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Effect of Molybdenum Oxide Anode Buffer Layer on the Performance of Inverted Small Molecular Organic Solar Cells

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Abstract

Small molecular organic solar cells (OSCs) with an inverted structure of indium tin oxide (ITO)/cesium carbonate (Cs2CO3)/C60/subphthalocya-nine(SubPc)/molybdenum oxide (MoO3)/Ag were fabricated and studied. By using the equivalent circuit model and transfer matrix theory, the influence of the thickness of MoO3 on the electrical and optical characteristics of the device was systematically investigated. The results indicate that at the optimized thickness of 15 nm, the power conversion efficiency was increased to 0.57 % under AM 1.5 solar illumination at an intensity of 100 mW/cm². The enhancement of the device performance was attributed to the optical spacer effect and the good protection of active layer from Ag diffusion and charge extraction without introducing more series resistance. Finally, the lifetime measurement showed that the stability of OSCs was remarkably enhanced by introducing inverted structure.

Keywords: Anode buffer layer, inverted organic solar cell, MoO3, transfer matrix theory

1. Introduction

Organic solar cells (OSCs) are considered as promising candidates for the next generation solar cells due to their potential low cost, highly tunable optical and physics properties, flexibility, and light weight [1]-[4]. In the past few years, many investigations on operating mechanism, synthesis of multifunctional materials, and novel device structure have been carried out, and the performance of the OSC devices have been greatly improved [5]-[7]. To date, the power conversion efficiency of 5.7 % has been achieved for small molecular devices [8], and 7 % for polymer devices [9].

However, the poor stability is still a major hurdle for practical usage of organic solar cells. One of the
most possible degradation reasons of OSCs is the material instability. For example, fullerene (C60), a commonly used acceptor material in small molecule OSC devices, is well known to be highly sensitive to the ambient air [10]-[11]. Moreover, the conventional structure usually consists of both an acidic poly (3,4-ethylenedioxythiophene):poly (stylene-sulfonate) (PEDOT:PSS) and a low work function metal cathode. The acidic PEDOT:PSS layer has been proven to be detrimental to the ITO electrode [12]-[13] and the low work function metal cathode is easy to react with oxygen and water [14]-[15]. All of them have a negative influence on the device lifetime. In order to improve the ambient stability of devices, inverted structure OSCs were fabricated. In the inverted structure, the ITO substrate, which is covered with a low work function buffer layer instead of hole-conducting PEDOT:PSS layer, acts as the cathode. On the contrary, PEDOT:PSS or certain high work function transition metal oxides (vanadium oxide (V2O5) [16]-[17], molybdenum oxide (MoO3) [16]), covered by a stable metal electrode, such as Ag or Au, serves as the anode. Particularly, the thickness of MoO3 anode buffer layer should be optimized as it has great influences on the electronic and optical properties of inverted OSCs.

In this work, inverted small molecular organic solar cells were fabricated using Cs2CO3 modified ITO as cathode and MoO3 modified Ag as anode. By optimizing the thickness of MoO3 layer, a power conversion efficiency of 0.57 % was achieved. The detailed analysis of the influence of anode buffer layer on the current density-voltage (J-V) characteristics of devices was investigated. Moreover, the series resistance, optical field distribution and absorption spectra were also compared and discussed. Finally, the degradation of devices without encapsulation was investigated, and it was found that the fabrication of OSCs with inverted structure is an effective approach to improve the devices stability.

2. Experimental

The schematic diagram of the inverted small molecule solar cells is shown in Fig. 1 (a), which has a structure of ITO (180 nm)/Cs2CO3 (3 nm)/C60 (40 nm)/SubPc (20 nm)/MoO3 (x nm)/Ag (100 nm). The ITO substrates with a sheet resistance of 10 Ω/sq were cleaned consecutively in ultrasonic baths containing detergent, acetone, ethanol, deionized water for 10 min each, and finally dried by high purity nitrogen blow. Prior to loading into a vacuum chamber, 0.2 wt % Cs2CO3 dissolved in 2-ethoxyethanol was spin coated on the substrates as the cathode. Then, C60, SubPc and MoO3 were used as purchased and deposited sequentially by an OLED-V (Shenyang Vacuum Co.) organic multifunctional vacuum deposition equipment at a rate of 1-2 Å/s at a pressure of 3×10^{-4} Pa. The molecular structures of major materials are shown in Fig. 1 (b). Finally, Ag was evaporated as anode at a rate of ~10 Å/s under a pressure of 3×10^{-3} Pa. The deposition rate and film thickness were in situ monitored using a quartz crystal oscillator mounted to the substrate holder. The active area of organic solar cell, defined by shadow mask, was 12 mm².

