Organic Solar Cells Based on PTB7:PC$_{71}$BM with Cs$_2$CO$_3$ as a Cathode Buffer Layer

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Bulk heterojunction solar cells were fabricated using poly[[4,8-bis[(2-ethylhexyl)oxy]benzo [1,2-b:4,5-b']dithiophene-2,6-diyl] [3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]-thiophenediyl] (PTB7) and [6,6]-phenyl C$_{71}$ butyric acid methyl ester (PC$_{71}$BM) after a layer of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was deposited on an indium tin oxide (ITO)-coated glass substrate. The fabricated structures were glass/ITO/PEDOT:PSS/PTB7:PC$_{71}$BM/Cs$_2$CO$_3$/Al with or without the cesium carbonate (Cs$_2$CO$_3$) buffer layer, and the effect of the buffer layer on the performance of the solar cells was investigated. The Cs$_2$CO$_3$ layer with a thickness of 0.8 nm significantly increased the short circuit current density, open-circuit voltages and fill factors of the solar cells, presumably because of the better contact between the active layer and the cathode and the work function shift of the aluminum cathode. As a result, the power conversion efficiency increased from 1.09 to 2.12%. However, when thickness of the Cs$_2$CO$_3$ exceeded 2 nm, significant degradation was observed. From the results of a stability test, it was suggested that the inserted Cs$_2$CO$_3$ layer had a minimal influence on the lifetime of the unpackaged devices.

Keyword: solar cell, bulk heterojunction, PTB7, PC$_{71}$BM, cesium carbonate

1. Introduction

Organic thin-film solar cells are especially interesting owing to their outstanding characteristics in terms of low-cost fabrication, light weight, and flexibility [1-5]. Tang [6] first reported a heterojunction solar cell composed of an organic electron donor layer (organic p-type semiconductor) and an organic electron acceptor layer (organic n-type semiconductor) using vacuum deposition systems. In 1995, bulk heterojunction (BHJ) solar cells fabricated using a solvent solution of a blended fullerene derivative of n-type C$_{60}$ and p-type poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene] semiconductors were reported, and the power conversion efficiency (PCE) of 1.5% was reported by Yu et al. [7]. BHJ solar cells can be fabricated by solution processes without using high-vacuum equipment [8-11]. Reyes et al. [12] reported a BHJ solar cell based on poly(3-hexythiophene) : [6,6]-phenyl C$_{61}$ butyric acid methyl ester (P3HT:PCBM). The solar cell was fabricated on a glass substrate, and it exhibited a PCE value as high as 4.9%. Sakurai et al. [13] clarified the nanostructures of these P3HT:PCBM active layers by synchrotron X-ray diffraction and helped establish the concepts of the BHJ solar cell. Vohra et al. [14] have recently reported that the performance of BHJ solar cells based on P3HT:PCBM could be improved by modifying the
vertical concentration gradient of these materials.

BHJ solar cells with an extremely high PCE of 7.4% have recently been reported, and these cells were fabricated using the p-type semiconductor poly[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b’]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b']-thiophenediyl] (PTB7), the n-type semiconductor [6,6]-phenyl-C_{71}-butyric-acid-methyl-ester (PC_{71}BM), and a calcium (Ca)-coated aluminum (Al) cathode on an indium tin oxide (ITO)-coated glass substrate [15]. Murray et al. [16] have recently reported BHJ solar cells based on PTB7:PC_{71}BM with a lithium fluoride (LiF) cathode buffer layer, and the BHJ solar cells exhibited a PCE value of 7.5%. These promising results inspired many publications on BHJ solar cells based on PTB7:PC_{71}BM, in which techniques were proposed to improve the performance of BHJ solar cells [17-28], and the highest efficiency of the similar BHJ structure of 9.215% was reported by He et al. [26].

On the other hand, it is known that the insertion of a cathode buffer layer such as zinc oxide, titanium oxide, or cesium carbonate (Cs_{2}CO_{3}) between the active layer and the electrode is effective in improving the efficiency of these organic solar cells [29-36]. Among these insulating interlayer materials, Cs_{2}CO_{3} is recently reported to be one of the best electron-injection materials [37-41]. For example, Wu et al. demonstrated that Cs_{2}CO_{3} can improve the device performance of organic light emitting diodes (OLEDs) due to the strong n-doping effect regardless of the cathode electrode materials from the results of ultraviolet photoemission spectroscopy (UPS) and x-ray photoemission spectroscopy (XPS) [39]. Li et al. [38] found that Cs_{2}CO_{3} decomposed into metallic Cs and gases during thermal evaporation following the reaction,

\[ 2 \text{Cs}_{2}\text{CO}_{3} \rightarrow 4\text{Cs} + \text{O}_{2} + 2\text{CO}_{2}. \quad (1) \]

