

Using organic thin-film transistors to characterize the interfacial composition of organic bulk heterojunction photovoltaic films

Calvin K. Chan¹, David S. Germack², Behrang H. Hamadani¹, Lee J. Richter³, Dean M. DeLongchamp², and David J. Gundlach¹

¹ Semiconductor Electronics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

² Polymers Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

³ Surface and Microanalysis Science Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

Abstract

Organic photovoltaic (OPV) cells are attractive for solution processable, flexible, and large-area solar energy conversion. Despite the potential cost advantages in manufacturing, the commercial viability of OPVs is currently inhibited by device instabilities and low power conversion efficiencies. OPVs using blended active layer materials to form bulk heterojunctions (BHJ) are receiving greater attention because the increased junction area raises the probability for exciton capture and dissociation. Although BHJ OPVs have shown modest performance improvements over their planar heterojunction counterparts, power conversion efficiencies still remain relatively low (<5%). Contributions to this limitation are not well understood, but given that charge collection at the electrodes is heavily dependant upon percolation pathways through a BHJ film, accurate characterization of the material composition within the film, as well as at the buried hole and electron interfaces is necessary.

In this work, the compositional structure at the bottom electrode-organic interface of BHJ OPVs was inferred using organic thin-film transistors (TFTs). Films consisting of poly(3-hexylthiophene):[6,6]-phenyl-C61-butyric-acid-methyl-ester (P3HT:PCBM) in a 1:1 mass ratio were spun-cast onto TFT structures with gate dielectric surface energies (γ) representative of the range used in typical OPV bottom contacts. In particular, high- γ SiO₂ and low- γ octyltrichlorosilane-modified SiO₂ (OTS8-SiO₂) were used. BHJ TFTs fabricated on bare SiO₂ showed ambipolar behavior indicative of a mixed P3HT/PCBM phase at the oxide-organic interface. However, films prepared on OTS8-SiO₂ exhibited hole-only transport indicative of P3HT-dominated channels. When the P3HT:PCBM TFTs were annealed to 140°C, which is typical in the processing of OPV devices, only hole transport was observed regardless of the gate dielectric. This suggests that P3HT-rich bottom interfaces form on both high- and low- γ surfaces after annealing. These observations were directly reflected in P3HT:PCBM OPVs fabricated on poly(3,4-ethylene dioxy thiophene):poly(styrene-4-sulfonate) (PEDOT:PSS) bottom contacts that have a surface energy similar to that of bare SiO₂. The annealed OPVs likely contained an enriched layer of hole-transporting P3HT at the hole-collecting bottom interface, and thus exhibited higher short-circuit currents (I_{sc}) and fill-factors (FF) as compared with non-annealed devices.

Near-edge x-ray absorption fine structure (NEXAFS) applied to the bottom interface of P3HT:PCBM films delaminated from SiO₂ and OTS8-SiO₂ substrates quantitatively confirm the changes in interfacial molecular composition with substrate surface energy and annealing. Also, NEXAFS performed on the top polymer-air interface showed a P3HT-rich layer where the typically top electron harvesting contact is made. The presence of an appreciable hole-transporting layer in this region likely contributes detrimentally to OPV device efficiencies. Interestingly, in all cases, the composition present at the bottom and top interfaces were different from the 1:1 mass formulation used to make the films, and conservation of mass requires a vertical composition gradient varying from the bottom interface to the top interface. Therefore, since the surface energy-dependant composition at the dielectric-organic interface does not necessarily represent the BHJ composition in the bulk or at the top interface, the use of TFTs to probe the bulk transport properties of OPVs must be applied cautiously. Nevertheless, this work demonstrates that TFTs still can be employed to infer the composition of blended organic films at OPV interfaces if the chemically-tailored gate dielectrics have surface energies representative of select electrodes used in OPVs.