Improving the efficiency of organic photovoltaic cells by introducing an ultrathin modification layer with a strong dipole moment

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A method to improve the efficiency of organic photovoltaic cells through inclusion of an ultrathin modification layer of Al_2O_3 or LiF sandwiched between poly(3,4-ethylenedioxythiophene)-polystyrene sulfonic acid (PEDOT:PSS) and indium tin oxide layers is developed. Because of the strong dipole moments of LiF and Al_2O_3 , either can enhance the built-in electric field, which increases the probability of the carriers reaching the corresponding electrode. In addition, the low work function of PEDOT:PSS can decrease the energy barrier for carrier transmission. A 21.7% improvement in the power conversion efficiency of experimental devices was achieved, mainly because the short circuit current was enhanced by almost 30%.

solar cell, modification layer, work function, photovoltaics

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Organic photovoltaic (OPV) devices have attracted tremendous interest because of their inherent advantages including low cost, large area, light weight and flexibility. The power conversion efficiency (PCE) of such devices has been reported to reach 6%–7% [1,2]. However, the efficiency of polymer solar cells is still lower than what is needed for practical application on a large scale. Besides significant effort focused on the bulk heterojunction (BHJ) photoactive layer, the properties of the interfaces between the photoactive layer and electrode or underlying buffer layer, e.g., Ohmic contact, interfacial cohesion, or charge traps, are of fundamental importance to the performance of OPV devices. This is because they can significantly affect the charge transport and collection processes as well as the built-in potential [3]. Therefore, control of these interfaces is essential to improve the PCE of OPV cells.

Poly(3,4-ethylenedioxythiophene)-polystyrene sulfonic acid (PEDOT:PSS) is one of the most popular anode modification materials because it can effectively improve the inter-

face between indium tin oxide (ITO) and the photoactive layer, significantly enhancing both the short-circuit current (J_{sc}) and the fill factor (FF). However, the ITO/PEDOT:PSS interface is not stable and chemical reactions finally result in degradation of the device performance [4]. Recently, Yoon et al. [5] introduced a plasma-oxidized silver layer with a thickness of 1 nm on top of ITO in poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM)-based BHJ solar cells, and improvements in J_{sc} and PCE of nearly 17.6% and 9.1%, respectively, were achieved. In this article, Al_2O_3 and LiF layers with a thickness of 1 nm are used to modify the interface between ITO and PEDOT:PSS. Al_2O_3 and LiF possess strong dipole moments, which can lower the work function (WF) of the anode, enhancing the built-in electric field and decreasing the energy barrier for charge carrier transmission to significantly improve both J_{sc} and PCE.

1 Experimental

PEDOT:PSS, P3HT and PCBM were purchased from Lu-

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minescence Technology Corporation. A 1 nm-thick layer of Al_2O_3 was formed on a clean ITO-coated substrate by the following two steps. First, a 1 nm-thick Al film was thermally evaporated on the ITO surface at 1.0×10^{-3} Pa. Second, the Al film, which actually oxidized to AlO_x , was oxidized in air at 150°C for more than 1 h to form Al_2O_3 . In contrast, the LiF layer was directly formed on the ITO substrate by thermal evaporation at 3.4×10^{-4} Pa. A film thickness detector (Taiyao Vacuum Technology FTM-V) was used to monitor the evaporation process, and the final thickness was determined by a profilometer (Veeco Dektak 150).

The anode substrate was prepared by spin-casting a thin layer of PEDOT:PSS on the Al_2O_3 or LiF-coated ITO surface. This was followed by spin-casting of the active layer of P3HT:PCBM (dissolved in chloroform with a weight ratio of 1:1, 20 mg/mL). LiF and Al cathodes were then deposited via thermal evaporation through a shadow mask at 3.4×10^{-4} Pa, giving an active device area of 0.16 cm^2 . Finally, thermal annealing was performed at 130°C for 5 min. The final structure of the experimental cells was ITO/LiF (or Al_2O_3 , 1 nm)/PEDOT:PSS(35 ± 3 nm)/P3HT:PCBM(130 ± 5 nm)/Al(100 nm).

In our experiments, control devices with the structure ITO/PEDOT:PSS(35 ± 3 nm)/P3HT:PCBM(130 ± 5 nm)/Al(100 nm) were also fabricated and tested. To minimize variation in the results that might arise due to different processing conditions, OPVs with different anode structures were fabricated in the same batch.

