Bilayer Polymer Solar Cells with Improved Power Conversion Efficiency and Enhanced Spectrum Coverage

Dhananjaya Kekuda and Chih-Wei Chu

Abstract. We demonstrate the construction of an efficient bilayer polymer solar cell comprising of Poly(3-hexylthiophene) (P3HT) as a p-type semiconductor and asymmetric fullerene (C70) as n-type counterparts. The bilayer configuration was very efficient compared to the individual layer performance and it behaved like a regular p-n junction device. The photovoltaic characteristic of the bilayers were studied under AM 1.5 solar radiation and the optimized device parameters are the following: Voc = 0.5 V, Jsc = 10.1 mA/cm², FF = 0.60 and power conversion efficiency of 3.6%. A high fill factor of ~0.6 was achieved, which is only slightly reduced at very intense illumination. Balanced mobility between p- and n-layers is achieved which is essential for achieving high device performance. Correlation between the crystallinity, morphology and the transport properties of the active layers is established. The External quantum efficiency (EQE) spectral distribution of the bilayer devices with different processing solvents correlates well with the trends of short circuit current densities (Jsc) measured under illumination. Efficiency of the bilayer devices with rough P3HT layer was found to be about 3 times higher than those with a planar P3HT surface. Hence it is desirable to have a larger grains with a rough surface of P3HT layer for providing larger interfacial area for the exciton dissociation.

Keywords: Bilayer solar cell, crystallinity of polymer, surface roughness.

PACS: 81.05.Fb; 81.05.ab; 81.10.Dn

INTRODUCTION

The Organic solar cells (OSCs) based on three dimensional networks of conjugated polymers and fullerene derivatives offer a great deal of potential for the effective photo conversion. Power conversion efficiencies of the OSCs have been steadily increasing through various device configurations and fabrication of organic solar cells with power conversion efficiencies in the range 3-7% are also demonstrated in recent years [1,2]. In order to achieve this, bulk hetero junction (BHJ) concept has been widely proved to be the best technique compared to the bilayer technique [3,4]. Indeed, it is desirable to have a percolating pathway for the carriers transporting to the electrodes and the interpenetrating networks proved to provide efficient charge separation and carrier extraction at the electrodes [5,6]. On the other hand, ever since Tang et al investigated bilayer organic solar cells [7], extensive work has been accomplished in the area of planar heterojunction organic solar cells [8] and tandem device structures. However, the efficiency in such bilayer structures is considerably lower compared to that of the bulk heterojunction devices. Currently, one of the bottlenecks for their poor efficiency is the lower interfacial area available for the exciton dissociation. Attempts to increase the interfacial area have been recently carried out by many researchers through the formation of initial rough surface. By achieving such a rough surface, one can anticipate bilayer devices to compete with the bulk heterojunction devices due to the fact that the directional photo induced charge transfer is guaranteed across the interface.

Among the most of the available conjugated polymers, regioregular poly(3-hexylthiophene) (P3HT) has been widely used due to its effective light absorption and high charge carrier mobilities. Moreover, they are easily soluble in most of the commonly available solvents which makes them ideal candidates for the solution processed devices. Due to the aforementioned factors, we used P3HT as the electron donor (p-type) active layer and fullerene C70 was used as electron acceptor. The present work reveals the high performance of the bilayer devices which is comparable to the most of the bulk heterojunction devices fabricated so far. Here, we present a clear correlation between the morphology of
the polymer layer and the device performance, with the device configuration ITO/PEDOT:PSS/P3HT/C_{70}/Al.

**EXPERIMENTAL DETAILS**

P3HT and fullerene C_{70} were received from Luminescence Technology Corp. and Material Technologies Research, respectively and were used without further purifications. Four different solvents were used for the P3HT film growth which include chloroform, xylene, 1,2 dichlorobenzene (DCB), and 1,2,4 trichlorobenzene (TCB). The cleaned ITO glass was then exposed to UV ozone for 15 minutes. It was then coated with a 30 nm PEDOT:PSS (Clevios™ P) at a speed of 4000 rpm for 60 sec. The substrates were heated at 130°C for 30 minutes and were immediately transferred to a glove box filled with N₂. Initial active layer, P3HT dissolved in different solvents, was then spun on the substrates at a spin speed of 2000 rpm for 60 seconds. The films were then transferred to a vacuum chamber where C70 was deposited under high vacuum at a rate of 0.5Å/sec. Finally, Al cathodes of area 0.1 cm² were deposited on the active layers through a shadow mask by conventional vacuum evaporation to complete the photovoltaic device. For the TFT fabrication, the films were grown on SiO₂ gate dielectrics and Au was used source-drain electrodes. At least ten identical devices were fabricated to test their reproducibility. The structural analysis of the P3HT films was performed by X-ray diffraction. The optical absorption spectra of the P3HT films processed in various solvents were recorded at room temperature using UV-visible spectrophotometer (V-650, Jasco). External quantum efficiency (EQE) of the bilayer devices was measured using a lock-in detector under a monochromatic light illuminated from a Xenon lamp. The dark and illuminated current-voltage characteristics were studied through Agilent 4156C semiconductor parameter analyzer.

