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Description	

Increase in Open-Circuit Voltage and Improved Stability of Organic Solar Cells by Inserting a Molybdenum Trioxide Buffer Layer

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ABSTRACT

We report an increase in open-circuit voltage (V_{oc}) by inserting an MoO_3 layer on ITO substrate to improve built-in potential of organic solar cells (OSCs). In the OSCs using 5,10,15,20-tetraphenylporphyrine (H_2TPP) as p-type material and C_{60} as n-type material, the V_{oc} effectively increased from 0.57 to 0.97 V with increasing MoO_3 thickness. The obtained highest V_{oc} (0.97 V) is consistent with the theoretical value estimated from the energy difference between the LUMO (-4.50 eV) of C_{60} and the HOMO (-5.50 eV) of H_2TPP layer. Importantly, the enhancement in the V_{oc} was achieved without affecting the short-circuit current density (J_{sc}) and the fill-factor (FF). Thus, the power conversion efficiency of the device increased linearly from 1.24% to 1.88%. We also demonstrated that a MoO_3 buffer layer enhances the stability of OSCs after photo-irradiation. We have investigated the stability of OSCs using H_2TPP and N,N' -di(1-naphthyl)- N,N' -diphenylbenzidine as p-type layer. Both devices with MoO_3 layer showed improved stability. These results clearly suggest that the interface between ITO and p-type layer affects device stability.

INTRODUCTION

In recent years, organic solar cells have attracted much attention as a new inexpensive renewable energy source. The increase in power conversion efficiency (η_p) and the improvement of stability of organic solar cells are key issues in the development of organic solar cells. The η_p of the solar cells depends on three device parameters, such as the open-circuit voltage (V_{oc}), the short-circuit current density (J_{sc}), and the fill factor (FF). Among those parameters, the J_{sc} can be improved by the use of bulk heterojunctions (e.g., the composite of p-type and n-type materials) as an active layer in both polymer [1] and small molecule-based solar cells. However, there is no enhancement effect on the V_{oc} by the use of bulk heterojunction structure. For the further improvement of η_p , it is essential to enhance V_{oc} , while keeping the corresponding J_{sc} . It has been shown that the V_{oc} depends on the energy difference between the lowest unoccupied molecular orbital (LUMO) of the electron acceptor material and the highest occupied molecular orbital (HOMO) of the electron donor material [2–4]. Recently, Mutolo et al. reported that V_{oc} of the solar cells increased in double heterojunction solar cells composed of boron subphthalocyanine chloride (HOMO level= -5.60 eV) and C_{60} (LUMO level= -4.50 eV) [5]. We have reported that V_{oc} increased by inserting a thin layer of CuPc and Zn-phthalocyanine (ZnPc) with higher HOMO level (-5.1 eV) at the interface of pentacene (HOMO= -5.0 eV) and C_{60} [6].

In this study, we found that a modification of ITO surface by a high work function metal oxide (molybdenum trioxide MoO_3) is very effective in increasing V_{oc} . We demonstrate the systematic control of V_{oc} as a function of the film thickness of MoO_3 buffer layer in organic solar

cells. The open-circuit voltage increased from 0.57 to 0.97 V as the thickness of MoO₃ film increased from 0 to 50 nm in the device structure of indium-tin-oxide ITO/ MoO₃ (x nm) / 5,10,15,20-tetraphenylporphine (H₂TPP, 10 nm) /C₆₀ (40 nm)/bathocuproine (10 nm) /Ag (100 nm). The values between V_{oc} and the ionization potential of MoO₃ (x nm) on ITO exhibit a linear relationship, where the work function values change from 4.92 to 5.92 eV with increasing x from 0 to 50 nm. We also found that a MoO₃ buffer layer enhances the stability of organic solar cells under photo-irradiation. We have investigated OSCs with the structure of ITO/ MoO₃ (0 or 20 nm)/ p-type layer/ C₆₀ (40 nm)/ Bathocuproine (BCP) (10 nm)/ Ag (100), where we use H₂TPP and *N,N'*-di(1-naphthyl)-*N,N'*-diphenylbenzidine (α -NPD) as p-type layer. Without MoO₃ layer, the devices showed a dramatic decrease in initial η_p under the same measurement conditions. However, both devices with MoO₃ layer showed excellent stability under the photo-irradiation. These results clearly indicate that the degradation occurs at the interface between ITO and p-type layer.

