

# Thursday Morning, October 31, 2013

## Electronic Materials and Processing

Room: 101 B - Session EM+AS+EN+TF-ThM

## Hybrid and Organic Electronics

Moderator: A.J. Muscat, University of Arizona, J.R.

Engstrom, Cornell University, J. Xue, University of Florida

8:00am **EM+AS+EN+TF-ThM1 When the Sequence of Thin Film Deposition Matters: Examination of Organic-on-Organic Heterostructure Formation using Molecular Beam Techniques and *In Situ* Real Time X-ray Synchrotron Radiation**, E.R. Kish, R.K. Nahm, A.R. Woll, J.R. Engstrom, Cornell University

Over the past several years significant advances have been made concerning our understanding of the growth of crystalline small molecule organic thin films consisting of a single component. An important challenge in organic electronics is to develop and improve methods to integrate both *p*-type and *n*-type small molecule organic semiconductors into the same device microstructure. Thus, developing an understanding of the molecular scale events that lead to heterojunction formation is essential. In this work we present results concerning nucleation and growth of a series of *n*-type organic semiconductors: PTCDI- $C_n$ , where the length of the alkyl tail ( $C_n$ ) attached to the perylene core of these molecules has been varied from  $n = 5, 8$  and  $13$ . In addition to examinations of the growth of these molecules themselves, we have also examined the growth of these molecules on ultrathin films of the *p*-type semiconductor pentacene, and vice-versa, the growth of pentacene on layers of PTCDI- $C_n$ . In this work we make use of molecular beam techniques to deliver PTCDI- $C_n$  and/or pentacene, and growth of these layers is monitored *in situ* and in real time using X-ray synchrotron radiation, and *ex situ* using atomic force microscopy. Concerning the growth of PTCDI- $C_n$  on 1 monolayer (ML) of pre-deposited pentacene we find substantial differences between the  $C_5$  and  $C_{13}$  variants of this molecule: X-ray intensity oscillations at the anti-Bragg scattering condition, signifying layer-by-layer (LbL) growth, are *much* more extended for the  $C_5$  variant. Interestingly, despite the extended nature of LbL growth for this molecule, the thin film crystallinity formed from  $C_5$  is significantly reduced when compared to the  $C_{13}$  variant, suggesting that the molecular interactions that provide the driving forces for crystallization, may also contribute to higher barriers for step-edge crossing events—highly crystalline but rough thin films. More dramatic differences emerge as we examine the sequence of deposition. While each perylene variant grows approximately layer-by-layer on 1 ML of pentacene for several layers of PTCDI- $C_n$ , when this order is reversed, and pentacene is grown on 1 ML of PTCDI- $C_n$ , dramatic changes occur: growth is immediately 3D, and a very rough morphology is formed. *Ex situ* analysis using AFM reveals that the thin film morphology is rougher than what would be formed from simple random deposition. Examination of multilayer structures, e.g., A/B/A/B... where A is PTCDI- $C_n$  and B is pentacene, shows that the growth of roughness tends to reflect this asymmetry, where the pentacene cycle tends to roughen the vacuum/film interface, while the PTCDI- $C_n$  cycle tends to smoothen the interface.

8:20am **EM+AS+EN+TF-ThM2 Scanning Tunneling Microscopy and Spectroscopy Study of Sliding Defects in  $\alpha$ -6T Films on  $C_{60}/Au(111)$** , D.B. Dougherty, J. Wang, North Carolina State University

Compared to the Si-based traditional inorganic electronics, mechanical flexibility is a tremendous advantage for organic electronics. The origin of mechanical flexibility is the relatively weak intermolecular interactions. In addition to flexibility, these weak interactions can also lead to structural disorder in organic thin films that has a significant impact on carrier transport in organic electronic devices [1]. A recent example can be seen in the analysis of the temperature dependence of carrier mobility in 2D  $\alpha$ -sexithiophene ( $\alpha$ -6T) field effect transistors (FET's) [2] which differ from 3D counterparts due to different sources of disorder.