**RESULTS AND DISCUSSION**

Boiling point (bp) of a solvent is a critical parameter for inducing crystallinity in P3HT. High boiling point solvents provide enough time for the P3HT crystallization process which can facilitate a highly crystalline growth. X-ray diffraction pattern of the P3HT film cast from four different solvents of different boiling points is displayed in Fig. 1a. As can be seen from the fig., slower evaporation of the solvent leads to better crystallization, stronger inter chain interaction and well defined crystalline peaks. While the peak intensity is a measure of the degree of crystallinity, it is clear that the films processed in TCB solvent posses intense diffraction peak compared to the films processed in other solvents. All the films exhibited a crystalline peak around 5.4 Å which corresponds to the (100) plane, representing inter planar distance of 1.61 Å. From the fig., it was found that the P3HT films processed in higher bp solvents had higher peak intensity and narrow half width of (100) diffraction peak compared to the films processed in lower bp solvents. The full width at half maximum (B) of these (100) reflections give an idea about the degree of crystallization and the crystal size (t) can be computed using the relation $t = \frac{0.9\lambda}{B \cos \theta}$ where λ is the wavelength of x-ray used and θ is the diffraction angle. P3HT crystallites drastically increase in size from ~ 8 nm for a chloroform processed films to ~ 19 nm for a TCB processed films. Such a large increase in the crystallite size also provides further insight into the effective charge transport and the origin of high field effect mobilities in our devices as discussed in the subsequent sections. Absorption spectra of these films were also studied and were displayed in Fig. 1b. As can be seen from the fig., all the films exhibited a similar breadth in their absorption with absorption peak located at 550 nm.

![FIGURE 1. (a) XRD pattern and (b) absorption spectra of P3HT films processed in different solvents (1). Chloroform (2) Xylene (3) DCB and (4) TCB.](image)
point solvents, which is essential for providing a large interface area in the bilayer solar cell structures as explained in the subsequent sections.

**FIGURE 2.** Atomic Force Microscopic images of P3HT films

Figure 3 shows the current-voltage characteristics of P3HT/C₇₀ solar cells under illumination of AM 1.5 radiation (100 W m⁻²) for all the devices. As can be seen from the fig., device parameters depend significantly on the solvent used for the P3HT layer processing. As explained previously, P3HT films processed in TCB solvent possess better crystallinity, higher surface roughness and high field effect mobility. Nearly 8 fold increase in surface roughness of the TCB processed P3HT provides a larger interface for the exciton dissociation compared to the chloroform processed near planar P3HT layers. Consequently, energy conversion efficiency was also higher for such devices. The current density values and the power conversion efficiency values were much higher than those reported for P3HT/C₆₀ bilayer devices. We attribute the high performance of our devices to the better crystallinity, high surface roughness of the P3HT and the balanced charge transport. The maximum conversion efficiency was 3.65 %, which is the highest value reported so far for the bilayer solar cells. Inset of Fig. 3 depicts the external quantum efficiency (EQE) of the bilayer devices with the P3HT layer processed in different solvents. Broad spectral coverage in the wavelength regime 400 – 600 nm was observed. It is worth mentioning that the devices had a better incident photon to collected electron efficiency for the devices with P3HT films grown in TCB solvent, which reciprocates the J-V characteristics. Even EQE results suggest that the high boiling point of the solvent for P3HT processing is necessary for obtaining superior transport properties. The EQE spectral distribution of the bilayer devices with different processing solvents correlates well with the trends of short circuit current densities (Jₛₑ) measured under illumination.

**FIGURE 3.** I-V characteristics of P3HT-C70 bilayer solar cells

In conclusion, we have demonstrated that bilayer organic solar cells can be the potential contenders for deriving high efficiency. The transport properties and crystallinity of the polymer films play a key role in obtaining the high current densities. Efficiency of the bilayer devices with rough P3HT layer was found to be about 3 times higher than those with a planar P3HT surface. This discovery infers that bilayer systems could also be used for achieving high efficiency solar cells through a balanced charge transport of the active layers and morphology control of the first layer.

**ACKNOWLEDGMENTS**

This work has been supported by National Science Council, Taiwan (98-2221-E-001-002) and Academia Sinica, Taiwan.

**REFERENCES**


231