The effect of solvent induced crystallinity of polymer layer on poly(3-hexylthiophene)/C\textsubscript{70} bilayer solar cells

Dhananjaya Kekuda\textsuperscript{a}, Hao-Shing Lin\textsuperscript{b}, Meng Chyi Wu\textsuperscript{b}, Jen-Shein Huang\textsuperscript{c}, Kuo-Chuan Ho\textsuperscript{c}, Chih-Wei Chu\textsuperscript{a,d,*}

\textsuperscript{a} Research Center for Applied Sciences, Academia Sinica, Taipei 11529, Taiwan
\textsuperscript{b} Department of Electrical Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan
\textsuperscript{c} Institute of Polymer Science and Engineering, National Taiwan University, Taipei 10617, Taiwan
\textsuperscript{d} Department of Photonics, National Chio-Tung University, Hsinchu 30013, Taiwan

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\textbf{Abstract}

A bilayer polymer solar cell is demonstrated with the device configuration ITO/PEDOT:PSS/poly(3-hexylthiophene)/C\textsubscript{70}/Al. In this article, we highlight the importance of polymer surface morphology, its crystallinity and mobility on device output parameters. The solvent used for polymer processing plays a major role in deciding these parameters and it was observed that high boiling point solvents are desirable for achieving large surface roughness of the polymer layer, which in turn provide more interface area in the bilayer device structure. Due to the increased interface area for exciton dissociation, these bilayer devices resulted in a maximum power conversion efficiency of 3.65\% under one sun radiation.

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\section{Introduction}

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, the bulk heterojunction (BHJ) concept has been widely proved to be a better technique compared with 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]. However, the chances of carriers travelling to wrong electrodes are quite high in complex blend systems. On the other hand, ever since Tang [7] investigated bilayer organic solar cells, extensive work has been accomplished in the area of planar heterojunction organic solar cells [8,9] and tandem device structures [10,11]. However, the efficiency in such bilayer structures is considerably lower compared with that of the bulk heterojunction devices.

Currently, one of the bottlenecks for their poor efficiency is the lower interfacial area available for exciton dissociation. Attempts to increase the interfacial area have been recently carried out by many researchers through the formation of an initial rough surface. Such a rough surface can be generated by many ways such as the thermal treatment, anodization process or through the lithographic techniques [12–14]. 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. These rough surfaces provide a vertical path to the charge carriers to transport to the electrodes and can hence avoid the complex network path for the carriers usually found in BHJ devices.

Among 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 [15]. 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 C\textsubscript{70} was used as an electron acceptor. The present work reveals the high performance of the bilayer devices, which is comparable to those of 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.
2. Experimental details

P3HT and fullerene C\textsubscript{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). Each solution was stirred overnight on a digitally controlled hot plate at 70 °C for uniform mixing and to get a homogeneous solution. The device fabrication process was initiated by cleaning of the ITO glass (sheet resistance 15 Ω/□) through a detergent and organic solvents and was subsequently dried using a nitrogen gun. The cleaned ITO glass was then exposed to UV ozone for 15 min. It was then coated with a 30 nm PEDOT:PSS (Clevios\textsuperscript{TM} P) at a speed of 4000 rpm for 60 s. The substrates were heated at 130 °C for 30 min and were immediately transferred to a glove box filled with N\textsubscript{2}. The initial active substrates at a spin speed of 2000 rpm for 60 s. After solvent layer, P3HT, dissolved in different solvents, was then spun on the substrates to complete the photovoltaic device. The device annealing was carried out at 150 °C for 30 min. For TFT fabrication, the films were grown on SiO\textsubscript{2} gate dielectrics and Au was used as source–drain electrodes. At least ten identical devices were fabricated to test their reproducibility. Structural analysis of the P3HT films was performed by X-ray diffraction. Optical absorption spectra of the P3HT films processed in various solvents were recorded at room temperature using a 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. Dark and illuminated current–voltage characteristics were studied through an Agilent 4156 C semiconductor parameter analyzer.

