Research Article


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We fabricated a poly[3-hexylthiophene] (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PC$_{61}$BM) organic photovoltaic cells (OPCs) using TiO$_x$ interfacial layer. We performed optimization processes for P3HT : PC$_{61}$BM with the TiO$_x$ layer. We found that a solution based TiO$_x$ layer coated at a spin speed of 3000 rpm improved the photon absorption of the active layer. An optimized TiO$_x$ layer was also used as the interfacial layer to investigate the stability of P3HT : PC$_{61}$BM OPC. After 70 days of storage, we observed that the short-circuit current density ($J_{SC}$) dropped by 16.2%, fill factor (FF) dropped by 10.6%, and power conversion efficiency (PCE) dropped approximately by 25%, while the open-circuit voltage ($V_{OC}$) remained relatively stable. We found that a solution based TiO$_x$ layer synthesized using a sol-gel chemistry method was very effective in protecting the active layer from degradation.

1. Introduction

Photovoltaic (PV) technology is considered an adequate way for solar energy use and for a limitless renewable clean energy. The electrical energy generated from solar energy appears as a noble solution for the immediate needs of having clean and renewable energy sources which is one of our desires to protect the environment. However, until now, Si materials have been used for current commercial solar cell applications. Recently, flexible organic materials have been introduced for photovoltaic applications and enabled innovative and reliable elements that were not possible by traditional technologies (e.g., flexible organic solar cells can be wrapped around surfaces, rolled up, or even painted onto structures). Organic solar cells can also replace expensive and rigid counterparts of Si solar cells with solution based, very cheap, and roll-to-roll fabrication process [1, 2]. Therefore, organic photovoltaic cells (OPCs) are considered very outstanding for low cost production by using solution processing which can effectively reduce the manufacturing costs. Typically, solar cells that are based on mixtures of conjugated polymers and [6,6]-phenyl C61-butyric acid methyl ester (PC$_{61}$BM) fullerene have been highly investigated [3]. Mixtures of conjugated polymer and fullerene form bulk heterojunction (BHJ) OPCs which are made of a blend of bicontinuous and interpenetrating donor and acceptor [3], maximizing interfacial area between the donor and the acceptor. In a polymeric BHJ organic solar cell, the photoactive blend layer is sandwiched between an indium tin oxide (ITO) anode and Al cathode. In this case, a high bandgap conjugated polymer donor is composed with a soluable nanosized acceptor. A fullerene derivative, [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), is a widely utilized acceptor. Conjugated polymer donor aids as the main solar photon flux absorbing component in the active layer and also as the hole transporting phase. Thus, the basic requirements to design an ideal polymer donor are a high bandgap feature to match the solar spectrum and fast hole mobility. With innovative BHJ structures, organic photovoltaic technology
has gradually advanced to power conversion efficiencies over 8% [4]. Even though the improvement in device efficiency has brought OPCs closer to commercial viability, the lifetime and reliability of OPCs should be substantially improved [5, 6]. The degradation of the active layer is clearly related to exposure to oxygen, air, and light [7]. To achieve the stability of OPCs, either the development of improved barrier materials for packing or the development of devices with less air sensitivity (or both) is required. Air stable OPCs have reportedly been achieved by inserting a solution based metal oxide as a buffer layer between the active layer and the metal cathode [8, 9]. For instance, a solution based titanium suboxide (TiO$_x$) with a thickness less than 30 nm has been reported to effectively minimize physical and chemical damages [10]. In this case, the TiO$_x$ layer serves as an effective barrier for oxygen permeation to improve device stability in an ambient atmosphere. In this study, we synthesized the solution based TiO$_x$ material by using the sol-gel chemistry method [10]. We fabricated OPCs composed of high bandgap polymer, poly(3-hexylthiophene-2,5-diyl) (P3HT): PC$_{61}$BM with the TiO$_x$ layer and performed a stability test.

