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## 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  $\text{MoO}_3$  layer on ITO substrate to improve built-in potential of organic solar cells (OSCs). In the OSCs using 5,10,15,20-tetraphenylporphyrine ( $\text{H}_2\text{TPP}$ ) as p-type material and  $\text{C}_{60}$  as n-type material, the  $V_{oc}$  effectively increased from 0.57 to 0.97 V with increasing  $\text{MoO}_3$  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  $\text{C}_{60}$  and the HOMO (-5.50 eV) of  $\text{H}_2\text{TPP}$  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  $\text{MoO}_3$  buffer layer enhances the stability of OSCs after photo-irradiation. We have investigated the stability of OSCs using  $\text{H}_2\text{TPP}$  and  $N,N'$ -di(1-naphthyl)- $N,N'$ -diphenylbenzidine as p-type layer. Both devices with  $\text{MoO}_3$  layer showed improved stability. These results clearly suggest that the interface between ITO and p-type layer affects device stability.

### INTRODUCTION

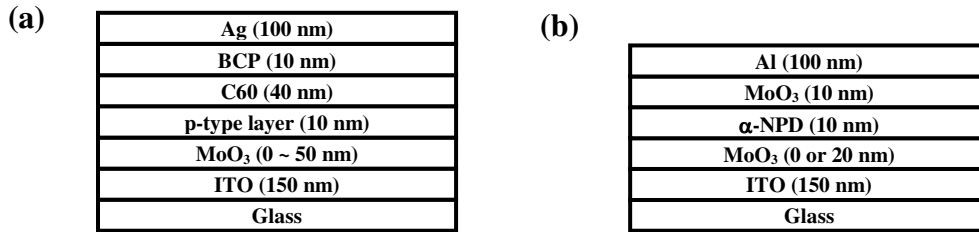
In recent years, organic solar cells have attracted much attention as a new inexpensive renewable energy source. The increase in power conversion efficiency ( $\eta_p$ ) and the improvement of stability of organic solar cells are key issues in the development of organic solar cells. The  $\eta_p$  of 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  $\eta_p$ , 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  $\text{C}_{60}$  (LUMO level= -4.50 eV) [5]. We have reported that  $V_{oc}$  increased by inserting a thin layer of  $\text{CuPc}$  and  $\text{Zn-phthalocyanine}$  ( $\text{ZnPc}$ ) with higher HOMO level (-5.1 eV) at the interface of pentacene (HOMO= -5.0 eV) and  $\text{C}_{60}$  [6].

In this study, we found that a modification of ITO surface by a high work function metal oxide (molybdenum trioxide  $\text{MoO}_3$ ) is very effective in increasing  $V_{oc}$ . We demonstrate the systematic control of  $V_{oc}$  as a function of the film thickness of  $\text{MoO}_3$  buffer layer in organic solar

cells. The open-circuit voltage increased from 0.57 to 0.97 V as the thickness of MoO<sub>3</sub> film increased from 0 to 50 nm in the device structure of indium-tin-oxide ITO/ MoO<sub>3</sub> (x nm) / 5,10,15,20-tetraphenylporphine (H<sub>2</sub>TPP, 10 nm) /C<sub>60</sub> (40 nm)/bathocuproine (10 nm) /Ag (100 nm). The values between  $V_{oc}$  and the ionization potential of MoO<sub>3</sub> (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 MoO<sub>3</sub> buffer layer enhances the stability of organic solar cells under photo-irradiation. We have investigated OSCs with the structure of ITO/ MoO<sub>3</sub> (0 or 20 nm)/ p-type layer/ C<sub>60</sub> (40 nm)/ Bathocuproine (BCP) (10 nm)/ Ag (100), where we use H<sub>2</sub>TPP and *N,N'*-di(1-naphthyl)-*N,N'*-diphenylbenzidine ( $\alpha$ -NPD) as p-type layer. Without MoO<sub>3</sub> layer, the devices showed a dramatic decrease in initial  $\eta_p$  under the same measurement conditions. However, both devices with MoO<sub>3</sub> 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/MoO<sub>3</sub> (0, 1, 5, 10, 20, and 50 nm) /p-type layer (10 nm) /C<sub>60</sub> (40 nm) /bathocuproine (BCP) (10 nm) /Ag (100 nm). (Fig. 1 (a)), where H<sub>2</sub>TPP and  $\alpha$ -NPD are used as p-type layers, C<sub>60</sub> 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. MoO<sub>3</sub> and organic layers were successively vacuum-deposited under a base pressure of 10<sup>-6</sup> 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 mm<sup>2</sup>.