EXPERIMENTAL DETAILS

The device structure studied in this work is ITO/MoO₃ (0, 1, 5, 10, 20, and 50 nm) /p-type layer (10 nm) /C₆₀ (40 nm) /bathocuproine (BCP) (10 nm) /Ag (100 nm). (Fig. 1 (a)), where H₂TPP and α -NPD are used as p-type layers, C₆₀ is used as n-type layer, and BCP is used as an exciton blocking layer. The devices were fabricated in the following ways: Glass substrates coated with an ITO layer were cleaned using ultrasonication in acetone, followed by ultrasonication in detergent, pure water, and isopropanol. The substrates were treated by UV ozone for 30 min and then annealed at 150°C for 10 min in air. MoO₃ and organic layers were successively vacuum-deposited under a base pressure of 10⁻⁶ Torr on the cleaned ITO layer. To complete the OSC structures, an Ag layer was vacuum-deposited through a shadow mask to define the active area of the devices to be 4 mm².

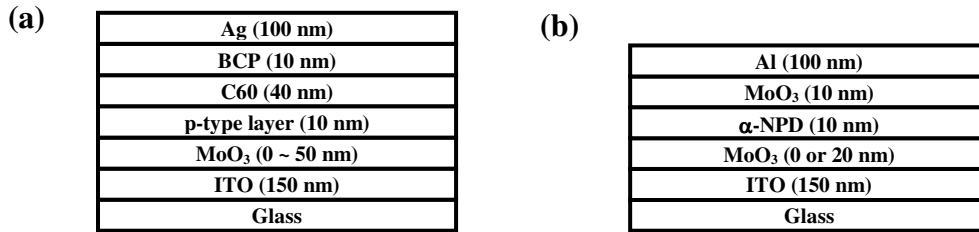


Figure 1. Schematics of structures of (a); organic solar cells and (b); hole-only devices.

To investigate the degradation mechanisms of the devices, the temporal change of the device characteristics after photo-irradiation was compared in the devices ITO/MoO₃ (0 and 20 nm) /p-type layer (10 nm)/C₆₀ (40 nm)/BCP (10 nm)/Ag (100 nm). We also fabricated hole-only devices with a glass substrate/ITO (150 nm)/MoO₃ (0 or 20 nm)/ α -NPD (70 nm)/MoO₃ (10 nm)/Al (100 nm) structure. In the hole-only structures, we used a high-work-function MoO₃ layer (-5.70 eV) at the α -NPD/Al interfaces to prevent injection of electrons from the cathode. The deposition rates were 0.03 nm/s for MoO₃, H₂TPP, α -NPD, and C₆₀, 0.1 nm/s for BCP, and 0.3 nm/s for Ag and Al. H₂TPP (99.0%) and C₆₀ (99.5%) were purchased from Aldrich and MTR, Ltd., respectively. H₂TPP (Fig. 3) and C₆₀ were sublimed in our laboratory before use. High purity BCP was provided by Nippon Steel Chemical Co., Ltd. and was used without further purification.

DISCUSSION

Dependence of V_{oc} on the thickness of MoO_3 layer

Figure 2a shows the current density-voltage (J-V) characteristics as a function of the film thickness of MoO_3 . The V_{oc} drastically increased from 0.57 V to 0.97 V as the MoO_3 film thickness increased from 0 nm to 50 nm. The value of 0.97 V is close to the maximum value estimated from the energy difference between the LUMO (-4.50 eV) of C_{60} layer and the HOMO (-5.50 eV) of H_2TPP layer. The linear relationship between the work function of ITO/ MoO_3 (x nm) and V_{oc} suggests that the observed increase in V_{oc} is the consequence of the enhancement of built-in potential generated between ITO/ MoO_3 and Ag.