2. Experimental Methods

To study the effect of the solution based TiO$_x$ layer on the performance and stability of the OPV device performance over a period of time, we fabricated OPCs with a structure of ITO/PEDOT : PSS/P3HT : PC$_{61}$BM/TiO$_x$/Al. The weight ratio for an active solution of P3HT : PC$_{61}$BM is 1 : 0.8 with a weight concentration (mg) of 30 : 24 in 2 mL chlorobenzene. The active solution was spun inside a glove box to form a thickness of approximately 100 nm. Immediately following, the active layer was annealed at 140° C for 2 min. The substrate was then allowed to cool down to room temperature inside the glove box. The TiO$_x$ solution was spun in air inside a fume hood environment. Al with an 80 nm thickness was used as the metal contact and deposited by an e-beam evaporator.

To synthesize TiO$_x$, sol-gel processing was performed by using an IKA rotary evaporator system. Prior to use, rotary and condensation flasks were cleaned using the standard method (trichloroethylene, acetone, methanol, ethanol, and DI water rinse between each solvent), blow dried with N$_2$ gas, and placed in an oven to dry for one hour. An empty flask was allowed to rotate at 50 rpm and 120°C in a silicon oil bath under a N$_2$ environment for one hour to ensure all moisture was removed from the system. The sol-gel procedure started with an injection of the precursors, in the following order: (1) titanium (IV) isopropoxide (Ti(OCH(CH$_3$)$_2$)$_4$, 5 mL), (2) 2-methoxyethanol (CH$_3$OCH$_2$CH$_2$OH, 20 mL), and (3) ethanolamine (H$_2$NCH$_2$CH$_2$OH, 2 mL) into the rotary flask connected with a water condenser and nitrogen gas inlet/outlet at room temperature. After stirring for one hour at room temperature, the mixed solution was heated at 80°C (using a silicon oil bath) for one hour, resulting in a dark orange colored solution. During this process, the inside of the flask must be in a dry N$_2$ environment and the mixed solution must be stirred continuously (600–800 rpm). The final step was to stir the mixed solution at the same speed at an elevated temperature of 120°C for another hour. At the end of the stirring process, we observed that the solution was transformed into a dark wine color. As a final step after cooling to room temperature, 10 mL of methanol was injected to extract the final solution of TiO$_x$ sol-gel product. Prior to applying the TiO$_x$ layer on the active layer, the TiO$_x$ sol-gel product was diluted by 1 : 200 in methanol [11]. When the TiO$_x$ layer deposited on the substrate was dried in the air, the condensation process started immediately resulting in the formation of Ti-O-Ti linkages [12, 13]. These reactions occurred very slowly because the alcohol solution inhibits contact of the TiO$_x$ with moisture. The condensation was significantly accelerated after spin casting forming solid TiO$_x$ films.

Absorption spectra were measured using a UV-Vis spectrophotometer. All films were measured on glass substrates and corrected for substrate absorption. The device active area was defined by cathode area (10.47 mm$^2$) as measured. Current density-voltage ($J$-V) characteristics were measured outside a glove box by using a Keithley 238 source measurement unit under air mass 1.5 G solar illumination (100 mW/cm$^2$).

### Table I: The photovoltaic parameters of P3HT : PC$_{61}$BM OPCs fabricated at different active layer thicknesses.

<table>
<thead>
<tr>
<th>Active layer thickness (nm)</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>87</td>
<td>8.8</td>
<td>0.605</td>
<td>0.59</td>
<td>3.14</td>
</tr>
<tr>
<td>98</td>
<td>10.0</td>
<td>0.610</td>
<td>0.62</td>
<td>3.78</td>
</tr>
<tr>
<td>121</td>
<td>7.4</td>
<td>0.599</td>
<td>0.57</td>
<td>2.52</td>
</tr>
<tr>
<td>146</td>
<td>6.0</td>
<td>0.598</td>
<td>0.55</td>
<td>1.97</td>
</tr>
</tbody>
</table>

