

Substrate-dependent interface composition and charge transport in films for organic photovoltaics

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(Received 25 March 2009; accepted 7 May 2009; published online 9 June 2009)

The buried interface composition of polymer-fullerene blends is found by near-edge x-ray absorption fine structure spectroscopy to depend on the surface energy of the substrate upon which they are cast. The interface composition determines the type of charge transport measured with thin film transistors. These results have implications for organic photovoltaics device design and the use of transistors to evaluate bulk mobility in blends. © 2009 American Institute of Physics.

[DOI: 10.1063/1.3149706]

Organic photovoltaic (OPV) devices are a promising technology for low-cost solar energy devices because their active layers can be processed from fluids, enabling high throughput fabrication. Critical barriers must be overcome to enable more widespread use of OPV devices. Power conversion efficiency (PCE) must be improved,¹ and device lifetime must be extended.² In bulk heterojunction (BHJ) OPV devices, the PCE strongly depends on the distribution of the absorber³ and electron acceptor⁴ within the BHJ (e.g., the blend morphology⁵). Interface composition is an important aspect of morphology because injection may depend on which BHJ components contact the cathode or hole transport layer. Vertical heterogeneity in BHJ composition (e.g., vertical segregation) could cause heterogeneities in photon absorption/exciton generation probability, morphology development, and the prevalence of hole and electron transport paths. The blend morphology and interface compositions are expected to depend on the components used and how they are processed, and strategies to control them will aid OPV technology development.

We use near-edge x-ray absorption fine structure (NEXAFS) spectroscopy⁶ to show that the interface composition of a BHJ film composed of a poly(3-hexylthiophene) (P3HT):phenyl-[6,6]-C₆₀ butyric acid methyl (PCBM) ester blend differs significantly from the formulation composition at its free and buried interfaces. The buried interface composition depends on the substrate surface energy (γ_{SUB}) upon which P3HT:PCBM is cast, and correlates to substrate-dependent charge transport in bottom-gated thin film transistors (TFTs). While TFTs are a valuable probe of charge transport, they are unlikely to provide useful information about bulk transport because the composition of the accumulation layer depends on the substrate (e.g., dielectric) chemistry and does not reliably reflect the BHJ interior.

The dependence of interface composition on γ_{SUB} was evaluated by comparing P3HT:PCBM films cast atop clean silicon dioxide (SiO₂) substrates to those cast upon sub-

strates modified with octyltrichlorosilane (OTS8). Silicon with a native oxide was cleaned by ultraviolet ozone for 10 min followed by water rinsing and N₂ drying, and used within 30 min. OTS8 surfaces were prepared as previously reported.⁷ The BHJ recipe employed here was modeled after Li *et al.*⁸ where 1:1 by mass P3HT:PCBM (Plexcore 2100, Plextronics Inc. and Nano-C Inc., respectively)⁹ at 30 mg/ml total concentration was dissolved in orthodichlorobenzene (DCB) and heated for ≈ 18 h at 60 °C. Films were spin cast at 500(2 π) rad/min (e.g., 500 rpm) for 60 s with an acceleration of 84(2 π) rad/min s (e.g., 84 rpm/s) in N₂. The films were then covered until dry (≈ 30 min). This procedure produces films ≈ 220 nm thick that achieve greater than 2% PCE in OPV devices. Films of neat P3HT and PCBM were spin cast at 1500(2 π) rad/min (e.g., 1500 rpm) from DCB.

The dynamics of film formation during spin coating can be complex, but vertical segregation is often expected in blends where the component γ_s are significantly different. The interface composition changes to minimize free energy, which is proportional to the difference between the effective γ of the blend and that of the material it contacts.¹⁰ The lowest γ component typically segregates to the free (top) interface. At a buried interface, segregation depends on γ_{SUB} , which ranges here from $\gamma_{\text{SiO}_2} = 77.4$ mN/m² to $\gamma_{\text{OTS8}} = 23.7$ mN/m².¹¹ The interfaces of P3HT:PCBM on SiO₂ should resemble those on poly(3,4-ethylene dioxy thiophene):poly(styrene-4-sulfonate) (PEDOT:PSS) because $\gamma_{\text{PEDOT:PSS}} = 45.7$ mN/m² is higher than the γ of either BHJ component.¹² We did not use PEDOT:PSS because of residue upon delamination (see below). Further, PEDOT:PSS cannot be used as a dielectric for TFTs because it is a conductor.