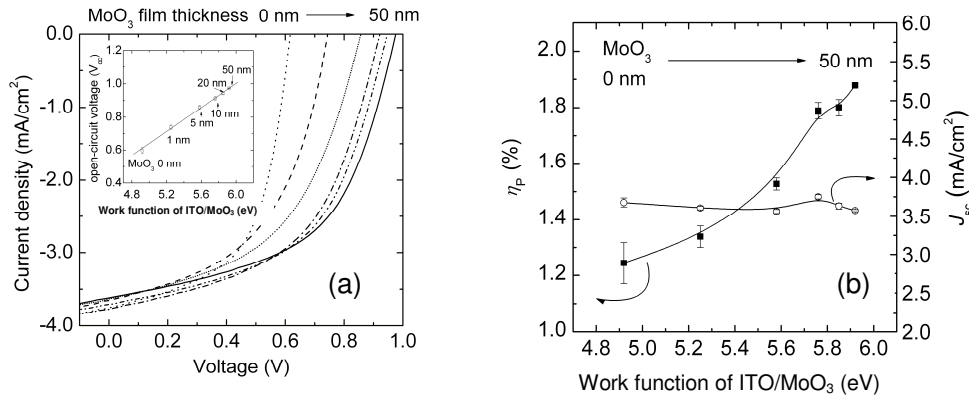


Figure 2. (a) Current density-voltage characteristics of ITO/ H_2TPP (10 nm)/ C_{60} (40 nm)/BCP (10 nm)/Ag (100 nm) under simulated AM1.5 solar illumination (100 mW/cm²). Inset: V_{oc} versus work function of ITO/ MoO_3 where the film thickness of MoO_3 was changed to 0, 1, 5, 10, 20, 50 nm. (b) The power conversion efficiency (η_p) and the short-circuit current density (J_{sc}) of the devices as a function of the work function of ITO/ MoO_3 .

Figure 2b shows the η_p and J_{sc} as a function of the work function of the ITO/ MoO_3 . The η_p of the device with MoO_3 layer increased from 1.24 % to 1.88% with increasing film thickness of MoO_3 . On the other hand, the J_{sc} was independent of the film thickness of MoO_3 . The FF of the device was also unchanged in the thickness range of 0 nm to 50 nm. (Data not shown) Thus, the enhancement of η_p is exclusively attributed to increase of V_{oc} by changing the film thickness of MoO_3 . Since the enhancement of V_{oc} does not affect other device parameters, further improvement of η_p may be achieved in the devices with a bulk heterojunction interface.

According to a metal-insulator-metal model and a p - n junction model, the origin of V_{oc} can be explained in two ways: (1) the difference in energy level between work functions of an anode and a cathode and (2) the difference in energy level between a HOMO of a p -type material and a LUMO of a n -type material [2-4]. Since depositing the MoO_3 on the ITO surface increases the work functions of the anodes [7], the increase in the V_{oc} is attributable to an increase in work function of the ITO/ MoO_3 anodes.

Effect of MoO₃ buffer layer on device stability

Figure 3 shows the changes of the J_{sc} , the V_{oc} , the FF , and the η_p for the OSCs with H₂TPP as a function of light irradiation time. While the OSCs with no buffer layer were drastically degraded with operational time, inserting the MoO₃ between the ITO and the H₂TPP suppressed the degradation. Although the η_p of the OSCs without the MoO₃ decreased to 37 % of its initial value after 60 min, the η_p of the OSC with the MoO₃ maintained 66 % of the initial value.

In addition to the H₂TPP OSCs, we investigated the stability of the α -NPD OSCs (Fig. 4). The η_p of the α -NPD OSC with the MoO₃ maintained 100 % of the initial value, while the α -NPD device without the MoO₃ decreased to 46 % of its initial value. In this device, we observed a slight increase in J_{sc} , FF , and η_p of the OSCs with MoO₃ after light irradiation. The origin of the increase in these parameters is not clear. As described later, we observed a similar increase of the dark current density in the hole-only α -NPD devices after light irradiation. One of the possible explanations of the increase in the J_{sc} might be a heating effect due to light irradiation [4]. These results clearly indicate that inserting the MoO₃ layer markedly improved OSC stability, and suggests that the degradation of the OSCs mainly occurs at the ITO/ p -type layer interfaces (*Vide infra*).

