Organic photovoltaic devices with a crosslinkable polymer interlayer

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Abstract...
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\textbf{A B S T R A C T}

Organic photovoltaic devices with a photo-crosslinkable interlayer were fabricated. This photo-crosslinkable interlayer acted as a leakage current reducing buffer layer. The performance of the small area OPV cell (0.04 cm\textsuperscript{2}) was enhanced by the increase in the short circuit current and the fill factor. When a larger area cell (1 cm\textsuperscript{2}) was used, the performance of OPV cell increased when the appropriate interlayer thickness was used. In the case of a 10 cm \times 10 cm module, the power conversion efficiency was about double than that without the interlayer. The insertion of the interlayer increased the current extraction by lowering the barrier height and attenuated the fill factor reduction by enhancing the rectification with a better leakage current sealing. From this study, it is clearly proved that the insertion of the appropriate photo-crosslinkable layer improves the performance of OPV devices, the effect was especially evident for large area cells.

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1. Introduction

Organic photovoltaics (OPVs) have received growing attentations because they have several advantages over traditional silicon-based or other inorganic solar cells, such as their excellent processability, light weight, and their capability to form large area devices at a low cost [1–10]. An efficient bicontinuous interpenetrating network structure, which can produce high conversion efficiency, can be easily obtained by the simple spin coating of a polymer blend solution [11–15]. Therefore, OPVs have the potential to provide low cost solar power conversion methods. Recent improvement of the power conversion efficiency utilizing bulk heterojunction interpenetrating network structures, low band gap materials, and advanced device fabrication methods (tandem cells, inverted cells, and parallel or series connections, etc.) draw great anticipations for commercial OPV devices in the near future [9,16–21]. Nonetheless, the conversion efficiency of OPV devices hitherto attainable is still not close to the approximate maximum value of 11% [22–25]. The best advantage of OPV is that it can be fabricated in a flexible form by printing technology. Recently many researchers have been focused on utilization of roll-to-roll processing to reduce the production cost [26,27].

Because of the relatively low conversion efficiency of OPV devices, they need a large scale photoactive area to achieve the desired power output [28,29]. However, the performance of a single OPV cell decreases with an increase in the active area because of the high resistivity caused by the increase in series resistance and the decrease in the fill factor. A close relationship between the device area and the conversion efficiency is now well established. In order to achieve the maximum power conversion efficiency for a large active area device, it is important to maintain the fill factor as the active area increases or at least minimize the reduction of the fill factor. A buffer layer has been used to attenuate this fill factor loss [30]; however, the solution processed overlaid structure forming the preparation characteristics of the OPV limits the use of high quality semiconductors because of the similarity in the solubility of the solvents used. One way of solving the problem for forming multi-layer structure was the utilization of insoluble polythiophene, which was prepared by the precursor method using thermo-cleaveable side chains [31,32]. In this work, we focus our efforts on using a photo-crosslinkable precursor as a buffer layer and study the influence of this interlayer on the device performance in terms of the short circuit current, the open circuit voltage, and the fill factor. The utilization of this crosslinkable interlayer allows a layer by layer processing of the solution coating technique. This method provides a distinct implementation advantage by using simple printing techniques, such as inkjet, gravure, offset and screen lithography, and soft contact transfer in the future application of printed electronics.

2. Materials and methods

2.1. Synthesis and basic characterization of photo curable precursor (T43)

\begin{equation*}
1.1.1.2.2.2^\prime.3.3^\prime.3^\prime-(1E,1E,1E)-2,2^\prime,2^\prime,2^\prime-(benzene-1,3,5-triyl)tris(ethene-2,1-diyl)tris(9H-carbazole-9,3-diyl))tris(ethene-2,1-diyl)
\end{equation*}
2.3. Characterization

deposition at 10 nm thick aluminum layer was evaporated by thermal vapor extraction, was deposited on top of the active layer and a 10 min. 0.8 nm thick LiF, which serves as a buffer layer for electron injection, was spincoated in air at 2000 rpm for 40 s to form an active layer was 220 nm; it was pre-annealed at 150 °C for 10 min. All of the processing was performed under a reduced pressure. The crude product was then purified by silica gel column chromatography (eluent: ethyl acetate/CH3Cl = 1:20) to obtain 0.55 g of a pure solid: yield 86%.

1H NMR (400 MHz, CDCl3): δ (ppm) 8.30 (s, 3H), 8.16 (d, J = 8.0 Hz, 3H), 7.76 (d, J = 8.0 Hz, 3H), 7.67 (s, 3H), 7.47 (m, 12H), 7.28 (m, 6H), 5.82 (m, 6H), 5.72 (t, 3H), 5.26 (m, 12H), 4.59 (t, 6H), 4.52 (t, 6H), 2.56 (t, 12H).

