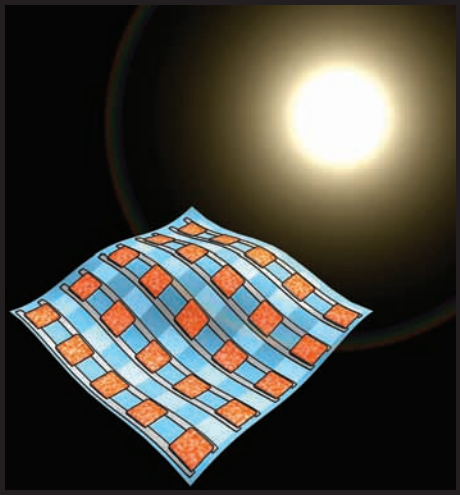
Organic Electronics and Photovoltaics

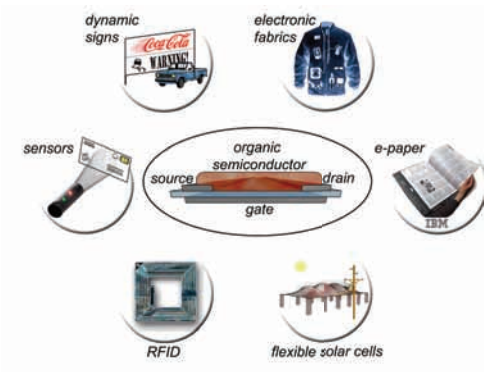


Objective

Our goal is to develop an integrated suite of non-destructive measurement methods to evaluate organic-based electrical devices and tie electrical and photovoltaic performance to the interfacial morphology of the active molecules in the device, thereby correlating it to particular chemical structures, fabrication methods, and processing parameters. By providing the measurement link for the structure - processing - performance paradigm, our methods will rationally accelerate product development, enable standard measurements, and provide a basis for quantitative comparisons in this emerging technology where device variability and optimization are still poorly understood.

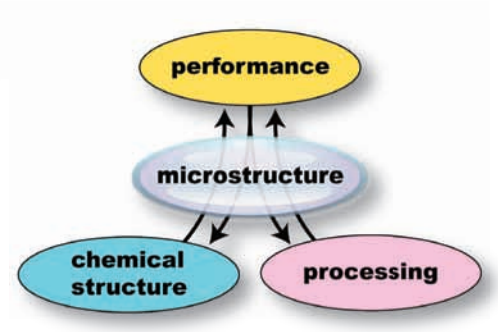
Impact and Customers

- Organic electronic devices are an emerging technology, with potential in displays, photovoltaics, sensors, logic, lighting, and radio-frequency identification tags. Their market is predicted to be $10 to $ 30 billion globally by 2010-2015.
- Our measurements provided critical structural insight that help guide materials development at Merck and Corning.
- NIST actively participates in the yearly International Summit on Organic Photovoltaic Stability hosted by the National Renewable Energy Laboratory (NREL)
- Collaborators include Seoul National University, Imperial College, Luna Innovations, Corning, Plextronics, Konarka, National Renewable Energy Laboratory, H.C. Starck, U. Chicago, UCSB, and Stanford.



Approach

Developing commercial products based on organic electronics requires materials that deliver predictable and reproducible performance. One advantage of these materials is their compatibility with versatile solution processing methods. However, this advantage can lead to unpredictable performance and poor reproducibility because the critical microstructure of the material forms dynamically as the solution dries. Many parameters influence the drying process and the microstructure formation is often hard to control. It can therefore be difficult to determine why new materials often underperform.



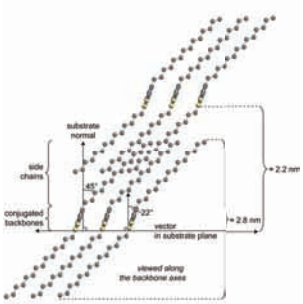
To address these challenges, we develop quantitative methods to correlate chemical structure and processing variables to performance via microstructure measurements. A combination of spectroscopic tools (IR, Vis, and X-ray), diffraction, and scanning probe microscopy provides sufficiently detailed characterization to isolate the contributions of individual structure and processing variables. This integrated measurement platform provides a rational basis for evaluating current processing methods, and it will further accelerate materials development by separating the molecular basis for electric performance from the process induced variability.

POLYMERS

Accomplishments

Conjugated, fused ring polymers with alkyl side chains constitute a general class of organic semiconductors, offering some of the best thin film charge mobilities to date. The detailed packing structure of these conjugated polymers that impacts their electrical performance, however, can be a challenge to determine.

We recently characterized the microstructure of pBTTTs, a series of polythiophene semiconductors with record-setting charge mobilities. The substrate-relative tilts of the pBTTT conjugated plane, side chains, and backbones were determined using a suite of spectroscopies. By combining this orientation information with spacing information from X-ray diffraction, we could discern important structure details. Notably, the conjugated planes have a preferred tilt, and the side chains are highly interdigitated.