In an effort to understand the origin of disorder in sexithiophene films relevant to 2D FETs, we have grown single layer  $\alpha$ -6T films on top of a  $C_{60}$  monolayer on Au (111). By utilizing Scanning Tunneling Microscopy and Spectroscopy, structural disorder effects in the  $\alpha$ -sexithiophene layer have been observed. Sexithiophene molecules form islands on  $C_{60}$  monolayer with apparent height about equal to the length of one single molecule. The  $\alpha$ -6T molecules assemble into "dimer strips" indicating the competition between interactions present in the  $\alpha$ -6T bulk crystal and interactions with  $C_{60}$  substrate. Random apparent height variations are observed that can be explained by vertical sliding defects in the layer, similar to other standing molecular films [3]. Remarkably, these defects have a minimal effect on the HOMO energy level, which is instead only strongly influenced by random

STM tip variations. This shows that intrinsic structural disorder in  $\alpha$ -6T films does not have a strong electronic impact.

\*This work was funded by NSF CAREER award DMR-1056861.

[1] Tessler et al., Adv. Mater. 21, 2741 (2009).

[2] Brondijk et al., Phys. Rev. Lett. 109, 056601 (2012).

[3] Kang et al., Appl. Phys. Lett. 86, 152115(2005).

8:40am **EM+AS+EN+TF-ThM3 Organic-Organic Heterostructures for Organic Electronics**, F. Schreiber, University of Tuebingen, Germany

INVITED

Functional organic materials and devices are becoming increasingly complex. Their preparation and growth is, not surprisingly, similarly complex, and the resulting structure will be determined by a competition between kinetics and thermodynamics, which is not trivial to predict in particular for multi-component systems. We discuss general concepts [1] and recent examples [2,3] of organics-based heterostructure growth in the context of kinetic effects compared to thermodynamic (equilibrium) structure.

These include unconventional roughening and smoothing behavior at interfaces as well as unconventional structural motifs, such as a frozen-smectic structure formed in a blend of organic semiconductors which form conventional crystals as pure compounds [4].

Particular attention is paid to the case of kinetically limited phase separation of a donor-acceptor pair (DIP:C60) used in organic photovoltaics [5]. This leads to asymmetric domain sizes near bottom vs top electrode due to the time (thickness) dependent phase separation with important implications for device modeling [1,6].

We also discuss the associated optical properties and the question of coupling between donor and acceptor components [7,8]. Finally, we comment on the implications for the optical and electronic properties as well as possible device applications with focus on organic photovoltaics [1,6].

Contributions by A. Hinderhofer, C. Frank, K. Broch, F. Anger, J. Novak, R. Banerjee, A. Gerlach, and S. Kowarik, are gratefully acknowledged.

[1] A. Hinderhofer and F. Schreiber, Organic-organic heterostructures: Concepts and applications, ChemPhysChem, 13 (2012) 628

[2] A. Hinderhofer et al., Templating effect for organic heterostructure film growth: Perfluoropentacene on diindenoperylene, J. Phys. Chem. C 115 (2011) 16155

[3] A. Hinderhofer et al., Structure and morphology of co-evaporated pentacene-perfluoropentacene thin films, J. Chem. Phys. 134 (2011) 104702

[4] A. Aufderheide et al., Mixing-induced anisotropic correlations in molecular crystalline systems, Phys. Rev. Lett. 109 (2012) 156102

[5] R. Banerjee et al., Evidence for kinetically limited thickness dependent phase separation in organic thin film blends, Phys. Rev. Lett. (2013)

[6] J. Wagner et al., High fill factor and open circuit voltage in organic photovoltaic cells with diindenoperylene as donor material, Adv. Funct. Mater. 20 (2010) 4295

[7] K. Broch et al., Optical evidence for intermolecular coupling in mixed films of pentacene and perfluoropentacene, Phys. Rev. B 83 (2011) 245307

[8] F. Anger et al., Photoluminescence spectroscopy of pure pentacene, perfluoropentacene and mixed thin films, J. Chem. Phys. 136 (2012) 054701

9:20am **EM+AS+EN+TF-ThM5 Importance of Interfaces in Graphene Transfer to Polymers**, E.H. Lock, Naval Research Lab, D. Delongchamp, National Institute of Standards and Technology (NIST), M. Laskoski, Naval Research Lab, M. Baraket, Lab de Chimie Inorganique et Biologique, France, S.P. Mulvaney, S.C. Hernandez, P.E. Sheehan, J.T. Robinson, Naval Research Lab, C. Jaye, D.A. Fisher, NIST, S.G. Walton, Naval Research Lab

Organic materials are widely used because they are cost effective and have excellent physical and mechanical properties. The polymers of interest in this work are polystyrene (PS) and ultra-high molecular weight polyethylene (UHMW PE). PS has been successfully used as electronics and biosensors platforms. UHMW PE is the material in lightweight high strength Dyneema and Spectra fibers for personal armor. However, to enable production of flexible and wearable electronic devices we need to transform the inherently low thermal and electrical polymer conductance. In order to maintain low cost it is technologically beneficial to modify only the surface of the polymer while preserving the bulk properties. This approach leads to development of hybrid materials. We recently reported production

of graphene/polystyrene (Gr/PS) hybrid material using a dry transfer print method [1]. Graphene is an excellent “coating” for a polymer because it is flexible and has high thermal and electrical conductivity. Furthermore, its remarkable chemical stability and low permeability allows for applications as barrier coating for plastics.