The thin Cs layer with an extremely low work function (1.9 eV) reduces the barrier height at the interface between the organics and the cathode. More recently, Huang et al. also indicated that thermally evaporated Cs_{2}CO_{3} decomposes into CsO and cesium suboxides, yielding a heavily doped n-type semiconductor, which exhibits a low work function [41]. This interfacial material tends to react with Al and create a Al–O–Cs complex, which further lowers the work function [41]. The energy level diagrams of all materials used in this study are shown in Fig. 1. Note that the HOMO level of Cs_{2}CO_{3} layer locates at 4.0 eV. It was also reported that significant increase of its Fermi level due to the Cs doping in the Cs_{2}CO_{3} film in the thicker Cs_{2}CO_{3} film than 1 nm was observed. Chen et al. reported a BHJ solar cell with Cs_{2}CO_{3} as a cathode buffer layer, and demonstrated the performance improvement of the BHJ solar cell using a vapor deposited 1-nm-thick Cs_{2}CO_{3} layer [18]. However, the influence of the thickness of the Cs_{2}CO_{3} layer was not reported. In this paper, we report the effect of inserting Cs_{2}CO_{3} layers with different thicknesses as a cathode buffer layer on the performance of BHJ solar cells based on PTB7:PC_{71}BM on a glass substrate.

![Energy level diagram of all materials used in this study.](image-url)

**2. Experimental**

The devices were fabricated on patterned indium tin oxide (ITO) glass substrates. The ITO substrates were cleaned in an ultrasonic bath with deionized water, acetone, and isopropanol sequentially and finally were rinsed in de-ionized water. After cleaning, the ITO glass was dried in an oven and then treated with UV ozone. By spin coating, the cleaned substrates were covered with a thin layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT-PSS) and subsequently baked at 120 °C for 60 min. The active layer of PTB7:PC_{71}BM (weight ratio=1:1.5) was spin coated from a solution of 1,2-dichlorobenzene on the top of PEDOT-PSS and subsequently baked at 120 °C for 60 min. The active layer of PTB7:PC_{71}BM (weight ratio=1:1.5) was spin coated from a solution of 1,2-dichlorobenzene on the top of PEDOT-PSS. Spin coating was performed at a speed of 1000 rpm for 20 s to deposit the active layer. The PTB7:PC_{71}BM-coated substrates were then dried in a glove box filled with dry nitrogen at room temperature before being transferred to a vacuum system to deposit the cathode layer. To complete the device, an interlayer of Cs_{2}CO_{3} (0.8, 2, and 3
nm) and Al (100 nm) were thermally evaporated through a shadow mask to define the device area 0.04 cm² under a vacuum of 1x10⁻⁴ torr. The solar cell device performance was measured with simulated AM1.5 irradiation (100 mW/cm²) using a xenon-lamp-based solar simulator. The current density–voltage (J–V) characteristics were measured with a Keithley 2400 source meter. All measurements were started under atmospheric conditions within 10 min after the device fabrication processes were completed. These measurements took almost 5 min, and these samples were stored in a desiccator until the subsequent repeated photovoltaic measurements of the devices in order to investigate the effect of the Cs₂CO₃ buffer layer on the long-term stability of the devices.

3. Results and Discussion

Figure 2 shows the J–V curves for the devices with and without the 0.8-nm-thick Cs₂CO₃ interlayer under the AM1.5G illumination (100 mW/cm²). Before the insertion of Cs₂CO₃, the open-circuit voltage, \( V_{oc} \) was 0.52 V; the short circuit current density, \( J_{sc} \) was 5.58 mA/cm²; the fill factor (FF) was 0.32, resulting in the PCE of 1.09%. On the other hand, after the insertion of Cs₂CO₃, \( J_{sc} \) increased to 8.55 mA/cm². In addition, the \( V_{oc} \) increased dramatically to 0.58 V, and a FF of 0.45 was achieved. The PCE was improved to be 2.12%.

Figure 3. Comparison of J–V curves of the devices with Cs₂CO₃ with different thicknesses, 0.8, 2.0, and 3.0 nm.

Table 1. Performance of the solar cells with or without Cs₂CO₃ buffer layer.