13C NMR (100 MHz, CDCl3): δ (ppm) 172.30, 171.32, 141.00, 140.44, 138.70, 135.02, 130.01, 129.31, 126.46, 126.29, 124.92, 123.67, 123.31, 120.76, 119.81, 119.03, 117.87, 109.06, 108.95, 106.75, 75.39; H, 5.25; N, 3.41.

2.2. The device fabrication

A PEDOT:PSS (poly(3,4-ethylene dioxythiophene)):poly(styrene sulfonate) aqueous dispersion (CLEVIOUS® PH-500) stock solution was spincoated in air at 2000 rpm for 40 s to form an about 35 nm thick film, then film was baked at 200 °C for 10 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box. The ITO glass was cleaned by boiling in chloroform, isopropyl alcohol, and acetone for 30 min in each solvent, then sonified for 15 min in a high purity nitrogen environment glove box.

A typical example of the sample preparation is as follows: 4.3 wt% of P3HT (purchased from Rieke Metals, EE grade) and PCBM (purchased from Nano-C) blend with a 1:0.6 ratio by weight was dissolved in anhydrous chlorobenzene and spincoated onto prepared PEDOT:PSS coated ITO glass with/without an interlayer at 2500 rpm for 40 s. The thickness of the resulting active layer was 220 nm; it was pre-annealed at 150 °C for 10 min. 0.8 nm thick LiF, which serves as a buffer layer for electron extraction, was deposited on top of the active layer and a 150 nm thick aluminum layer was evaporated by thermal vapor deposition at 10^-6 to 10^-7 Torr; the prepared device was post annealed at 120 °C for 10 min. All of the processing was performed in a glove box with a high purity nitrogen environment. The active cell areas were 0.04 cm² for the small area, 1 cm² for the large area, and 36.4 cm² for the largest area module.

2.3. Characterization

The thickness of the coated film was measured with a surface profiler (TENCOR®, P-10 α-step). The surface morphology of the samples was studied using a tapping mode atomic force microscope (Digital Instruments Multimode) equipped with a nanoscope IIIa controller. The absorption spectra of the films were obtained using a photodiode array type UV–Vis spectrometer (HP 8453). An Oriel Class A type solar simulator (IEC 904) with an Oriel Reference Cell (calibrated data traceable to NREL) was used as a light source; all of the measurements were performed under a 1 sun condition (AM 1.5 100 mW/cm²). The measurements were not corrected for reflection losses and for light absorption in the ITO electrode. The I–V characteristics were determined with a Keithley 2400 source-measure unit.

3. Results and discussions

The chemical structure of the photo curable precursor used in this study is given in Fig. 1(a). This crosslinkable precursor was designed to possess carbazole moieties for a high hole transporting characteristic and pentadienyl moieties for photo-crosslinking sites. UV–Vis spectral changes due to cure process are shown in Fig. 1(b). The decrease in 300 and 350 nm represents the disappearance of the double bond in pentadiene photoreactive groups. In order to study its effectiveness as a buffer layer, the energy levels (HOMO, LUMO, and energy band gap) were studied using a cyclic voltamogram and UV–Vis spectroscopy. The band energy diagrams are given in Fig. 2. The HOMOs of the photo-crosslinked interlayer material and the P3HT are very close to that of the PEDOT, which serves as a hole extraction layer, so these interlayers can form an ohmic contact with the hole extraction layer. As a result of this ohmic contact, the contact resistance is reduced due to a reduction of the barrier height. Meanwhile LUMOs of interlayer are much bigger than that of P3HT or PCBM, therefore, this interlayer can be acted as an electron blocking layer. Insertion of this electron block layer can improve device performance by reducing separated charge quenching (i.e. electron).

Fig. 1. Chemical structure of the UV crosslinkable polymer.
The surface roughness is another important factor affecting the device performance, because OPV devices are made with a very thin (100–200 nm) active layer. We used AFM to compare the surface roughness of the PEDOT and the interlayer. As shown in Fig. 3, the surface roughness was reduced from ~3 nm to ~2 nm when the ITO was coated with the PEDOT (Fig. 3(a) and (b)). After the photo-crosslinking procedure, the surface roughness slightly increased to about 3 nm (Fig. 3(c)). The annealing of the P3HT:PCBM active layer caused a severe deterioration in the surface roughness by about a 10 nm scale. From this image analysis, it was concluded that the photo-cured interlayer would not cause any surface roughness problems. When we compared the AFM images of active layer morphology with and without interlayer, there was not much morphological difference between these two active layers. Therefore, we concluded that the interlayer did not cause any affect on the morphology of active layer and it is understandable since the thickness of the interlayer was only 5 nm thick.