The composition of the P3HT:PCBM film interfaces was measured using NEXAFS partial electron yield (PEY) on NIST beamline U7A at the National Synchrotron Light Source of Brookhaven National Laboratory. To access buried interfaces, the films were delaminated from their substrates using a variation in a previously reported technique.^{13,14} Instead of an elastomer stamp, we deposited ≈ 10 μm of parylene (Parylene-C with SCS PDS-2010) onto the film for

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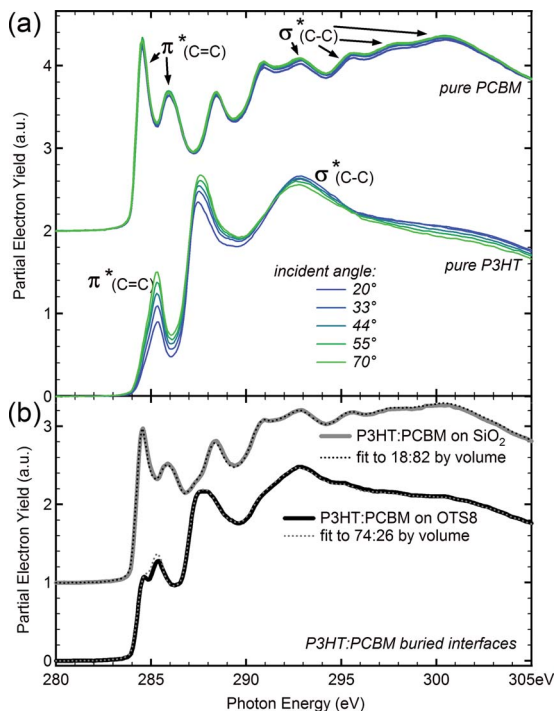


FIG. 1. (Color online) (a) Neat P3HT and PCBM NEXAFS spectra. (b) Spectra of the P3HT:PCBM buried interface on OTS8 and SiO₂ with composition fits. Spectra offset for clarity. Standard uncertainty in PEY is $\pm 2\%$; photon energy ± 0.2 eV.

support. The former substrates were evaluated with NEXAFS and had no P3HT or PCBM residue. The PEY spectra were collected with a grid bias of -50 V, providing a surface-weighted signal such that $\approx 50\%$ originates within 2 nm of the interface, and $\approx 75\%$ originates within 4 nm. The volume probed correlates closely to the TFT charge accumulation layer.¹⁵

NEXAFS spectra of neat P3HT and PCBM are shown in Fig. 1(a), respectively. The spectra were collected at several incident angles to evaluate orientation. The changes in intensity of the P3HT $1s \rightarrow \pi^*$ demonstrate the relatively edge-on orientation of the conjugated plane typically observed for high performance TFTs.¹⁶ PCBM shows no orientation due to its radially symmetric fullerene cage. P3HT and PCBM have distinct NEXAFS spectra due to their different π^* bond architectures, therefore, they can be discriminated at BJJ film interfaces.

The NEXAFS spectra in Fig. 1(b) reveal the buried interface composition of P3HT:PCBM films. The spectrum of P3HT:PCBM in contact with the low γ_{SUB} OTS8 resembles neat P3HT, while the spectrum of P3HT:PCBM in contact with the high γ_{SUB} SiO₂ resembles neat PCBM. The interface compositions can be quantified if we assume that the mean free paths of photons and electrons through PCBM and P3HT are equivalent; a blend spectrum can then be fitted to a linear combination of pure component spectra weighted by volume fraction. Fits were performed at the orientation-independent $\approx 55^\circ$ incidence. The P3HT:PCBM interface with SiO₂ was $\approx 18\%$ P3HT whereas the interface with OTS8 was $\approx 74\%$ P3HT. Independent of substrate treatment, the free surfaces (polymer-N₂ interfaces) were 75% to 80% P3HT. These compositions differ significantly from the $\approx 58\%$ P3HT expected from formulation.