A xenon lamp with an illumination power of 100 mW/cm² was used as an illumination source. The current-voltage curves in dark and under illumination were measured with a Keithley 4200 programmable voltage-current source. The absorption spectra were measured with a SHIMATZU UV1700 system. All the measurements were performed in air at ambient circumstance without device encapsulation.

![Fig. 1. (a) Schematic diagram of inverted organic solar cell and (b) Molecular structures of SubPc and C60 in this study.](image)
Fig. 2. Current density-voltage (J-V) characteristics of ITO (180 nm)/Cs2CO3 (3 nm)/C60 (40 nm)/SubPc (20 nm)/MoO3 (x nm)/Ag devices under illumination with an intensity of 100 mW/cm².

Table 1: Photovoltaic performance of cells with different thickness of MoO3 layer. The value is the median of four individual samples for each configuration.

<table>
<thead>
<tr>
<th>Thickness of MoO3 layer (nm)</th>
<th>$V_{OC}$ (V)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>FF</th>
<th>$\eta_p$ (%)</th>
<th>$R_S A$ (Ω cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>0.30</td>
<td>4.55</td>
<td>0.31</td>
<td>0.41</td>
<td>10.98</td>
</tr>
<tr>
<td>5</td>
<td>0.27</td>
<td>5.28</td>
<td>0.29</td>
<td>0.42</td>
<td>10.32</td>
</tr>
<tr>
<td>15</td>
<td>0.39</td>
<td>5.29</td>
<td>0.28</td>
<td>0.57</td>
<td>7.7</td>
</tr>
<tr>
<td>25</td>
<td>0.38</td>
<td>3.81</td>
<td>0.35</td>
<td>0.52</td>
<td>12.04</td>
</tr>
</tbody>
</table>

3. Results and Discussion

3.1. Enhancement of open circuit voltage

Various thicknesses ($x=2.5, 5, 15$ and 25 nm) of MoO3 were inserted between donor and Ag in inverted structure. Fig. 2 shows the Current density-voltage (J-V) characteristics of inverted organic solar cells with various MoO3 thicknesses under illumination with an intensity of 100 mW/cm² and the effect of MoO3 layer thickness on the photovoltaic parameters of devices is shown in Table 1. It can be seen that $V_{OC}$ increases from 0.30 to 0.39 V when the film thickness of MoO3 varies from 2.5 to 15 nm and then saturates for thicker MoO3 layer. It has been reported that the energy difference between the highest occupied molecular orbital (HOMO) of donor material (D) and the lowest unoccupied molecular orbital (LUMO) of acceptor material (A) [18] and the work function difference between two electrodes [19] can both affect the $V_{OC}$. The changes of $V_{OC}$ is consistent with the logarithmical dependence of the work function of MoO3 ($\Phi_B$) on the layer thickness [20]-[21]. The increase in $\Phi_B$ reduces the energy difference between the valence band of MoO3 and the highest occupied molecular orbital (HOMO) of SubPc to form a better contact at the donor/anode interface, which is beneficial to the hole extraction and the enhancement of the $V_{OC}$. However, when the thickness of MoO3 is further increased, the $\Phi_B$ is almost no change and $V_{OC}$ reaches its saturate value correspondingly.

3.2. Effects of Optical Field Distribution on Short Circuit Current

Short circuit current ($J_{SC}$) is slightly increased as the thickness of MoO3 layer increases from 2.5 to 15 nm and then decreased. Particularly, the device with 15 nm thick MoO3 layer has the maximum $J_{SC}$ of 5.28 mA/cm². As well known, $J_{SC}$ is limited by external quantum efficiency ($\eta_{EQE}$) and can be expressed as

$$J_{SC} \approx \frac{q}{\hbar c} \eta_{EQE} (\lambda, 0) S(\lambda) d\lambda$$  \hspace{1cm} (1)$$

Here, the $\eta_{EQE}$ is the product of the efficiencies of following four steps: (1) absorption efficiency of the incident photons ($\eta_A$), (2) the efficiency of photogenerated excitons that diffuse to the charge
separation interface ($\eta_{ED}$), (3) the charge transfer efficiency ($\eta_{CT}$) and (4) the charge collection efficiency ($\eta_{CC}$). In the present devices, $\eta_{ED}$ and $\eta_{CT}$ should be unchanged with different thickness of MoO$_3$ since the thickness of the active layer was the same. Therefore, JSC was influenced by absorption efficiency $\eta_A$ and charge collection efficiency $\eta_{CC}$.

