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Predicting current from cross section images of organic photovoltaic devices

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ABSTRACT

The morphology of organic photovoltaics plays a significant role in the resulting power conversion efficiency of the device. In this study, we used Focused Ion Beam (FIB) and Energy Filtered Transmission Electron Microscope (EFTEM) techniques to create cross sections of solar cells and to study the phase separation and morphology. Combining the images obtained from EFTEM with simple absorption and exciton diffusion models, we are able to predict the short circuit current (J_{SC}) of these devices. The predicted current of the ideal device, annealed at 160 °C for 20 min, showed that 36% of the current comes from island areas, suggesting short distance hopping is responsible for some charge collection. For a device annealed at 160 °C for 10 h, the model estimates 15% of the current coming from island areas. This information suggests that over-annealed devices experience a current drop due to large phase separation and not from an increase in non-geminate recombination.

1. Introduction

Organic photovoltaic (OPV) devices may provide a promising low-cost alternative to traditional thin-film solar cells. The fact that they can be solution processed provides a means for roll-to-roll development and the possibility of greatly reduced costs versus other photovoltaic technologies [1,2]. Unfortunately, challenges still remain. Short exciton lifetimes and high rates of recombination require large donor/acceptor interfaces, causing most high efficiency devices to have a bulk heterojunction (BHJ) architecture. One major need in this area is a better understanding of the morphology of these devices and how it affects their performance [3–5]. Novel characterization techniques are required to better probe the morphology of these devices.

Much work has been done on the interaction between light and the organic materials of the active layer in order to optimize OPV devices. Absorption modeling was done in the past to increase the device efficiency [6]. These studies find the optimal thickness of a device with respect to maximizing both light absorption and carrier collection. Other absorption models were used to find the interaction between light and the active layer. Moule et al. used a Fresnel matrix to predict J_{SC} and found it to closely match their experimental values [7]. Shaw et al. used a transfer matrix to model the absorption and find the diffusion length in poly(3-hexylthiophene-2,5-diyl): [6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM) devices [8]. Work has also been carried out to compare the absorption of P3HT and PCBM and concluded that the low absorption of PCBM needs to be offset by P3HT to form an efficient device. This study was also able to make an estimate of the exciton collection from various phases of P3HT: PCBM devices, as we propose to do in this article [9]. Interesting predictions of the device morphology combined with Monte Carlo simulations can also provide accurate estimates of the charge collection, but this data lacks detailed information about the bulk morphology [10].

In order to better understand the BHJ structure, many studies have investigated the bulk morphology of OPV devices. 2-D surface morphology mapping has been done using precise optical techniques, revealing morphology and photo collection at the surface [11]. This method provides interesting details about surface morphology, but cannot probe the bulk. Atomic force microscopy (AFM) studies also provide rich details of surface morphology, but cannot reveal details important to device operation, such as phase separation and donor/acceptor distribution. Neutron studies have proven useful for determining material distribution and have helped resolve the debate about material distribution in OPV [12]. In a previous report from our group Transmission Electron Microscopy (TEM) studies combined with energy filtering and analytical techniques [13] have also been used to study bulk morphology. This technique provides

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the most detailed information about the inner workings of the device. More references and information on morphology characterization can be found in the recent review by Pfanmöller [14].

Energy filtered TEM (EFTEM) is a powerful characterization technique and can be used to reveal contrast between the materials used for a device. More information regarding EFTEM can be found in section 3.1 or in our previous work [15,16]. Although EFTEM is a very powerful technique and can resolve OPV morphology from a convoluted blend of nano-scale phase separation to clear images, it has some limits. Sample preparation using the FIB is both costly and time consuming, taking up to 20 h per sample including TEM imaging. The images also only provide a 2-D glimpse into a 3-D structure, leaving questions as to the true state of island phases. Keeping these limits in mind, EFTEM cross sections still offer accurate glimpses into the morphology and phase separation of OPV devices.

2. Experimental

2.1. Device fabrication

Devices were fabricated on Indium Tin Oxide (ITO) coated glass substrates (8–12 Ω, Delta Technologies). Substrates were cleaned in a sonicating bath using, sequentially, detergent, water, acetone, isopropyl alcohol, and finally rinsed with water. Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) was spin coated onto the substrates to create a 20 nm layer which was annealed at 130 °C for 10 min in a nitrogen filled glove box. P3HT and PCBM, purchased from Rieke metals and Nano-C respectively, were mixed in a 1:0.8 ratio in di-chloro benzene and stirred overnight at 50 °C. The P3HT:PCBM mixture was spin coated on the PEDOT:PSS layer to create a 150 nm layer. The samples were then annealed at 160 °C for the specified time. After annealing, the samples were loaded into a thermal evaporation chamber. The 100 nm Al contact was evaporated at a base pressure of $< 9 \times 10^{-6}$ mbar at a rate of 0.2 nm/s. Fig. 1

2.2. FIB sample prep

Samples were prepared for EFTEM using a focused ion beam (FIB) system (Auriga FIB 60). Samples were milled using a gallium ion beam to create cross section lamella of functional solar cells that were approximately 50 nm thick. Further information regarding this sample preparation can be found in our previous work [15,16]. Once the lamella samples were prepared, they were placed onto a copper TEM grid and transferred to the TEM (LIBRA 120® PLUS, Zeiss with an operating voltage of 120 kV).

