

Photocurrent Mapping of Polymer Photovoltaic Cells

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Abstract: Multi-wavelength near-field scanning photocurrent microscopy correlates photocurrent generation with morphology. Photocurrent generation in a P3HT:PCBM bulk heterojunction solar cell appears enhanced in the vicinity of a PCBM crystallite and the goal is to determine a qualitative concentration map from differential spectral absorption and photocurrent contribution of constituent materials.

1. Introduction

Currently the best organic photovoltaic device is one made from a 1:1 poly(3-hexylthiophene):[6,6]-phenyl-C61 butyric acid methyl ester (P3HT:PCBM) blend [1,3]. It is known that device performance is enhanced by annealing the film [2] for a set period after the material blend is spun onto the surface and it has been noted that crystals form in the annealed films [4]. It is thought that these are PCBM based on by X-ray microscopy [4] but the crystals will have a P3HT capping layer of unknown thickness and the surrounding material is then an unknown blend of the two constituents. The photocurrent generated in the vicinity of these crystallites differs from that generated away from the crystallites [5].

The near-field scanning photocurrent microscopy (NSPM) technique [5] uses tapered optical fibre NSOM probe to illuminate small ($\sim 0.3 \mu\text{m}^2$) areas of the device via chopped laser light as shown in figure 1. The probe tip is brought close to the aluminium electrode surface of the device using an AFM feedback loop. The tip is then rastered across the surface of the device performing the dual function of an AFM tip, thus creating a topographical map of the surface, and generating photocurrent in the device voxel illuminated directly by the tip. The photocurrent is measured using a phase-locked loop at the chopper frequency and when coupled with the position of the tip, yields a photocurrent map of the surface. Multiple wavelengths may be transmitted through the fibre probe sequentially to build a wavelength dependent photocurrent map of topological features identified within the device.

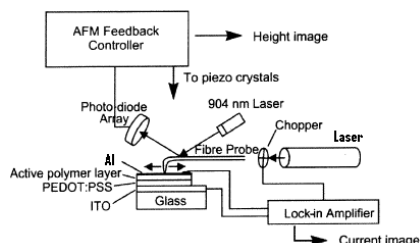


Fig1. NSOM photocurrent mapping

This ability to probe the wavelength dependent photocurrent of a morphological feature is unique to the technique.

2. Experimental

The device to be investigated is formed from the solvated blended materials spun as a film from the

solution onto a transparent Indium Tin Oxide (ITO) electrode upon a glass slide as shown in figure 2. The devices produced for photocurrent mapping have a thin transparent aluminium layer to allow the light from the probes to penetrate into the active 100nm thick layer of P3HT:PCBM.

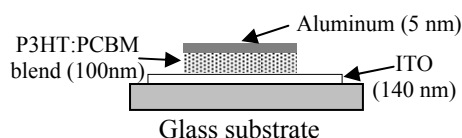


Fig 2. Device architecture

This 5nm thick aluminium layer serves as the electrode and is added by evaporation, after spinning and before the device is annealed at 140 °C for 4 minutes. This process causes the materials to undergo a partial phase separation, with the PCBM forming large crystallites as may be seen in figure 3 [4].

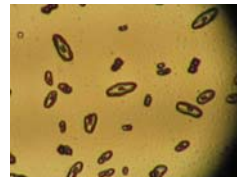


Fig 3. Optical micrograph of annealed P3HT:PCBM film

These crystallites may be 200nm high above the surface of the blended film as measured by atomic force microscopy (AFM).

By recording the absorption profile of each material in the film, wavelengths which are preferentially absorbed by one material or the other may be selected. 409nm light is absorbed roughly equally by both materials, the 532nm light is absorbed preferentially by the P3HT and the 633nm light is absorbed preferentially by the PCBM as shown in figure 4. Photocurrent generated at these wavelengths is as a result of the presence of these materials.