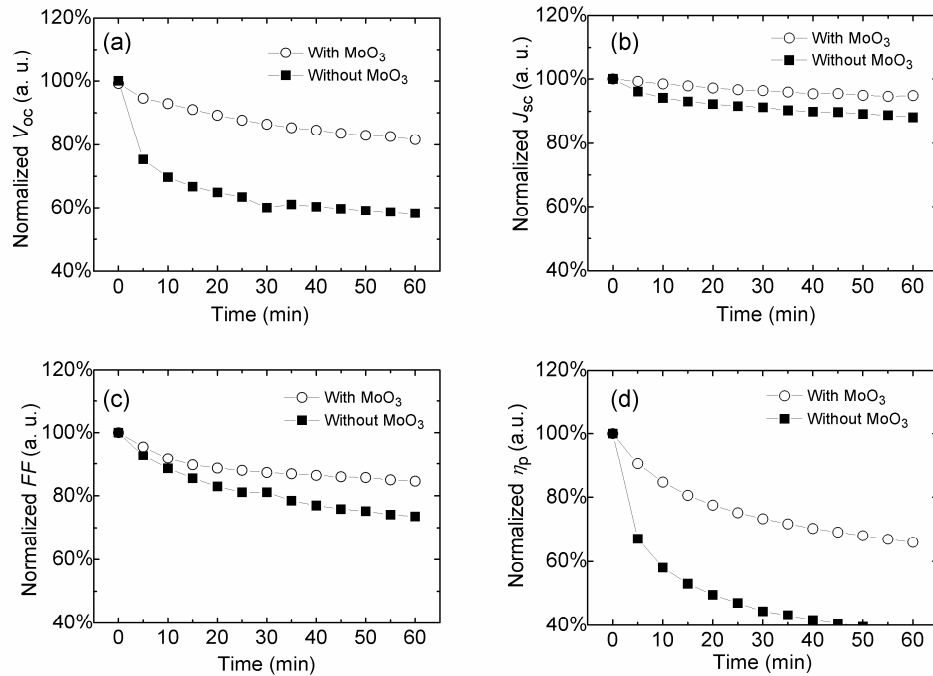


Figure 3. Changes of (a) V_{oc} , (b) J_{sc} , (c) FF , and (d) η_p for H₂TPP OSCs with and without MoO₃ buffer layer under light irradiation.

