Photovoltaic Properties of Organic Thin-Film Solar Cell Using Various Exciton-Diffusion Blocking Materials

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We studied the photovoltaic properties of organic thin-film solar cell using 8-hydroxyquinoline aluminum (Alq3), 3,4,9,10- Perylenetetracarb-oxylichianhydride (PTCDA) and Bathocuprine (BCP) as an exciton-diffusion blocking layer. Although the use of Alq3 caused comparative high open-circuit voltage, it led to much poor short-circuit current. The introduction of optimum thick BCP layer improved photovoltaic properties but the increase in BCP thickness incurred the reduction of those properties. Organic thin-film solar cell with PTCDA showed stable photovoltaic properties in spite of the increase in PTCDA thickness. PTCDA was found to be one of excellent exciton-diffusion blocking materials. Keywords: organic thin-film solar cell, exciton-diffusion blocking layer

1. Introduction

Although organic thin-film solar cells (OTSs) have been investigated for a few decades, the conversion efficiency had stayed in a low value of <1[1]. But C. W. Tang reported ca. 1% of conversion efficiency in single heterojunction cell that consist of organic donor and acceptor molecules in 1986[2]. The bulk heterojunction cell proposed by Hiramoto et al. improved the conversion efficiency rapidly[3]. Also in donor-acceptor heterojunction, the cell using the acceptor material C60 with long exciton diffusion length achieved high conversion efficiency of 3.6%[4]. In addition, very high efficiency of >5% is reported for tandem cell stacked two cells in series with Ag nanoclusters[5]. On the other hand, Kim et al. reported conversion efficiency of ca. 5% by using conductive polymer P3HT and soluble fullerene derivative PCBM[6, 7]. Organic thin-film solar cells have many attractive advantages; light-weight. They do not require any electrolyte as compared with conventional dye-sensitized solar cells[8]. Since they can be fabricated at no more than 100°C, it is easy to fabricate the cells on various common plastic films.

In this paper, we investigate the photovoltaic properties of OTSs with various exciton-diffusion blocking layers (EBL) and discuss the conduction mechanism of photo carrier in OTS.

2. Experimental

We used copper Phthalocyanine (CuPc) as an electron donor and fullere, C60 as an electron acceptor and 8-hydroxyquinoline aluminum (Alq3), 3, 4, 9, 10- Perylenetetracarb- oxylicdianhydride (PTCDA), Bathocuprine (BCP) as an exciton-diffusion blocking layer (EBL). Figure 1

![Chemical structures of organic materials](image)

Fig. 1 Chemical structures of organic materials.
shows the chemical structures. The cell structure is ITO/ CuPc/ C<sub>60</sub>/ EBL/ metal cathode. All materials were purified (purity > 99.9%). We used a specific ITO substrate (Ra=0.9 nm) for organic light emitting diodes from Gomiatric Co. as transparent anode. All organic layers were deposited by vacuum evaporation method at room temperature under ca. 3×10<sup>-3</sup>Pa. Deposition rates were 0.15-0.20 nm/s. Metal cathodes were deposited at 3-6×10<sup>4</sup>Pa. The area of sandwich cell was 2×2mm<sup>2</sup>. Unfortunately, the specimens were exposed twice times by atmosphere after the depositions of organic layers and the metal cathode.

We measured absorption spectra with a spectrophotometer (U-3000; Hitachi Ltd.). The ionization potentials of organic films and the work functions of ITO and metal were estimated by means of an atmosphere ultraviolet photoelectron analysis device, AC-2 (Riken Keiki). We defined the ionization potential of organic thin film as the highest occupied molecular orbital (HOMO) and estimated the lowest unoccupied molecular orbital (LUMO) from HOMO and the threshold energy of optical absorption spectrum. The PV properties were measured through a squared hole of 2×2mm<sup>2</sup> under AM1.5, 100mW/cm<sup>2</sup> using solar simulator (XIL-03E, SERIC) in vacuum. We measured the current - voltage characteristics using a source measurement unit (2400; Keithley) in low vacuum.