However, production of graphene/polymer hybrids is not trivial because graphene has to be transferred from the growth substrates (e.g. copper foil, SiC) to polymers without introducing chemical and structural defects. In this talk we will show that there may be a “trade off” between the use of attachment chemistries to ensure good transfer, and the resultant performance of the transferred graphene. More aggressive attachment chemistries ensure transfer success at the cost of compromising the transport properties of graphene. Different interface preparation approaches may prove to be optimal for different applications, depending on whether transfer yield or surface conductivity is more important. This work was supported by the Naval Research Laboratory Base Program. S. C. Hernandez and M. Baraket were postdoctoral National Research Council fellows during the completion of this work.

---

[1] E. H. Lock, et. Al. “High-quality uniform dry transfer of graphene to polymers”, *Nano Letters* 12, 102 (2012).

9:40am **EM+AS+EN+TF-ThM6 Towards Organic Electronics: Methods for the Selective Deposition of Semiconductors and Metals**, Z. Shi, J. Yang, K. Borner, A. Ellsworth, A.V. Walker, University of Texas at Dallas

Robust methods for the chemically selective deposition of metals, semiconductors, biomolecules and other substances are developed and applied in the construction of complex two- and three-dimensional structures. This work has important applications in molecular and organic electronics, sensing, biotechnology and photonics. These methods are easily parallelized, afford precise nanoscale placement and are compatible with photolithography. This work has important applications in photovoltaics, molecular and organic electronics, sensing, photonics and other technologies.

Several recent developments in our laboratories are discussed including the chemical bath deposition (CBD) and atomic layer deposition (ALD) of ZnO and the formation of Cu and Cu<sub>x</sub>S “wires” on micron-scale patterned surfaces. We demonstrate that the deposition selectivity and film morphology can be controlled by the deposition technique, the experimental conditions and the underlying substrate chemistry. Optimization and further development of these techniques requires a detailed understanding of the reaction pathways involved in the interaction of organic thin films with metals, organometallic compounds, ions, and other compounds.

11:00am **EM+AS+EN+TF-ThM10 Organic Thin-Film Transistors Manufactured by Vacuum-Evaporation in a Roll-to-Roll Web-Coater Exploiting a Flash-Evaporated Polymer Gate Dielectric**, Z. Ding, G. Abbas, H. Assender, University of Oxford, UK, D.M. Taylor, E. Patchett, A. Williams, Bangor University, UK, J. Morrison, S. Yeates, University of Manchester, UK, L. Lin, University of Leeds, UK

We have developed a process to make bottom gate top contact organic thin-film transistors (OTFTs) in a roll to roll vacuum web coater environment. The vacuum based all-evaporated process allows a solvent-free deposition to make organic/inorganic multilayer structures for thin-film electronic devices on a flexible substrate, at high speed. The polymeric gate dielectric layers have been fabricated by flash evaporation of acrylic monomers followed by radiation curing of E-Beam or Plasma onto a polymer film with pre-patterned metal gates. We now report our work on improving the performance of OTFTs by including modification of the dielectric surface, using new dielectric materials and new semiconductors. With a non-polar dielectric surface, charge carrier mobility of 1cm<sup>2</sup>/Vs; on/off current ratio of 10<sup>8</sup>, sub-threshold slope of 0.3V/decade and saturated output curve was routinely achieved in DNTT transistors. The devices showed good stability in ambient environment with no need of encapsulation. Inverters and ring oscillators based on these transistors were fabricated successfully. The effect of mechanical deformation; aging time and aging environment on these thin-film devices were also investigated in this work.