We performed the contact angle study (Krüss DS-100 Drop Shape Analyzer) of the surfaces of the PEDOT and photo-crosslinked interlayer. As shown in Fig. 4, the surface of interlayer is more hydrophobic since the contact angle measurement of PEDOT surface is 41.5° (calculated surface energy is 58.2 mN/m) while that of interlayer is 59° (calculated surface energy is 46.7 mN/m). Utilizing reported surface energy values of PCBM and P3HT [28], of which the surface energy was 37.8 and 26.9, respectively. From these results, it is clear that overlay coating of PCBM:P3HT blend will be more nicely coated on interlayer than PEDOT surface. This better adhesion should help the device performance.

Fig. 3. AFM topography images: (a) ITO, (b) PEDOT on ITO, (c) T43 on PEDOT/ITO and (d) P3HT:PCBM on T43/PEDOT/ITO.
circuit voltage, the short circuit current density, the fill factor, and the power conversion efficiency at an AM 1.5 condition without the interlayer (i.e. the reference cell) were, 0.586 V, 8.86 mA/cm², 0.649, and 3.38, respectively. When the ~5 nm thick photo-crosslinked interlayer was inserted between the PEDOT and the active layer, their values changed to 0.588 V, 9.96 mA/cm², 0.693, and 4.06, respectively. The power conversion efficiency of the device with the interlayer increased by about 20% compared to that of the cell without an interlayer. Fig. 5(b) and (c) show the logarithmic $I-V$ characteristics plot of the small area cell (active area: 0.04 cm²) with and without the interlayer for dark and photo state, respectively. As shown in figures, device with 5 nm thick interlayer showed the lowest dark current while the highest photocurrent. From this plot, it is clear that this interlayer prevented shunt leakage at dark state. The shunt resistance and series resistance of the device measured from $I-V$ plot was $6.40 \times 10^4$ and $9.78 \Omega \text{cm}^2$ for without the interlayer (reference device) and $2.34 \times 10^5$ and $4.86 \Omega \text{cm}^2$ for with interlayer. From these resistances, it is clear that this interlayer is formed by ohmic contact and it also plays role of leakage current preventing layer. Fig. 6 compares the incident photon to current collection efficiency (IPCE) spectrum of devices with and without the interlayer. The reference device shows the typical spectral response of P3HT:PCBM blend film with a maximum IPCE of ~66% at 516 nm, similar with the other report[33]. For the device with the interlayer, the extracted current was increased due to the interlayer and the maximum IPCE increased to 71% at 516 nm.

The interlayer thickness effects were studied by changing the interlayer thickness; the results are summarized in Table 1. The short circuit current density was increased with a decreasing interlayer thickness, whereas the open circuit voltages were not changed. The devices with and without the interlayer were identical except for the interlayer between the hole extraction layer (PEDOT) and the active layer (all of the devices were prepared under identical conditions), therefore, the difference in the short circuit current and the power conversion efficiency should originate from the decrease in the barrier height between the PEDOT layer and the active layer due to the insertion of the interlayer. The open circuit voltage, which represents the built-in potential in the fabricated devices is mainly determined by the energy difference between the HOMO of the donor material and the LUMO of the acceptor material, which contact to form the heterojunction. Since the device structures were identical with and without the interlayer, and since the HOMO levels of the

<table>
<thead>
<tr>
<th>Interlayer thickness (nm)</th>
<th>Open circuit voltage (V)</th>
<th>Short circuit current density (mA/cm²)</th>
<th>Fill factor</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (reference)</td>
<td>0.586</td>
<td>8.859</td>
<td>0.649</td>
<td>3.376</td>
</tr>
<tr>
<td>52</td>
<td>0.587</td>
<td>9.038</td>
<td>0.657</td>
<td>3.695</td>
</tr>
<tr>
<td>26</td>
<td>0.587</td>
<td>9.564</td>
<td>0.657</td>
<td>3.695</td>
</tr>
<tr>
<td>12</td>
<td>0.589</td>
<td>9.762</td>
<td>0.654</td>
<td>3.765</td>
</tr>
<tr>
<td>5</td>
<td>0.588</td>
<td>9.964</td>
<td>0.693</td>
<td>4.061</td>
</tr>
</tbody>
</table>

Fig. 5. (a) $I-V$ characteristics of the small active area cell (0.04 cm²), (b) log $I-V$ plots of the small active area cell (0.04 cm²) (dark current), and (c) log $I-V$ plots of the small active area cell (0.04 cm²) (photocurrent).