These NEXAFS results clearly indicate vertical segregation in P3HT:PCBM films that is strongly influenced by

γ_{SUB} . If the P3HT:PCBM film behaves as a miscible blend,¹⁰ then segregation can occur independently at each interface. The segregation can be correlated with the γ of the BJJ components because PCBM ($\gamma_{\text{PCBM}} = 37.8$ mN/m²) has a higher γ than P3HT ($\gamma_{\text{P3HT}} = 26.9$ mN/m²). At the free interface and the buried low γ_{SUB} (OTS8) interface, enrichment with low- γ P3HT minimizes free energy. At the high γ_{SUB} (SiO₂) interface, enrichment with high- γ PCBM minimizes free energy. These results may be related to the dependence of polymer:PCBM film morphology on substrate chemistry,¹⁷ but more subtly since our films on OTS8 and SiO₂ had similar morphology. The dependence of interface composition on γ_{SUB} has ramifications for OPV device engineering. For the typical P3HT:PCBM film on PEDOT:PSS, the buried interface is expected to be PCBM rich, creating a possible hole injection barrier. Similarly, the composition at the free interface where the cathode would be deposited is P3HT rich, creating a possible electron injection barrier. Improvements in OPV performance can be anticipated from the development of hole transport layers with lower γ , electron acceptors with lower γ (or absorbers with higher γ), and inverted devices.¹⁸

The hole and electron mobilities of the BJJ are critical elements of models used to interpret and predict OPV device behavior. Charge carrier mobilities in the vertical direction have been difficult to obtain from diodes, so TFT measurements have been used.¹⁹ This strategy has at least two limitations. The first is that TFT measurements cannot evaluate the mobility anisotropy prominent in neat P3HT^{16,20} and in blends. The second is that charge transport in TFTs occurs within the first few nanometers of the BJJ adjacent to the dielectric¹⁵ and should be sensitive to interface segregation.

The charge transport of the P3HT:PCBM buried interfaces was measured using bottom contact, bottom-gated TFTs fabricated on heavily doped silicon wafers with 200 nm thermal SiO₂ as the gate dielectric. Gold source and drain contacts were deposited by physical vapor deposition and patterned by photolithography and lift-off. Clean SiO₂ and OTS8-modified surfaces were prepared on the substrates with patterned electrodes, and P3HT:PCBM films were cast as reported for the NEXAFS samples. Electrical characteristics were measured in Ar using an Agilent 4155C.⁹ TFTs were tested using bias conditions appropriate for accumulation of either holes or electrons.

The dependence of interface charge transport on γ_{SUB} is revealed in Fig. 2, which shows drain current (I_D) as a function of V_{DS} . The P3HT:PCBM films on OTS8 exhibited unipolar (hole-only) operation similar to neat P3HT TFTs, as demonstrated by the hole accumulation and transport in Fig. 2(a). The diodic characteristics observed at biases for n -type behavior are consistent with hole-only operation [Fig. 2(b)], with increasing hole depletion as V_{GS} becomes more positive. Since the accumulation layer is formed in the first few nanometers near the dielectric, this result confirms that the OTS8 interface of the BJJ was P3HT rich. A field-effect mobility of 2×10^{-3} cm² V⁻¹ s⁻¹ was extracted for the device biased in the saturation regime of operation. The mobility was less than our neat P3HT (2×10^{-2} cm² V⁻¹ s⁻¹ on SiO₂), but consistent with other reports.¹⁶