3. Results and discussion

Figures 2(a) and 2(b) show the absorption spectra of 20nm-thick films of Alq3, BCP, PTCDA and those of 20nm-thick C<sub>60</sub> and 10nm-thick CuPc thin films, respectively. Alq3 is widely used as comparably stable electron-transport material for organic light-emitting diodes (electron mobility, 10<sup>-3</sup> cm<sup>2</sup>/Vs[9,10]). BCP is very popular EBL for organic thin-film solar cells[11,12]. PTCDA has a perylene derivative with a simpler structure than 3,4,9,10-perylenetetracarboxyl-bis-benzimidazole (PTCBI) reported by Tang[2]. And many researchers often reported the film structure and electronic state on metals for PTCDA[13-16]. PTCDA has the lowest threshold of absorption and BCP has the highest of all EBL. Since the energy gap between HOMO and LUMO for C<sub>60</sub> is reported to be 1.7 eV[17,18], the exciton migration of C<sub>60</sub> can be efficiently suppressed by use of PTCDA.

From the viewpoint of exciton generation, since BCP has the strong absorption in the ultraviolet region, BCP cannot be photoexcited by visible light. Although Alq3 has the absorption in visible light region, Alq3 shows poor generation efficiency of exciton because of low absorption coefficient. On the other hand, PTCDA has large absorption coefficient in visible light region.
Figure 3 shows the current density-voltage characteristics of ITO/CuPc(10nm)/C_{60}(20nm)/BCP(20nm)/Al under irradiation. From this property, open-circuit voltage (Voc), short-circuit current (Jsc), fill factor (FF), and power conversion efficiency (PCE) are estimated to be 0.37V, 2.4mA/cm², 0.47 and 0.42%, respectively.

Figure 4 shows the current density-voltage characteristics of ITO/CuPc(10nm)/C_{60}(20nm)/Alq3(15nm)/Al under irradiation. The Voc is estimated to be 0.75eV. This value is much larger as OTS and almost twice higher than that of OTS with BCP. However, The Jsc is sub-μA/cm² order and 4-orders lower than those of the other specimens. The J-V is convex upward in the fourth quadrant and FF is estimated to be 0.21 and poor.

Figure 5 shows the current density-voltage characteristics of ITO/CuPc(10nm)/C_{60}(20nm)/PTCDA(20nm)/Al under irradiation. Voc, Jsc, FF and PCE are estimated to be 0.42V, 2.5mA/cm², 0.57 and 0.57%, respectively. The Jsc is the same value as that of BCP. However, since FF is improved by the use of PTCDA, the PCE is higher than that of the OTS with BCP. Table 1 shows the summary on device performance of OTSs with a different EBL.

<table>
<thead>
<tr>
<th>EBL</th>
<th>Voc [V]</th>
<th>Jsc [mA/cm²]</th>
<th>FF</th>
<th>PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCP</td>
<td>0.37</td>
<td>2.4</td>
<td>0.47</td>
<td>0.42</td>
</tr>
<tr>
<td>Alq3</td>
<td>0.75</td>
<td>2.2x10⁻⁴</td>
<td>0.21</td>
<td>3x10⁻⁴</td>
</tr>
<tr>
<td>PTCDA</td>
<td>0.42</td>
<td>2.5</td>
<td>0.57</td>
<td>0.57</td>
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</tbody>
</table>

Table 1 the summary on device performance of OTSs with various different EBLs.

In Figure 6, the energy diagram of C_{60} and EBL materials (top, BCP; middle, Alq3; bottom, PTCDA) is shown. The unit of energy level is eV. The broken line between LUMO and HOMO for BCP (top) shows the carrier transport level. However, its energy is incorrect.
Figure 6 shows the energy diagram of C₆₀ and EBL materials[19]. Only PTCDA has lower LUMO than C₆₀. In the use of PTCDA as EBL, however, since the barrier height of electron from PTCDA to Al increases, the extraction efficiency of electron to Alq3 is thought to decrease. Since the LUMOs of Alq3 and BCP are much lower than that of C₆₀, the electron transfer from EBL to C₆₀ is thought to be suppressed. But in fact, the Jsc of OTS with BCP is much higher than that of OTS with Alq3, and the PCE with OTS with BCP is the same order as that of OTS with PTCDA.