11:20am **EM+AS+EN+TF-ThM11 Interface Science of Emerging Thin Film Photovoltaic Technologies: The Role of Interface Composition on Charge Harvesting Efficiencies**, N.R. Armstrong, University of Arizona  
**INVITED**

Organic solar cells, while still not at the efficiencies of more mature PV technologies, are improving in efficiency at the fastest rate of all PV technologies. There are nevertheless significant technical and scientific challenges to be overcome before OPVs can be a legitimate energy conversion technology. This talk will review our recent work in

understanding the role that electrical contacts play in determining the performance characteristics of OPVs. We discuss both the role of the contact/active layer interface, and the roles of electron- or hole-selective interlayer materials in modifying the properties of the contact, for both small molecule and polymer based OPVs.

We will focus first of all on the characterization small molecule systems (correlating UPS, conducting tip AFM, and device performance), where the contact can dictate the efficiency of charge harvesting through specific interactions between small molecule components and the contact. We find that for several systems orientation, charge redistribution, heterogeneity of charge harvesting, local fields and leakage currents are all influenced by these interactions.

We secondly deal with electron-selective interlayers (e.g. ZnO, TiO<sub>2</sub>), and the role of surface/interface composition in controlling their selectivity. Interlayer materials, typically with thicknesses of 10-50 nm, are increasingly required to ensure efficient and selective charge harvesting in bulk-heterojunction polymer and small molecule based organic solar cells (OPVs) and even in solar cells based on nanocrystalline semiconductors. Selectivity is typically achieved by choosing band edge energies in interlayer materials which provide for efficient collection of only one charge carrier and minimization of surface recombination velocities. New approaches to oxide interlayers will be shown, using conventional (sol-gel) and sputtering approaches, and chemical vapor deposition, focusing on the surface characterization of electronically relevant defect states which appear to control charge selectivity, sub-micron heterogeneity in charge collection, and OPV efficiency.

# Authors Index

**Bold page numbers indicate the presenter**

## — A —

Abbas, G.: EM+AS+EN+TF-ThM10, 2  
Armstrong, N.R.: EM+AS+EN+TF-ThM11, **2**  
Assender, H.: EM+AS+EN+TF-ThM10, 2

## — B —

Baraket, M.: EM+AS+EN+TF-ThM5, 1  
Borner, K.: EM+AS+EN+TF-ThM6, 2

## — D —

Delongchamp, D.: EM+AS+EN+TF-ThM5, 1  
Ding, Z.: EM+AS+EN+TF-ThM10, **2**  
Dougherty, D.B.: EM+AS+EN+TF-ThM2, **1**

## — E —

Ellsworth, A.: EM+AS+EN+TF-ThM6, 2  
Engstrom, J.R.: EM+AS+EN+TF-ThM1, **1**

## — F —

Fisher, D.A.: EM+AS+EN+TF-ThM5, 1

## — H —

Hernandez, S.C.: EM+AS+EN+TF-ThM5, 1

## — J —

Jaye, C.: EM+AS+EN+TF-ThM5, 1

## — K —

Kish, E.R.: EM+AS+EN+TF-ThM1, 1

## — L —

Laskoski, M.: EM+AS+EN+TF-ThM5, 1  
Lin, L.: EM+AS+EN+TF-ThM10, 2  
Lock, E.H.: EM+AS+EN+TF-ThM5, **1**

## — M —

Morrison, J.: EM+AS+EN+TF-ThM10, 2  
Mulvaney, S.P.: EM+AS+EN+TF-ThM5, 1

## — N —

Nahm, R.K.: EM+AS+EN+TF-ThM1, 1

## — P —

Patchett, E.: EM+AS+EN+TF-ThM10, 2

## — R —

Robinson, J.T.: EM+AS+EN+TF-ThM5, 1

## — S —

Schreiber, F.: EM+AS+EN+TF-ThM3, **1**  
Sheehan, P.E.: EM+AS+EN+TF-ThM5, 1  
Shi, Z.: EM+AS+EN+TF-ThM6, 2

## — T —

Taylor, D.M.: EM+AS+EN+TF-ThM10, 2

## — W —

Walker, A.V.: EM+AS+EN+TF-ThM6, **2**  
Walton, S.G.: EM+AS+EN+TF-ThM5, 1  
Wang, J.: EM+AS+EN+TF-ThM2, 1  
Williams, A.: EM+AS+EN+TF-ThM10, 2  
Woll, A.R.: EM+AS+EN+TF-ThM1, 1

## — Y —

Yang, J.: EM+AS+EN+TF-ThM6, 2  
Yeates, S.: EM+AS+EN+TF-ThM10, 2