In contrast to unipolar transport on OTS8, ambipolar transport was observed for P3HT:PCBM on SiO₂, similar to earlier reports.^{19,21,22} For biases corresponding to hole accu-

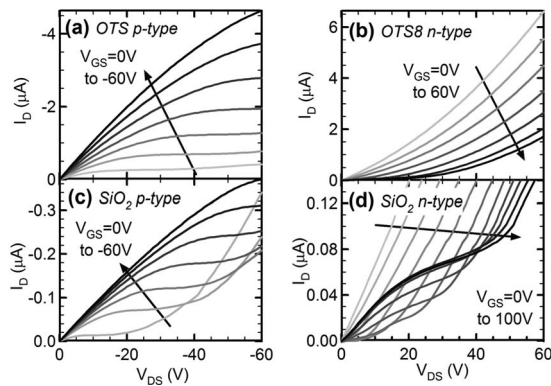


FIG. 2. Output characteristics of P3HT:PCBM transistors with [(a) and (b)] OTS8-treated and [(c) and (d)] clean SiO₂ dielectrics. The transistor gates were biased in 10 V steps from 0 to -60 V according to hole accumulation [(a) and (c)] and from 0 to +60 V or +100 V according to electron accumulation [(b) and (d)]. Arrows indicate increasing V_{GS} magnitude. Standard uncertainty in current is $\pm 1\%$.

mulation and transport [Fig. 2(c)], *p*-type behavior was observed at low drain-source bias. When the magnitude of V_{DS} became sufficiently high to inject electrons from the drain contact, ambipolar operation was achieved and an exponential increase in drain current was observed. As expected, an increasingly negative V_{GS} suppressed the ambipolar behavior, so the current-voltage characteristics for $V_{GS} = -60$ V were consistent with a well saturated unipolar (hole-only) device. Ambipolar transistor behavior was also confirmed for the same device when biasing the TFT for electron accumulation and transport [Fig. 2(d)]. At low gate bias, only diodic behavior is observed; similar to that on OTS8. At more positive V_{GS} , electron injection, accumulation, and transport became more favorable, and unambiguous *n*-type transistor behavior was observed. The substrate dependence of charge transport cannot be explained by differences in trap character because SiO₂ typically suppresses electron transport in organic TFTs.²³ The ambipolar behavior of the P3HT:PCBM on SiO₂ is consistent with a PCBM rich interface.²⁴ Our results clearly indicate that TFT measurements with devices employing the most common gate dielectric interfaces (clean hydrophilic SiO₂ or SiO₂ rendered hydrophobic) are not representatives of the BHJ interior composition and should not be used to estimate bulk transport properties.

The thermal stability of the interfaces was explored by heating the P3HT:PCBM films to 140 °C for 40 min in N₂. For films on OTS8, heating did not change the interface composition, and the TFTs exhibited only a decrease in off current that is likely due to residual solvent removal. For films on SiO₂, heating caused the transport to change from ambipolar to unipolar (hole-only). Further, NEXAFS indicated that heating increased the amount of P3HT at the buried interface from $\approx 18\%$ to $\approx 49\%$. This heating-induced change in composition and charge transport atop SiO₂ is attributed to the appearance of micron-scale PCBM crystallites that could be viewed with an optical microscope (not shown). The PCBM crystallites were poorly connected and did not span TFT contacts, so that charge transport could occur only through the well-connected P3HT-rich matrix, producing hole-only behavior.

The substrate dependence of interface composition in BHJ films has implications for OPV device design. Interfacial engineering strategies may cause changes in the vertical segregation of the BHJ.¹⁸ Importantly, any modifications targeting injection barriers via work function engineering may have the unintended consequence of altering the BHJ interface composition. Future measurements of BHJ vertical composition distributions as a function of substrate characteristics will likely contribute to a framework for predicting OPV device characteristics for a given combination of interfacial chemistries, BHJ components, and processing conditions.

The authors thank R. J. Kline and C. L. Soles for helpful discussions. D.S.G., C.K.C., and B.H.H. thank the NRC RAP for financial support.

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