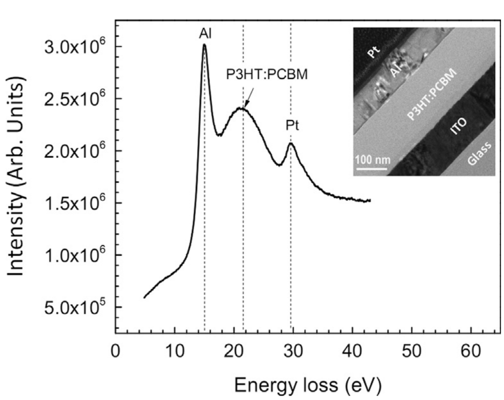

Fig. 1. EELS spetrum of a P3HT:PCBM solar cell. The P3HT:PCBM peak is composed of a P3HT peak and a PCBM peak, with peak positions of 21.5 eV and 25 eV, respectively. Inset: Cross section of a solar cell.

3. Results and discussion

3.1. EFTEM images

Both P3HT and PCBM exhibit broad plasmon resonance peaks which can be measured using electron loss spectroscopy (EELS). Work by Herzing et al. has shown P3HT to have a resonance peak at 22.2 eV and PCBM to have a resonance peak at 25.5 eV [17]. By analyzing the sample using an energy loss filter, we can preferentially remove most of the P3HT or PCBM signature from the signal. All EFTEM images shown here were taken with a 30 eV energy loss filter with a 7 eV window width applied, effectively darkening the P3HT signal and leaving the PCBM rich regions bright. We performed EFTEM on two samples annealed for different times (Fig. 2).

The 30 eV filter applied to the EELS signal creates a contrast in the active layer that is not visible using traditional TEM techniques. Groups in the past have attempted to use defocused TEM [18] to image the difference between donor and acceptor materials. Unfortunately, defocused TEM has been shown to provide questionable results [12]. EFTEM creates a superior contrast and has been confirmed to work on P3HT:PCBM systems [3,17] as well as many other materials systems [19,20]. Combining EFTEM with the FIB cross section preparation technique, cross sections made from functioning devices give us the ability to see phase separation and charge collection pathways in actual devices.

Sample preparation with an FIB produces 50 nm thick lamella samples. Due to the thickness being larger than the observed phase size, some stacking of P3HT and PCBM regions is expected. Thus, the maps shown here provide the dominant material in each region. Although this study is only looking at a 2D cross section, the region is fairly large and can provide some estimate of the morphology of the total device. A difference can be observed between the 20 min and 10 h annealed devices (Figs. 2a and 2b). Larger areas and more contrast are apparent in the 10 h device due to increased phase separation.

Even with an energy loss filter applied, the raw images produced by EFTEM (Figs. 2a and 2b) need additional contrast. After rotating and cropping the image to contain only the active layer with the ITO side on the top of the image, we filtered the image. By applying a threshold filter to the image (Fig. 2b) we were able to obtain an image that is highly contrasted. To achieve the binary image in Fig. 3, we applied an averaging filter to the image using Matlab. To reduce noise and increase contrast, we binned the original image pixels into regions of 2.5 nm. We then applied a cutoff, making every pixel darker than average black and lighter than average white. The average in each region was determined by averaging the regions surrounding it. This was to smooth any non-uniformity in the image due to different thicknesses in the lamella.

After obtaining a rough black and white image, we then smoothed the image, removing isolated pixels. These isolated pixels may be due to noise. Unfortunately, this also removes mixed regions from the device, creating a 2-phase image and ignoring all mixed regions. Although this may be a problem, exciton separation occurs at P3HT:PCBM interfaces, which will predominantly occur at the interface between P3HT rich and PCBM rich regions. Using this binary image (Fig. 3), we were able to create a Matlab program to analyze the absorption and exciton collection in the device.

3.2. Phase separation

By creating a map of P3HT and PCBM rich regions, as seen in Fig. 3, we were able to explore the vertical phase separation in the device. Summation of the PCBM pixels in each row led to the plot of PCBM concentration in the device (Fig. 4). A high PCBM concentration at the PEDOT:PSS interface is very apparent, which causes a decrease in charge transfer. A buildup of PCBM also exists