3. 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 [17,18]. 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 figure, 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 possess 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 (1 0 0) plane, representing inter-planar distance of 1.61 Å. From the figure, it was found that the P3HT films processed in higher bp solvents had higher peak intensity and narrow half width of (1 0 0) diffraction peak compared with the films processed in lower bp solvents. The full width at half maximum (B) of these (1 0 0) reflections gives an idea about the degree of crystallization and the crystal size (t) can be computed using the relation $t = (0.9\lambda)/(B\cos\theta)$, where $\lambda$ is the wavelength of X-ray used and $\theta$ is the diffraction angle. P3HT crystallites drastically increase in size from ~8 nm for chloroform processed films to ~19 nm for TCB processed films. Such a large increase in the crystallite size also provides further insight onto effective charge transport and origin of high field effect mobilities in our devices as discussed in the subsequent sections. Absorption spectra of these films were also studied and a displayed in Fig. 1b. As can be seen from the figure, all the films exhibited a similar breadth in their absorption with absorption peak located at 550 nm [19]. A slight red-shift in the absorption maxima is also observed in the case of films processed in high bp solvent such as DCB and TCB and two shoulders also emerge in the spectra at 550 and 603 nm, which account for the crystalline π stacking of P3HT [5].

The interface area available for exciton dissociation in bilayer solar cells primarily depends on the surface property of the first layer and hence it needs to be monitored carefully. Surface morphology of the P3HT films processed in different solvents is displayed in Fig. 2. Surface roughness of the P3HT films cast from
One of the prerequisites for the high efficiency solar cells is that balanced mobility is essential for achieving high device performance as explained below.

Fig. 4 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 and the device parameters are listed in Table 1 for the films processed in different solvents. As can be seen from the figure, device parameters depend significantly on the solvent used for the P3HT layer processing. As explained previously, P3HT films processed in the TCB solvent possess better crystallinity, higher surface roughness and high field effect mobility [22]. Nearly 8 fold increase in surface roughness of 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 [23]. We attribute the high performance of our devices to better crystallinity, high surface roughness of the P3HT and the balanced charge transport. The maximum 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 [23]. We attribute the high performance of our devices to 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 bilayer solar cells. Inset of Fig. 4 depicts the external quantum efficiency (EQE) of the bilayer devices with the P3HT layer processed in various 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 (EQE) of the bilayer devices with the P3HT layer processed in various 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 ratio.

Photovoltaic parameters of P3HT/C70 bilayer devices with P3HT layer processed in various solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>R_a (nm)*</th>
<th>μ_eff (cm²V⁻¹s⁻¹)</th>
<th>J_sc (mA/cm²)</th>
<th>V_oc (V)</th>
<th>FF</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform</td>
<td>1.14</td>
<td>2.8 × 10⁻³</td>
<td>4.61</td>
<td>0.53</td>
<td>0.43</td>
<td>1.04</td>
</tr>
<tr>
<td>Xylene</td>
<td>4.83</td>
<td>1.1 × 10⁻³</td>
<td>8.66</td>
<td>0.51</td>
<td>0.53</td>
<td>2.34</td>
</tr>
<tr>
<td>DCB</td>
<td>8.62</td>
<td>3.2 × 10⁻³</td>
<td>9.36</td>
<td>0.51</td>
<td>0.53</td>
<td>2.53</td>
</tr>
<tr>
<td>TCB</td>
<td>9.20</td>
<td>1.0 × 10⁻²</td>
<td>10.65</td>
<td>0.52</td>
<td>0.64</td>
<td>3.56</td>
</tr>
</tbody>
</table>

* rms roughness of P3HT.
4. Conclusion

In conclusion, we have demonstrated that bilayer organic solar cells can be the potential contenders for deriving high efficiency. Proper monitoring of the morphology of the polymer films is a key issue to obtain the desired rough surface, which helps in enhancing the interfacial area. In addition, transport properties and crystallinity of the polymer films play a key role in obtaining 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 can 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.

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References