the QDs. Use of the ZnO layer reduced the injection voltage for a brightness of $\sim 200 \text{ cd/m}^2$ from ~ 11 to $\sim 2.6 \text{ V}$ (green light), and improved the stability with time. For example, an unencapsulated QD-LED with a ZnO nanoparticle layer exhibited a stable $\sim 200 \text{ cd/m}^2$ brightness for 18 hrs in ambient air, while a comparable device without the ZnO layer degraded from 80 to 6 cd/m^2 in 3 hrs under the same conditions. The reasons for these improvements will be discussed.

11:20am **EM-WeM11 Effects of Different Organic Passivation Layers on the Electrical Stabilities of Flexible Organic Thin Film Transistors under Cyclic Bending**, *Y.G. Seol, J.S. Park, J.H. Ahn, N.-E. Lee*, Sungkyunkwan University, Korea

One of the critical issues for applications of flexible organic thin film transistors (OTFTs) for flexible electronic systems is the electrical stabilities of the OTFT devices, including variation of the current on/off ratio ($I_{\text{on}}/I_{\text{off}}$), leakage current, threshold voltage, and hysteresis, under repetitive mechanical deformation. In particular, repetitive mechanical deformation accelerates the degradation of device performance at the ambient environment. In this work, electrical stabilities of the pentacene organic thin film transistors (OTFTs) employing various passivation layers were investigated under mechanical cyclic bending. Flexible bottom-gated pentacene-based OTFTs fabricated on flexible polyimide substrate with poly-4-vinyl phenol (PVP) dielectric as a gate dielectric were passivated by the solution-processed, evaporated, and plasma-deposited organic layers. For cyclic bending experiment of flexible OTFTs, the devices were cyclically bent up to 10^5 times with 5 mm bending radius. In the most of the devices after 10^5 times of bending cycles, the off-current of the OTFT with no passivation layers was quickly increased due to increases in the conductivity of the pentacene caused by doping effects from O_2 and H_2O in the atmosphere, which leads to decrease in the $I_{\text{on}}/I_{\text{off}}$ and increase in the hysteresis. With passivation layers, however, the electrical stabilities of the OTFTs were improved significantly. In particular, the OTFTs with plasma-deposited organic layers showed the best electrical stabilities up to the bending cycles of 10^5 times compared to the devices with the solution-processed or thermal-evaporated organic layer. Changes in electrical properties of cyclically bent OTFTs with different organic passivation layers will be compared and discussed in detail.

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