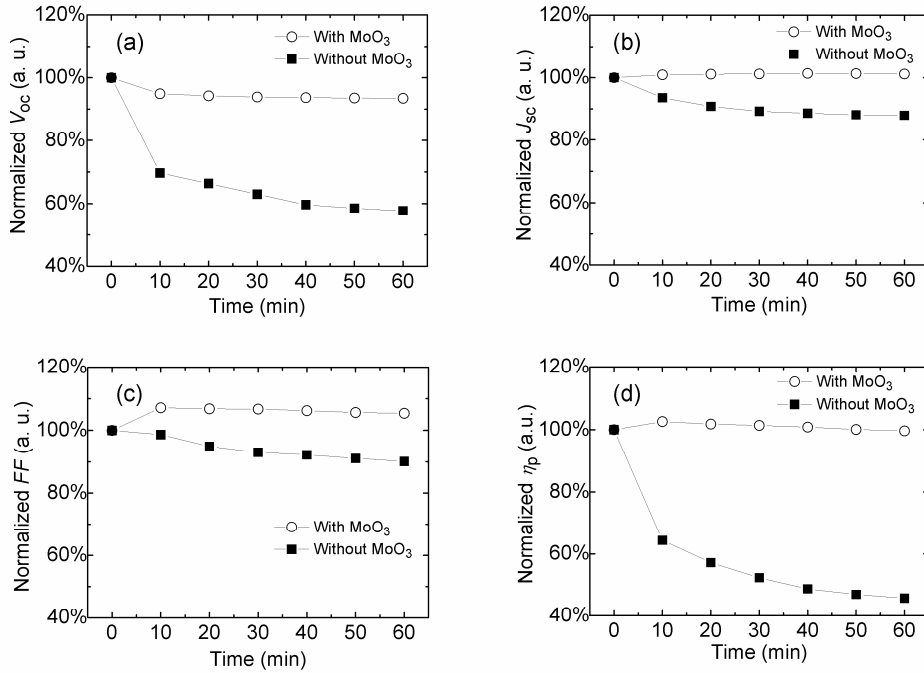


Figure 4. Changes of (a) V_{oc} , (b) J_{sc} , (c) FF , and (d) η_p for α -NPD OSCs with and without MoO₃ buffer layer under light irradiation.

To get insights about the anode/ α -NPD interfacial degradation, we fabricated the hole-only α -NPD devices. Figure 5 shows the changes of the J - V characteristics of the hole-only devices during light irradiation. The hole-only α -NPD device without the MoO₃ layer was markedly degraded by light irradiation. The current density at the forward bias, where ITO electrode was biased positively, significantly dropped to 0.7% of its initial value, while the current density at the reverse bias was unchanged. On the other hand, we observed no degradation in the device with the MoO₃ layer, in either forward or reverse bias directions, after light irradiation. Instead, we observed a slight increase in current density due to light irradiation.

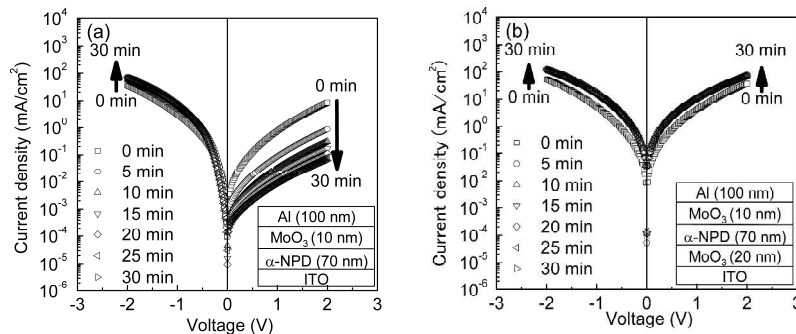


Figure 5. Change of J - V characteristics of α -NPD hole-only devices (a) without MoO₃ and (b) with MoO₃ under light irradiation. Insets show structures of hole-only devices.

These results suggest that the decrease in the current density in the forward bias region is not caused by an increase in resistance of the α -NPD bulk layer, but is caused by an increase in hole injection barrier height between the ITO and the α -NPD after light irradiation. In other words, the relative position of the HOMO level of the α -NPD to the Fermi level of the ITO might be shifted in the direction of increasing the hole injection barrier height after light irradiation. We attribute the shift of the relative energy level position to a vacuum level shift caused by a chemical reaction between the ITO and the α -NPD [8,9]. Moreover, the difference in Fermi levels of ITO and Ag are probably reduced by the vacuum level shift. In this case, the built-in potential of the OSCs decreases, resulting in the reduction of the V_{oc} . The insertion of the MoO_3 would prevent this reduction and, therefore, enhance device stability.

CONCLUSIONS

In conclusion, we have demonstrated that the V_{oc} increased from 0.57 to 0.97 V with the MoO_3 film thickness, due to enhanced built-in potential with increasing MoO_3 thickness. The highest V_{oc} (0.97 V) is consistent with the theoretical value estimated from the energy difference between the LUMO of C_{60} layer and the HOMO of H_2TPP layer. We have found that the OSC degradation occurs at the ITO and α -NPD interface under light irradiation, and that the degradation can be prevented by inserting a MoO_3 layer between ITO and the p-type layer. These findings would be beneficial for developing high performance organic solar cells.

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