3. Results and Discussion

The active layer solution was prepared at a ratio of P3HT (30 mg) : PC$_{61}$BM (24 mg) (1 : 0.8 wt%) in 2 mL chlorobenzene and was stirred at a temperature of 50°C overnight inside a glove box atmosphere (H$_2$O, O$_2$ < 0.1 ppm). Due to excellent miscibility and solubility of both P3HT and PC$_{61}$BM in chlorobenzene a much finer domain size results [14], which is beneficial for both increasing light harvesting and for better charge transport [15]. For the active layer thickness, we fabricated four OPCs with four different active layer thicknesses of 87 nm, 98 nm, 115 nm, and 146 nm corresponding to spin coating speeds of 1500 rpm, 1250 rpm, 1000 rpm, and 750 rpm, respectively. Prior to depositing the active layer, a blend active layer of P3HT : PC$_{61}$BM was filtered through a 0.45 µm PTFE filter. We measured the active layer thickness by using a Veeco Dektak stylus profilometer. Optimum layer thicknesses must be determined to improve the optical field distribution across the cell, as well as to properly balance charge transport and current collection at the electrodes. In general, high efficiency OPCs have been reported with an active layer thickness of approximately 100 nm [16]. Our experiment agrees with these results. Figure 1 shows the J-V curves of the OPV cells fabricated at different thicknesses of the active layer. We found that a 98 nm thickness of the active layer yielded the best results with an FF value of approximately 62% and a power conversion efficiency (PCE)
value of 3.8%. As shown in Table 1, as the active layer thickness of OPV cells increases, the short-circuit current density ($J_{SC}$), fill factor (FF), and PCE values decrease, due mainly to the buildup of space charge, the increase of the series resistance, and recombination issues [17]. When the active solution was less than 100 nm, we observed the decrease in the PCE value slightly, possibly due to the decreased light absorption. Optimized fabrication processes with active layer thickness of 100 nm yielded the best performance of a P3HT:PC$_{61}$BM organic solar cell with a FF of 63.4% and a PCE of 4.14% (see Figure 1(b)).

To investigate the stability of TiO$_x$ interfacial layer for P3HT:PC$_{61}$BM solar cell, ITO/PEDOT:PSS/P3HT:PC$_{61}$BM/TiO$_x$/Al solar cell structure should be optimized. Once TiO$_x$ is synthesized using sol-gel processes, TiO$_x$ was spin-cast between P3HT:PC$_{61}$BM and the Al electrode. It should be noted that TiO$_x$ has been used as the optical spacer to optimize absorption within the active layer by redistributing the light intensity between the active layer and the reflecting electrode [10]. To investigate the role of the TiO$_x$ layer, TiO$_x$ solutions was spin-cast on 100 nm-thick P3HT:PC$_{61}$BM photoactive layer at different spin speeds of 1000 rpm, 2000 rpm, and 3000 rpm. The corresponding thicknesses of TiO$_x$ were 20, 14, and 8 nm which were measured by Dektak stylus profilometer. Other studies have

Figure 1: (a) $J$-$V$ characteristics of P3HT:PC$_{61}$BM OPCs fabricated at different thicknesses of the active layer and (b) the best P3HT:PC$_{61}$BM OPC with active layer thickness of 100 nm.

Figure 2: UV-Vis absorption profile of P3HT:PC$_{61}$BM with/without TiO$_x$ in which TiO$_x$ was spin-casted at different spin speeds of 1000, 2000, and 3000 rpm.

Figure 3: $J$-$V$ characteristics of P3HT:PC$_{61}$BM OPCs fabricated at different spin speeds of the TiO$_x$ solution.
reported that optimal thicknesses of the TiO\textsubscript{x} layer for OPV devices are in the 5 nm–20 nm ranges [18]. A P3HT:PC\textsubscript{61}BM photoactive layer coated without a TiO\textsubscript{x} layer was used as a reference cell. Subsequently, the P3HT:PCBM/TiO\textsubscript{x} samples without Al electrode were annealed at 90°C for 10 minutes. Figure 2 shows UV-VIS spectra of P3HT:PC\textsubscript{61}BM and P3HT:PC\textsubscript{61}BM/TiO\textsubscript{x} with different spin-speeds of the TiO\textsubscript{x} solution. As shown in Figure 2, the relative maxima of absorption were influenced by both the polymer and fullerene. There is a local peak in the UV range at ~330 nm, influenced by the PC\textsubscript{61}BM in the blend, and three peaks in the visible ranges of ~510, ~555, and ~605 nm, due to the presence of P3HT. These peaks are very consistent with published data, which also show the absorption peaks in the exact same ranges [19]. However, the increase in the spin speed of TiO\textsubscript{x} solution led to the increase in the light absorption. UV-VIS measurement indicates that a spin speed of 3000 rpm yields the highest light absorption. For instance, the light absorbance at 500 nm for a sample with spin speed of 3000 rpm increased up to 25% compared to a sample without a TiO\textsubscript{x} layer. Figure 3 shows the J-V characteristics of the OPCs fabricated at different spin speeds of the TiO\textsubscript{x} solution. The device fabricated with a TiO\textsubscript{x} layer spun at a speed of 3000 rpm produced the best performance with a FF of 50% and PCE of 3%.