To get more insights of relationship between the absorption efficiency $\eta_A$ of inverted cells and the thickness of

Fig. 3. Normalized electric field $\frac{|E_j(x)|^2}{|E_0(x)|^2}$ distribution of devices with different thickness of MoO$_3$.

MoO$_3$ layer, one-dimensional transfer matrix method [22] was used to simulate the optical field distribution within the devices. The optical electric field ($E_j(x)$) at an arbitrary position inside layer $j$ is given in terms of the electric field of the incident wave ($E_0$) by Eq.(2) [23]

$$E_j(x) = E_j^+(x) + E_j^-(x) = (t_j^+ e^{-ik_j x} + t_j^- e^{ik_j x}) E_0^+$$

where $\xi_j = 2\pi(n_j + i \cdot k_j) / \lambda_j$, $n_j$ and $k_j$ are the optical index and extinction coefficient, $t_j^+ = E_j^+(x) / E_0^+$ and $t_j^- = E_j^-(x) / E_0^-$ are the electric field propagating in positive and negative direction, respectively. Fig. 3 shows the normalized electric field $\frac{|E_j(x)|^2}{|E_0(x)|^2}$ distribution for a single wavelength illumination (590 nm, the maximum absorption peak of SubPc) of the devices. It can be seen that the intensity maximum trends to shift to the center of the active layer when MoO$_3$ thickness increases from 2.5 to 25 nm, however, the relative optical intensity decreases with increase of MoO$_3$ thickness. This implies that the MoO$_3$ layer acts as an optical spacer on $J_{SC}$. By comparing the absorption of SubPc/C$_{60}$ devices without and with 5 nm MoO$_3$ shown in Fig. 4, it is obvious the shape of the spectra has almost no difference, indicating high optical transparency of MoO$_3$. Moreover, the light absorption intensity of SubPc is enhanced while that of C$_{60}$ is reduced, which confirmed the optical spacer effect of MoO$_3$.

Fig. 4. Absorption spectra of inverted OSC devices without and with 15 nm MoO$_3$. Inset: Absorption spectra of SubPc and C$_{60}$.

3.3. Effects of series resistance on short circuit current

$J_{SC}$ is affected not only by the optical spacer effects, but also by the charge collection efficiency
(ηCC), which is reflected by series resistance (RSA). To prevent damage to the donor during Ag deposition, a sufficient thickness of MoO3 buffer layer is required. But increase in film thickness will lead to higher series resistance (RSA), including the bulk resistance of organic materials and electrodes and contact resistance between organic layer and electrodes. By fitting the dark J-V curves we obtain the RSA of devices with different thickness of MoO3. The parameters are summarized in Table 1. It can be seen that a thin (2.5 and 5 nm) layer of MoO3 cannot effectively protect the organic materials from metal diffusion, leading to a high contact resistance between SubPc and Ag electrode. However, when the thickness of MoO3 increased to 25 nm, the increase in bulk resistance of MoO3 becomes dominant. The combined effects of reduced contact resistance and increased bulk resistance as increasing the thickness of MoO3 results in a minimum RSA = 7.7 Ω cm^2. This is in good agreement with the variation of JSC.

As shown in Table 1, the maximum fill factor (FF) of 0.35 has been achieved in the device with 25 nm thick MoO3 layer. It may be attributed to the small electron leakage current owning to the increase in ФB. Finally, the maximum ηp of 0.57 % was achieved with the optimal thickness of 15 nm MoO3, revealing a good absorption, a good protection of active layer and a good charge transport. Beside power conversion efficiency, the stability of OSCs has been recognized as another important area of research in both academic and commercial settings. By comparing the lifetime of inverted and conventional devices, the stability of inverted structure is better than that of the conventional devices. The in-depth study of the devices stability will be carried out in the following work.

4. Conclusions

In summary, the effect of MoO3 layer thickness on the performance of inverted organic solar cells was analyzed by transfer matrix theory and equivalent circuit model. It was found that with the increasing of thickness of MoO3, VOC is enhanced due to the increase in work function difference between two electrodes. In addition, the device with 15 nm thick MoO3 layer has the maximum JSC of 5.28 mA/cm^2, suggesting a balance between the protection of active layer, charge collection, charge transport, and optical spacer effect. As a result, the power conversion efficiency of 0.57 % has been achieved at the optimized thickness of 15 nm, which play an important role in forming good interface contact between active layer and metal electrode. The enhancement of device stability indicates that inverted structure gives a promising way for fabrication of high performance organic solar cells if the power conversion efficiency is as high as the conventional structure.

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