Soft X-Ray Beam Induced Current Technique

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Abstract. Direct mapping of the charge transport efficiency of polymer solar cell devices using a soft X-ray beam induced current (SoXBIC) method is described. By fabricating a polymer solar cell on an x-ray transparent substrate, we demonstrate the ability to map polymer composition and nanoscale structure within an operating solar cell device and to simultaneously measure the local charge transport efficiency via the short-circuit current. A simple model is calculated and compared to experimental SoXBIC data of a PFB:F8BT bulk-heterojunction device in order to gain greater insight into the device operation and physics.

1. Introduction
It is well known that the nanoscale structure determines the exciton splitting and charge transport properties of bulk-heterojunction polymer photovoltaic devices. However the precise details of these effects hide in the entangling of the different steps of energy capture in the device. Comparison of nanoscale composition images from scanning transmission X-ray microscopy (STXM) with conventional macroscopic efficiency testing of polymer solar cells has proven that such testing is insufficient for determining the influence of nanoscale structures [1]. A more direct way to measure nanoscale device efficiency is required to further understanding in this area. To this end, we have developed a method to produce charge transport efficiency images via X-ray beam induced current (XBIC) [2] in a STXM instrument, simultaneously measuring of conventional STXM transmission images for the calculation of composition maps.

2. SoXBIC Principle
Traditional STXM spectromicroscopy uses a zone plate to focus soft X-rays onto a thin sample, measuring the transmitted intensity. In the soft X-ray beam induced current (SoXBIC) technique, the transmitted light is still utilized to map composition as in normal STXM operation, however the absorbed soft X-ray photons also create charge carriers of the active polymer layer, and produce a measureable current between the device electrodes. Therefore, measuring the short-circuit current, provides a current signal for each pixel in the recorded image to complement the transmission data.

The soft X-ray photons of the SoXBIC beam have considerably more energy than the visible photons absorbed in normal solar cell operation. Hence, rather than the formation of an exciton that must be split before the charges can be transported to the device electrodes, the soft X-ray photon produces one or more high energy photo- and Auger electrons, which then creates a cascade of lower energy, secondary electrons and a corresponding number of positively charged molecules. The large number of free charges created by each absorbed soft X-ray photon renders the nature of the original absorption event insignificant. Since SoXBIC does not involve the creation nor splitting of excitons,
the technique is a measure of only the soft X-ray absorption and charge transport properties of the device. Further, since the soft X-ray absorption properties of materials are easily characterized and modeled, SoXBIC allows the charge transport properties to be isolated. The spatial spread of this secondary electron cascade is limited to about 10 nm [3] and so SoXBIC charge transport maps have the same spatial resolution as the simultaneous STXM composition maps.

3. Experiment
Poly(9,9'-dioctylfluorene-co-bis-N,N'-(4, butylphenyl)-bis-N,N'-phenyl-1,4-phenylenediamine) (PFB) and poly(9,9'-dioctylfluorene-co-benzothiadiazole) (F8BT) were purchased from American Dye Source with molecular weights (polydispersity) of 23k (2.7) and 38k (2.3) respectively. PEDOT:PSS was purchased as Baytron P from H.C. Starck.

The lower indium-tin oxide (ITO) electrode was magnetron sputtered onto a silicon nitride membrane in a 5 mTorr Ar atmosphere at ~0.5 As\(^{-1}\) with a base pressure of 10\(^{-7}\) Torr. Polymer layers were spin-cast; PEDOT:PSS at 4 krpm and then 1:1 PFB:F8BT from p-xylene at 3 krpm. 30 nm of Al were then thermally evaporated 1-2 As\(^{-1}\) (in a base pressure of 10\(^{-6}\) Torr) to form the top electrode and complete the device. The connection pads of the ITO layer were exposed by wiping away the polymer with acetone and then isopropanol and electrical connections were made to the ITO and AL electrodes by wedge-bonding fine gold wires.

The device was mounted (oriented such that the probing soft X-rays enter the device through the aluminium electrode) in the 5.3.2. STXM at the Advanced Light Source in Berkeley, USA, and the electrodes connected to a Keithley 6517A Electrometer in short-circuit. The output of the electrometer was connected to a voltage-to-frequency converter and the resulting pulses counted and recorded by a PC. STXM images were recorded with a dwell time of 500 ms and a pixel size of 50 nm at 280, 284.7, 285.2, 285.7, 286.6, 289 and 320 eV (in order of ascending photon energy) with both the transmitted intensity and current signals recorded simultaneously.

4. Results and Discussion
The composition map of the segregated PFB:F8BT layer of the device, shown in figure 1, exhibits a domain structure ~0.5 \(\mu\)m in size and domain purities of about 59% and 65% for the PFB- and F8BT-rich domains, respectively. This differs from the 50% and >90% domain purities in structures greater than one micron that was previously observed in similar blend films [1], likely because of the much lower molecular weight of the polymer materials.

Figure 2 shows the modelled and observed SoXBIC current images and figure 3 presents the spatially averaged currents, normalised against the photon flux. While there is considerable noise in the experimental images, it is clear that the PFB:F8BT segregated domain pattern is present in the 320 eV and 284.7 eV current images and is just observable in the 280 eV and 287.7 eV images as well. The fact that the pattern observed in the current images does not reverse contrast, even at 284.7 eV, where F8BT absorbs more strongly than PFB, suggests that the PFB-rich phase may have better charge transport properties than the F8BT-rich phase. Previous current mapping experiments at visible wavelengths have also shown enhanced current from the PFB-rich domains [4].
Of the model variants shown in figures 2 and 3, the “full collection” model is the simplest and involves a straightforward calculation of the number of photons absorbed between the device electrodes, multiplied by the photon energy (assumed proportional to the number of charges induced per photon). A further consideration of beam damage was added to account for lower than expected current signal at higher photon energies by subtracting a scaled cumulative sum of the total charges induced by the preceding image scans. Note that the SoXBIC charge generation applies equally to all device layers that lie between the electrodes and hence the model also includes contributions due to charges induced in the PEDOT:PSS layer. The other, “boundary”, model assumes that the PFB:F8BT layer is a poor conductor of holes and the PEDOT:PSS is a poor conductor of electrons such that only charges close to the polymer/polymer interface (within 10 nm was the condition utilised here) are contributing to the device current. The effect of PFB:F8BT phase-dependent charge transport on the variation in total current with photon energy was also investigated, but found to not differ significantly from the corresponding models (figure 3) that ignore PFB:F8BT phase effects beyond that of the initial soft X-ray absorption. The “boundary” model appears to be a slightly better fit to the experimental current signal data, both in terms of total current and current image contrast, however the data presented here is not of sufficient quality to draw further conclusions on the device operation.

Figure 2. SoXBIC current images. High (low) current values are represented by bright (dark) pixels. Image size is 1.9 µm by 1.8 µm.

Figure 3. Photon flux normalised and spatially averaged, modelled and experimental currents. Spatial variations in current (image contrast), are shown via line width.

5. Conclusions
We have demonstrated the experimental measurement of charge transport maps with nanoscale structures that correspond to the observed PFB:F8BT phase domain structures within the active polymer layer of a polymer solar cell device. While the lack of contrast reversal in the current signal data suggests that PFB-rich domains have better charge transport properties than F8BT-rich domains, the data presented here is not of sufficient quality to draw further conclusions on the device operation.

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