MAR06-2005-004021

Abstract for an Invited Paper
for the MAR06 Meeting of
the American Physical Society

NEXAFS measurements of the development of interfacial order in organic semiconductor thin films.

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Interest in organic semiconductors has increased because of their potential use in new electronics applications such as radio frequency identification tags, biosensors, or photovoltaics. The development of solution processable organic semiconductors has made it possible to take advantage of low-cost processing methods such as spin coating, dip coating, or ink-jet printing onto flexible substrates. However, the performance of these materials in devices is difficult to control and new processing methods can deliver unexpected results. These deviations are often due to variability in film microstructure that leads to variability in carrier transport properties. The microstructure is sensitive to processing variables because they influence the dynamic assembly process of the material as it dries from a solution to a solid thin film that is crystalline or semicrystalline. To quantify structural changes, we employ synchrotron-based near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, which measures the soft X-ray excitation of 1s electrons to unfilled molecular orbitals. For a polymer semiconductor, regioregular poly(3-hexylthiophene) (P3HT), we show that variations in the spin-coating process may be a source of differences in the P3HT microstructure because of changes in complex balance of inertial forces and solvent evaporation during the solidification of the film from solution. The morphology of semicrystalline polymers such as P3HT is affected by the rate of solidification; slower solvent removal rates result in materials closer to their equilibrium structure. For thermally convertible, oligomeric organic semiconductors, we show that the formation of interfacial order of the molecules is affected by the oligomer length.