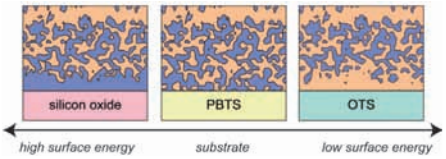


The detailed packing structure of pBTTT.

Our measurements explain why pBTTT delivers exceptional charge mobility, recently displacing P3HT (poly(3-hexylthiophene) as the industry benchmark for performance. P3HT has a similar structure, but the side chains are disordered and do not interdigitate. The interdigitation promote registry between the crystalline layers, enhancing long range order and improving performance.

Conjugated polymers, when blended with an electron acceptor such as the fullerene PCBM, can be used in organic photovoltaic (OPV) cells with substantial promise for producing low-cost solar power. OPV cells are currently limited by modest efficiency and limited stability, both significantly below theoretical expectations. The efficiency of OPV cells is related to the details of the nanoscale phase separation of the two components that occurs while the blend film dries. The domain size, shape, and distribution are critical to cell efficiency, but are challenging to measure. We recently established a suite of advanced measurements to address this challenge.

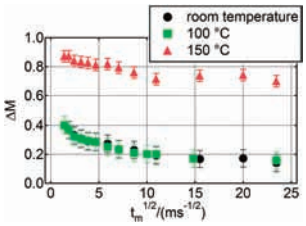
In a recent OPV vertical segregation study, we prepared solar cells made of blends of P3HT and PCBM, and related changes in device performance to changes in the stratified film layers that form upon drying. We used Near-Edge X-ray Absorption Fine Structure (NEXAFS) Spectroscopy to directly measure the composition of the layers that interact with the device electrodes. The NEXAFS results correlated with good agreement to three-layer model fits of the films from spectroscopic ellipsometry.



The vertical domain distribution of P3HT (orange) and PCBM (blue) in OPV films cast atop varying substrate surface energies.

Surprisingly, the most commonly used OPV deposition conditions result in suboptimal compositions at both the top and bottom interfaces of the film. We found that the surface free energy of the substrate strongly influenced the composition of the blend film at the buried substrate interface. By demonstrating how to control the composition of this interfacial layer, we provided simple guidelines to make new OPV ink systems for more efficient printable solar cells.

We also recently demonstrated that ^{1}H spin diffusion NMR can be a valuable method to estimate the domain size distribution in OPV active layers. A distribution of domain sizes was observed in P3HT/PCBM blend bulk samples that ranged over hundreds of nanometers. Unannealed samples exhibited a large amount of PCBM in small domains (1 nm to 5 nm) and smaller amounts in moderate (tens of nm) and large (> 200 nm) domains. Annealing the samples at 100 °C had no effect on the morphology as evidenced from ^{1}H spin diffusion NMR, grazing-incidence diffraction, and calorimetry, but phase separation was observed after annealing at 150 °C. The ^{1}H NMR showed conclusively that phase separation remained incomplete even for high temperature processing. Efforts are underway to directly apply this method to the thin films that are used in OPV devices. Results should lead to rational OPV blend formulation strategies that control phase segregation.



^{1}H spin diffusion of P3HT/PCBM blends. Significant segregation is observed after annealing at 150°C.

This year our team presented seventeen invited lectures, including ACS and MRS meetings and other academic and industrial venues, and published ten peer-reviewed manuscripts. In FY10, we will extend measurement development to address 3-D domain distributions in OPV films using microscopy and scattering techniques. We will also develop measurements that identify the chemical origins of performance loss in aging OPV devices.

Learn More

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Publications

Germack DS, Chan CK, Hamadani BH, Richter LJ, Fischer DA, Gundlach DJ, DeLongchamp DM, Substrate-dependent interface composition and charge transport in films for organic photovoltaics, Appl. Phys. Lett. 94: 233303 (2009)

DeLongchamp DM, Kline RJ, Jung Y, Germack DS, Lin EK, Moad AJ, Richter LJ, Toney MF, Heeney M, McCulloch L, Controlling the Orientation of Terraced Nanoscale "Ribbons" of a Poly(thiophene) Semiconductor, ACS Nano 3 (4): 780-787 (2009)

Salleo A, Kline JR, DeLongchamp DM, Chabinyc ML, Microstructural characterization and change transport in thin films of conjugated polymers, Adv. Mater. (accepted): (2010)

Gundlach DJ, Royer JE, Park SK, Subramanian S, Jurchescu OD, Hamadani BH, Moad AJ, Kline RJ, Teague LC, Kirillov O, Richter CA, Kushmerick JG, Richter LJ, Parkin SR, Jackson TN, and Anthony JE, Contact-induced crystallinity for high-performance soluble acene-based transistors and circuits, Nature Mater. 7 (3): 216 (2008)