The change of J-V characteristics of the P3HT:PC\textsubscript{61}BM OPV device fabricated with TiO\textsubscript{x} layer was monitored with a storage time. It should be noted that most data reported in the literature show very short period of time [20, 21]. We extended our study to a 70-day storage time. We compared the degradation trend of the device by evaluating their \( J_{SC}, V_{OC}, FF, \) and PCE values as a function of the storage time. OPCs were stored inside glove box with Al foil to protect the device from light. Every five days, OPCs were taken and characterized outside the glove box and were restored inside the glove box. Figure 4 shows the J-V characteristic of an OPC with a TiO\textsubscript{x} layer as a function of storage time. After 70 days
of storage, we observed that the $V_{OC}$ was relatively stable, the $J_{SC}$ dropped by 16.2%, the FF dropped by 10.6%, and the PCE dropped approximately by 25%. We observed that the $J_{SC}$ value dropped linearly over the entire storage time with a loss rate of approximately $-0.0155$ mA cm$^{-2}$ per day. The $V_{OC}$ value dropped only about 1% after 70 days of the storage time; therefore, it could be considered the most stable organic photovoltaic parameter. This is a fact that the $V_{OC}$ value is intrinsically dependent on the energy levels of the active materials and the morphology of the active layer [22, 23]. Without TiO$_2$, the PCE of OPCs dropped to 0% within a day.

The degradation of organic solar cells is attributed to many factors including phase separation of organic blends, oxidation of metal electrodes, chemical degradation of photoactive layer caused by moisture, oxygen and/or light, and others reported in [24]. Particularly, organic materials such as P3HT and PC$_{61}$BM are susceptible to chemical degradation from O$_2$ and H$_2$O [25]. To improve the stability of organic solar cells, the interfacial layers such as TiO$_x$, MoO$_3$, and ZnO were inserted between the active layer and the electrodes [26, 27]. These interfacial layers have been proven to slow down the degradation between the active and the electrode [28]. Recently, Li et al. reported the stabilization mechanism of organic solar cells with thin TiO$_x$ layer [29]. The surface of TiO$_x$ layer has –OR (OR= OCH$_2$(CH$_3$)$_2$) and –OH function groups. In the presence of light, TiO$_x$ undergoes photochemical oxidation reaction (see (1)), resulting in trapping O$_2$ within the TiO$_x$ layer (see (2)), which protects underlying organic blends from oxygen attack. The hydrolysis of isopropoxide function groups (–OR) (see (3)) results in protecting the underlying organic blends from water attack as

$$\text{Ti(IV)} + h\nu \rightarrow \text{Ti(III) (e$^{-}$)} \quad (1)$$

$$\text{Ti(III) (e$^{-}$)} + \text{O}_2 \rightarrow \text{Ti(IV)} - \text{O}_2^{-} \quad (2)$$

$$\text{Ti(OR)$_4$} + \text{H}_2\text{O} \rightarrow \text{HO-Ti(OR)$_3$} + \text{H-OR} \quad (3)$$

As a result, sol-gel derived TiO$_x$ serves as a passivation layer for protection of underlying organic blends from the oxygen and water attack. Therefore, the TiO$_x$ layer plays a significant role in preventing the degradation of organic solar cells.

4. Conclusion

We investigated the effect of the stability of P3HT:PC$_{61}$BM based solar cells. In this study, we used a sol-gel TiO$_x$ material as the interfacial layer between the active layers of P3HT:PC$_{61}$BM and the Al cathode. After 70 days of storage, the OPCs remained relatively stable, indicating that the $V_{OC}$ was relatively stable, the $J_{SC}$ dropped by 16.2%, the FF dropped by 10.6%, and the PCE dropped approximately by 25%. Data on the degradation of solar cell performance with TiO$_x$ are presented indicating that significant improvements are observed with TiO$_x$ layer protection.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References