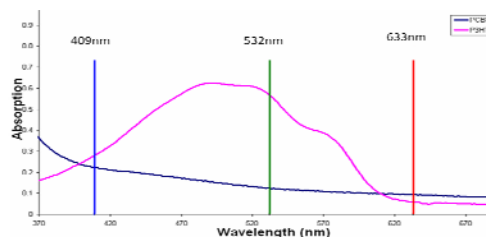


Fig.4 Spectral absorption of constituents

3. Results and Discussion

A topographic map of a crystallite and the corresponding photocurrent map is presented in figure 5 below. This photocurrent map was generated using the 409nm light. By comparing the two, we are able to see that there seems to be enhanced photocurrent generation around the crystallite, while there is less generated in the bulk of the crystal. This would tend to indicate that there is an optimised blend ratio of P3HT to PCBM surrounding the crystallite, while the blend further from the crystallite is slightly worse, and the blend ratio within the crystallite is far from optimal.

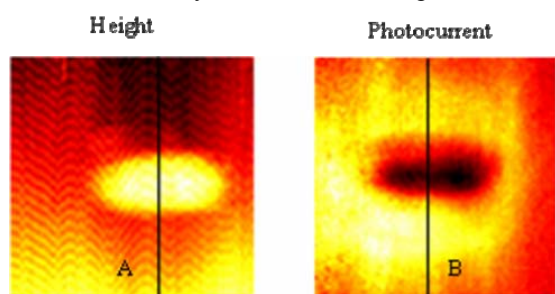


Fig. 5 Height and photocurrent map recorded at 409nm.

It is possible to use this image to calculate the external quantum efficiency (EQE) at any point in the map. This can be done by determining the absolute current which is flowing from the device, and by carefully measuring the power of the light transmitted through the NSOM tip. In general, measuring the transmitted optical power is difficult due to the highly diffracted nature of the light, however this can be overcome by placing the tip inside an integrating sphere, which should collect all the light leaving the tip. After the power is known, it is a simple case of calculating the ratio of electrons out (from the current) to the number of photons incident (from the light power measurement).

It is often more instructive to look at the cross-section of the images than to look at the maps themselves to give a much more direct comparison between the current and height maps. In figure 6 below, a cross-section of the height and current maps is presented. The location of the cross-section is indicated by the dark lines labelled A and B running through the images in figure 5.

From figure 6 we can see that the EQE doubles between the inside of the crystallite and the edge, while there is a 50 percent increase between the film and the edge of the crystallite.

If EQE maps could be created using 532nm light and 633nm light it could be possible to distinguish between current generated in the P3HT and PCBM thus creating a compositional map of the surface. It could then be possible to determine the optimal blend ratio for the materials in the organic photovoltaic cell.

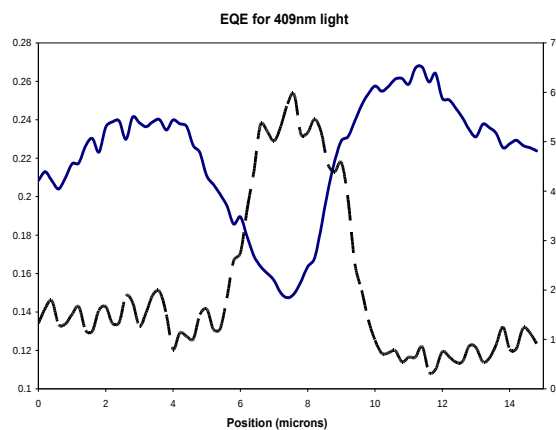


Fig. 6 The cross-section of the height (dashes) and current (solid) maps. The current map has been converted into EQE shown on the left hand scale. The height in nm is shown on the right hand scale.

4. Conclusion

The NSPM technique allows us to correlate charge generation in organic photovoltaics with the morphology of the film. We note that charge is not generated evenly throughout the film, with enhanced current generation occurring at the interface area of the crystallite and the surrounding film. Therefore, the device performance can be improved if the morphology can be controlled to create a film with a greater interface area between the crystallites and the film.

It could also be possible to use multi-wavelength NSPM to determine the optimal blend ratio for organic photovoltaic devices.

5. References

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6. Acknowledgements

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