<table>
<thead>
<tr>
<th>Cs₂CO₃ thickness (nm)</th>
<th>( J_{sc} ) (mA/cm²)</th>
<th>( V_{oc} ) (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.58</td>
<td>0.52</td>
<td>0.32</td>
<td>1.09</td>
</tr>
<tr>
<td>0.8</td>
<td>8.55</td>
<td>0.58</td>
<td>0.45</td>
<td>2.12</td>
</tr>
<tr>
<td>2.0</td>
<td>7.10</td>
<td>0.44</td>
<td>0.28</td>
<td>0.87</td>
</tr>
<tr>
<td>3.0</td>
<td>6.03</td>
<td>0.53</td>
<td>0.40</td>
<td>1.27</td>
</tr>
</tbody>
</table>

It is also important to discuss the effect of the Cs₂CO₃ buffer layer on the stability of the BHJ solar cells based on PTB7:PC₇₁BM. Since Cs₂CO₃ has hygroscopicity, it will be important to see if the Cs₂CO₃ has a negative impact to accelerate degradation of the BHJ solar cells. Figure 3 shows the time dependent change of normalized PCEs for the BHJ solar cells with or without the Cs₂CO₃ buffer layer. Both devices showed a rapid decrease in PCE as a function of time. However, the device with the Cs₂CO₃ buffer layer exhibited improved stability over the device without the Cs₂CO₃ buffer layer. In fact, the device with the buffer layer showed a nearly 30% reduction in PCE after the...
storage of 250 h, while the device without the Cs$_2$CO$_3$ buffer layer showed an almost 45% reduction in PCE.

Figure 4. Time dependent degradation of BHJ solar cells with or without Cs$_2$CO$_3$ buffer layer.

The degradation of the BHJ solar cells with the Cs$_2$CO$_3$ buffer layer thicker than 2 nm may be explained as follows. When Cs$_2$CO$_3$ is 0.8 nm-thick, the number of Cs donors in the Cs$_2$CO$_3$ film is small. Thus, the Fermi level shift by the Cs doping is small, only a small amount of the Fermi level shift in the Cs$_2$CO$_3$ layer occurs, and the Fermi level of Al layer aligns with the Fermi level of Cs$_2$CO$_3$. This may lead to the ohmic contact between PC$_{71}$MB and the Al cathode associated with tunneling of electrons locating either side of PC$_{71}$BM or Al cathode. This will result in the increase of $V_{oc}$ of the BHJ solar cell. On the other hand, when the thickness of the Cs$_2$CO$_3$ is larger than 2 nm, the Fermi level shifts due to Cs doping in Cs$_2$CO$_3$ layer becomes larger [41]. The Fermi level of the vacuum deposited Cs$_2$CO$_3$ was reported to 2.2 eV from the vacuum level. If the Fermi level of the cathode Al layer aligns with this level as described in Fig 4(b), the cathode energy level becomes too high for the photo electrons to flow into the cathode. In fact, some BHJ solar cells with the thickness of 2-3 nm Cs$_2$CO$_3$ layer exhibited even reversed photo current was observed possibly due to electron-hole generation within the semiconducting Cs$_2$CO$_3$ layer. The possible cause of the fluctuation of the BHJ solar cells with the Cs$_2$CO$_3$ buffer layers thicker than 3 nm may be owing to the uncontrolled Cs doping in the Cs$_2$CO$_3$ during processing. Thus, it will be very important to control the thicknesses of the Cs$_2$CO$_3$ buffer layer to less than 1 nm to suppress overwhelming shift of the work function of the Al cathode layer upon introducing Cs$_2$CO$_3$ buffer layer.

4. Conclusion

BHJ solar cells were fabricated using PTB7 and PC$_{71}$BM. The fabricated structures were glass/ITO /PEDOT:PSS/PTB7:PC$_{71}$BM/Cs$_2$CO$_3$/Al with or without the Cs$_2$CO$_3$ buffer layer, and the effects of the Cs$_2$CO$_3$ buffer layer on the performance of the solar cells were investigated. The Cs$_2$CO$_3$ layer with a thickness of 0.8 nm significantly increased the $V_{oc}$ and FF of the solar cells. However, when the thickness of the Cs$_2$CO$_3$ exceeded 2 nm, significant degradation was observed. Possible reasons for the degradation of solar cells were discussed based on the Fermi level shift of the Cs$_2$CO$_3$. From the results of a stability test, it was suggested that the inserted Cs$_2$CO$_3$ layer had a minimal influence on the lifetime of the unpackaged devices.

References