Figures 7(a) and 7(b) show the EBL thickness dependence of photoconduction for OTSs with BCP and PTCDA for OTSs with BCP and PTCDA, respectively. The photocurrent of OTS with BCP strongly depends on BCP thickness and it is little observed for OTS with ≥30nm-thick BCP layer. The photocurrent of PTCDA is saturated with PTCDA thickness.

Figures 8a, 8b, 8c and 8d show the EBL thickness dependence of Voc, Jsc, FF and PCE, respectively. Voc is almost constant in spite of increase in both EBL thicknesses. Therefore, Voc is thought to depend on the relationship between

![EBL thickness dependence of photoconduction for OTSs with BCP and PTCDA](image)

Figs. 8 The EBL thickness dependence of Voc (a), Jsc (b), FF (c) and PCE (d) for OTSs with BCP and PTCDA.
materials. Both $i_{sc}$ gradually show an initial increase with EBL thickness. In OTS with BCP, $i_{sc}$ rapidly decreases beyond 20nm and then is much lower than that of OTS without EBL. Both FF are improved until 10nm, but FF of OTS with PTCDA keeps almost constant until 40nm, while FF of OTS with BCP remarkably decreases above 10nm. From these results, the PCE of OTS with PTCDA is saturated with increase of PTCDA thickness and the optimum PCE of OTS with BCP can be obtained at BCP thickness of 15nm.

Despite BCP which has smaller LUMO than $C_{60}$ is used as EBL, electrons in $C_{60}$ can be transported to Al electrode through BCP layer. This electron transfer from $C_{60}$ to Al electrode cannot be explained by energy diagram. However, Forrest’s group reported that localized state in bandgap may be produced as a carrier transport site[4,20]. Therefore, it is suggested that electrons in $C_{60}$ do not move by passing LUMO level of BCP after obtaining an activation energy but do through the localized states to Al electrode. In fact, our BCP thickness dependence is found to support the formation of localized state in bandgap. We have already reported that BCP thin films are very soft and that the surface morphology of BCP thin film is changed by a small atomic force of scanning probe in AFM measurement[19].

On the other hand, the high carrier transportation of PTCDA is thought to cause the thickness independence of photovoltaic properties. PTCBI which has a similar chemical structure shows the thickness independence[21]. The optimum thickness is reported to be 10nm. The PCE of OTS with PTCBI rapidly decreases with PTCBI thickness beyond 10nm. The Voc, $i_{sc}$, and FF of OTS with PTCBI and Al electrode are shown to be 1.15V, 0.125mA/cm², and 0.25, respectively. Figure 8 shows the current density-voltage characteristics of ITO/PTCDA(95nm) or BCP(100nm)/Al. The current of PTCDA thin film is 7 orders higher than that of BCP thin film. The feature that thick EBL thickness does not affect the photovoltaic properties is thought to be similar to NTCDA[22]. However, we do not have an experience with fabrication of 1 μm-thick PTCDA as EBL. In future, we will have to check it in detail.

In the case of BCP, the use of metal with lower workfunction is expected to give higher extraction efficiency of electron to metal electrode because of lower barrier height of electron. However, when LiF/Al electrode is used instead of Al electrode, Voc and $i_{sc}$ decrease [23]. Therefore, the extraction efficiency of electron for OTS with BCP is not improved using metal with lower workfunction. On the other hand, since PTCDA has larger LUMO than BCP, it is preferable Au rather than Al. As a result, it is advantage that stable Au can be used as a metal electrode although Au is an expensive material.

The Voc of OTS is reported to be determined by the energy gap between HOMO of donor molecule and LUMO of acceptor molecule in the optimum case [24,25]. However, since the selections of EBL material and metal will affect the built-in potential in OTS cell, we think that the photovoltaic properties of OTS can be controlled by the combination material condition.

4. Conclusions

We studied the effect of exciton-diffusion blocking material on photovoltaic properties of OTS based on CuPc and $C_{60}$. Consequently, we concluded that PTCDA is better than BCP as EBL in the viewpoint of the stability of film structure and tractability. However, the use of Alq3 as EBL increased Voc but deceased the other parameters.

Acknowledgement

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References