2 Results and discussion

Figure 1 shows the current density-voltage (J - V) characteristics of the OPVs with ITO anodes with different surface modifications under AM 1.5 G filtered illumination from a calibrated solar simulator with an overall intensity of 100 mW/cm^2 . The extracted device parameters are summarized in Table 1. The control cell exhibits a PCE of 2.76% with a relatively high FF of 51.6%. The open circuit voltage (V_{oc}) and J_{sc} are 0.60 V and 8.89 mA/cm^2 , respectively. The J - V curves of the cells containing Al_2O_3 and LiF layers almost overlap, and an evident enhancement in J_{sc} is observed compared to the control cell. For the LiF-modified cell, J_{sc} is improved by 27% from 8.89 to 11.3 mA/cm^2 . In contrast, the Al_2O_3 -modified cell exhibits a 29% enhancement in J_{sc} from 8.89 to 11.5 mA/cm^2 . Both cells enhance the PCE by 21.7% from 2.76% to 3.36%. However, both Al_2O_3 and LiF lead to a decreased FF. Because Al_2O_3 and LiF both have a high resistance, this phenomenon can be explained by the higher series resistance of the OPV cells containing an additional layer. It also can be seen that the V_{oc} of the cells is almost the same (~ 0.6 V). This is because V_{oc} is primarily determined by the difference in WF between the lowest unoccupied molecular orbital (LUMO) of the acceptor and highest occupied molecular orbital (HOMO) of the donor

Figure 1 J - V characteristics of OPV devices containing different anodic modifications under illumination.

Table 1 Performance parameters of OPV cells with different anode structures

	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
Control cell	8.89	0.60	51.6	2.76
ITO/LiF/PEDOT:PSS	11.3	0.58	51.2	3.36
ITO/ Al_2O_3 /PEDOT:PSS	11.5	0.58	50.4	3.36

[6,7], and consequently the influence of the electrode WF on V_{oc} is negligible [8].

Figure 2 shows the effects of modification layers of different thickness on the performance of the OPV cells. As mentioned above, LiF and Al_2O_3 exhibits similar features as an anodic modification layer, so here we only discuss Al_2O_3 . Figure 2 shows that there is an obvious deterioration in the performance of the OPV cells as the thickness of the Al_2O_3 layer is increased from 1 to 5 nm. The optimal thickness of Al_2O_3 is expected to be 1 nm. As the thickness of Al_2O_3 increases, V_{oc} decreases slightly compared to J_{sc} , which drops sharply from 11.5 to 5.33 mA/cm^2 because of the

Figure 2 J - V characteristics plotted to illustrate the effects of different thicknesses of Al_2O_3 on the photovoltaic performance of the experimental cells.

strong insulating character of Al_2O_3 [9]. In addition, because the Al_2O_3 layer is oxidized from Al, any unoxidized Al will force the OPV cell to invert, causing the performance of the OPV cell to deteriorate abruptly.

To clarify the origin of the enhancement in J_{sc} in the experimental solar cells, optical transmission spectra for the experimental and control cells without an Al electrode were measured from 300 to 800 nm by an ultraviolet-visible-infrared spectrometer. As illustrated in Figure 3, the transmission spectra for the experimental and control cells are very similar with only a slight difference at around 400 nm. This small difference could not cause the almost 30% enhancement in current observed in our experiment. Moreover, the coverage of the modification layer on ITO is very low with the formation of small islands, so optical-field redistribution is unlikely to explain the enhancement in J_{sc} . Therefore, reason for the improvement in J_{sc} is increased efficiency of carrier collection at the electrode.

Figure 4 shows the energy band diagram for the experimental OPV cells, which provides evidence for a possible mechanism for the influence of Al_2O_3 and LiF layers on the cell performance. Because of the strong dipole moment of Al_2O_3 and LiF, even a monolayer of these materials will induce a mass of interfacial dipoles that can lower the WF of PEDOT:PSS, which really functions as the anode. On the one hand, the lowered WF of PEDOT:PSS so it approaches the HOMO of the donor material can help hole carriers to transfer to the anode more easily because the energy barrier is decreased [5]. On the other hand, it can effectively enhance the built-in electric field of the OPV cells [9,10]. This is because the built-in electric field is primarily determined by the difference in WF between the anode and cathode materials when the thickness of the photoactive layer is the same. In addition, the chemical structure at the interfaces between the Al cathode and the photoactive layer may cause the WF of Al to be larger than 4.2 eV because of the formation of Al-O bonds at Al/polymer interface caused by post-annealing [11]. Therefore, the built-in electric field in a

Figure 3 Transmission spectra of experimental and control cells without an Al electrode.

Figure 4 Energy band diagram for the experimental OPV cells.

device can be improved by addition of a thin layer of a material with a strong dipole moment.

In the P3HT:PCBM blended layer, carriers may recombine if the transport time is longer than the carrier lifetime. The built-in electric field, which is directed from the cathode towards the anode, is the driving force for holes and electrons moving towards each corresponding electrode. Thus, a larger internal electric field can help charge carriers reach to each electrode in a shorter time, which eventually generates a higher efficiency of charge carrier collection. As a consequence, both J_{sc} and PCE are obviously improved.

3 Conclusion

In summary, a method to modify the interface between PEDOT:PSS and the anode was developed because this interface is not stable, which can result in degradation of device performance. An obvious improvement in PCE for OPV devices was achieved, mainly because of an enhanced J_{sc} , by using a thin film of Al_2O_3 or LiF between ITO and PEDOT:PSS. Both LiF and Al_2O_3 possess a strong dipole moment, so an enhanced built-in electric field is expected to be the main reason for the improved J_{sc} . Furthermore, the decreased energy barrier between the anode and HOMO of the donor material can also increase J_{sc} . Our results match well with the belief that V_{oc} is primarily determined by the offset between the LUMO of the acceptor and HOMO of the donor in OPV cells.

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