Fig. 6. IPCE plots of the small active area cell (0.04 cm²) in photo state.
PEDOT and the interlayer material were very close to each other, the open circuit voltages should not change with the change in the thickness of the interlayer. As shown in Fig. 5(a), the series resistance slightly decreased with a decreasing interlayer thickness, therefore there was a slight increase in the short circuit current density with the decreasing interlayer thickness. The most noticeable change was the fill factor. The shunt resistance representing the rectification of the device was enhanced noticeably, as shown in Fig. 5(a). As a result of this improvement, the fill factor increased from 0.649 for the reference cell to 0.693 for the optimum thickness interlayer, which was about 5 nm thick. From this study, it can be concluded that this photo-crosslinkable interlayer can prevent the flow of leakage current like TiO used in an n-type interlayer [25,33].

In order to study the charge transporting characteristics of this interlayer, TFT devices were fabricated to measure the hole mobility within this photo-crosslinked interlayer. The measured hole mobility of the interlayer was 4.81 \times 10^{-3} \text{cm}^2/\text{V s}, which was very close to or lower than that of the P3HT in the active layer. Therefore it was clear that the short circuit current enhancement was caused by the barrier height reduction of the interlayer. A similar result was reported by Kang et al. [34] in that the short circuit current and the fill factor could be enhanced even with a high resistance hole transporting buffer layer, i.e. polytetrafluoroethylene, if this buffer layer had a low barrier height [35,36].

We applied this interlayer for the cells to a higher active area (i.e. changed the cell area from 0.04 to 1 cm²). The larger area cells were prepared by the same methods as used for the preparation of the smaller cells. Fig. 7 shows the I–V characteristics of the large cell with and without an interlayer. The open circuit voltage, the short circuit current density, the fill factor, and the power conversion efficiency at an AM 1.5 condition without the interlayer (i.e. the reference cell) were, 2.88 V, 1.00 mA/cm², 0.271, and 0.78%, respectively. The module with the interlayer was 2.94 V, 1.56 mA/cm², 0.296, and 1.36%, respectively. The power conversion efficiency of the module with the interlayer increased by about 2 times compared to that of the cell without an interlayer.

As predicted, the performance of the OPV module decreased with an increase in active area because of the high resistivity caused by the increase in the series resistance and a decrease in the fill factor. In order to achieve the maximum power conversion efficiency for a large active area device, it is important to maintain the fill factor as the active area increases. These module experiments clearly showed that the insertion of an interlayer curtailed the reduction of the fill factor. This attenuation of the fill factor

Finally, this interlayer study was applied to a large area 10 cm x 10 cm module, which had active cell area of 36.4 cm², as shown in Fig. 8(a). The I–V characteristics of these modules are shown in Fig. 8(b). The open circuit voltage, the short circuit current density, the fill factor, and the power conversion efficiency at an AM 1.0 condition without the interlayer (i.e. the reference cell) were, 3.38–2.53, a 25% reduction), whereas that for the cell with an interlayer was only 20% (i.e. 4.06–3.27). This was caused by the selective diode contact of the interlayer, which led to a better ohmic resistance to the holes and better blocking to the electrons; this effect was enhanced when the active area was increased.

Fig. 7. I–V characteristics of the large active area cell (1 cm²).

Fig. 8. (a) Schematic diagram of 10 cm x 10 cm module and (b) I–V characteristics of the 10 cm x 10 cm module.
can be achieved by enhancing the rectification with a better leakage current sealing as proved in the increased shunt resistances.

4. Conclusion

In order to maximize the expected capability of OPVs as a future renewable energy source, it is very important to have device fabrication methods suitable for multi-layer printable techniques and an enhanced large area performance. In this study, we used a photo-crosslinkable interlayer, which acts as a buffer layer, not only for a leakage current reducing layer, but also for a multi-layer printable insoluble layer. Since this interlayer is photo-crosslinkable, it can be used in a solution process to form an overlaid structure for polymer semiconductors with a similar organic solvent solubility. This will be an important factor for future organic photovoltaic applications, which will be fabricated using various printing methods with a similar solubility. This interlayer also played an important role in enhancing the rectification and the charge extraction. The influence of the increase in the rectification was severe for modules with a larger active area. In this study, we clearly proved that an insertion of an appropriate photo-crosslinkable layer improved the performance of OPV devices.

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