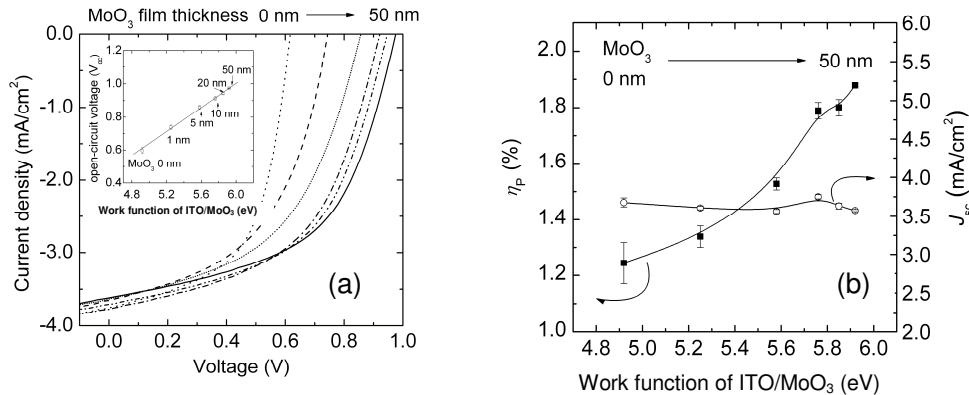
**Figure 1.** Schematics of structures of (a); organic solar cells and (b); hole-only devices.

To investigate the degradation mechanisms of the devices, the temporal change of the device characteristics after photo-irradiation was compared in the devices ITO/MoO<sub>3</sub> (0 and 20 nm) /p-type layer (10 nm)/C<sub>60</sub> (40 nm)/BCP (10 nm)/Ag (100 nm). We also fabricated hole-only devices with a glass substrate/ITO (150 nm)/MoO<sub>3</sub> (0 or 20 nm)/ $\alpha$ -NPD (70 nm)/MoO<sub>3</sub> (10 nm)/Al (100 nm) structure. In the hole-only structures, we used a high-work-function MoO<sub>3</sub> layer (-5.70 eV) at the  $\alpha$ -NPD/Al interfaces to prevent injection of electrons from the cathode. The deposition rates were 0.03 nm/s for MoO<sub>3</sub>, H<sub>2</sub>TPP,  $\alpha$ -NPD, and C<sub>60</sub>, 0.1 nm/s for BCP, and 0.3 nm/s for Ag and Al. H<sub>2</sub>TPP (99.0%) and C<sub>60</sub> (99.5%) were purchased from Aldrich and MTR, Ltd., respectively. H<sub>2</sub>TPP (Fig. 3) and C<sub>60</sub> 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 $\text{MoO}_3$ layer

Figure 2a shows the current density-voltage (J-V) characteristics as a function of the film thickness of  $\text{MoO}_3$ . The  $V_{oc}$  drastically increased from 0.57 V to 0.97 V as the  $\text{MoO}_3$  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  $\text{C}_{60}$  layer and the HOMO (-5.50 eV) of  $\text{H}_2\text{TPP}$  layer. The linear relationship between the work function of ITO/ $\text{MoO}_3$  (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/ $\text{MoO}_3$  and Ag.



**Figure 2.** (a) Current density-voltage characteristics of ITO/ $\text{H}_2\text{TPP}$  (10 nm)/ $\text{C}_{60}$  (40 nm)/BCP (10 nm)/Ag (100 nm) under simulated AM1.5 solar illumination (100 mW/cm<sup>2</sup>). Inset:  $V_{oc}$  versus work function of ITO/ $\text{MoO}_3$  where the film thickness of  $\text{MoO}_3$  was changed to 0, 1, 5, 10, 20, 50 nm. (b) The power conversion efficiency ( $\eta_p$ ) and the short-circuit current density ( $J_{sc}$ ) of the devices as a function of the work function of ITO/ $\text{MoO}_3$ .

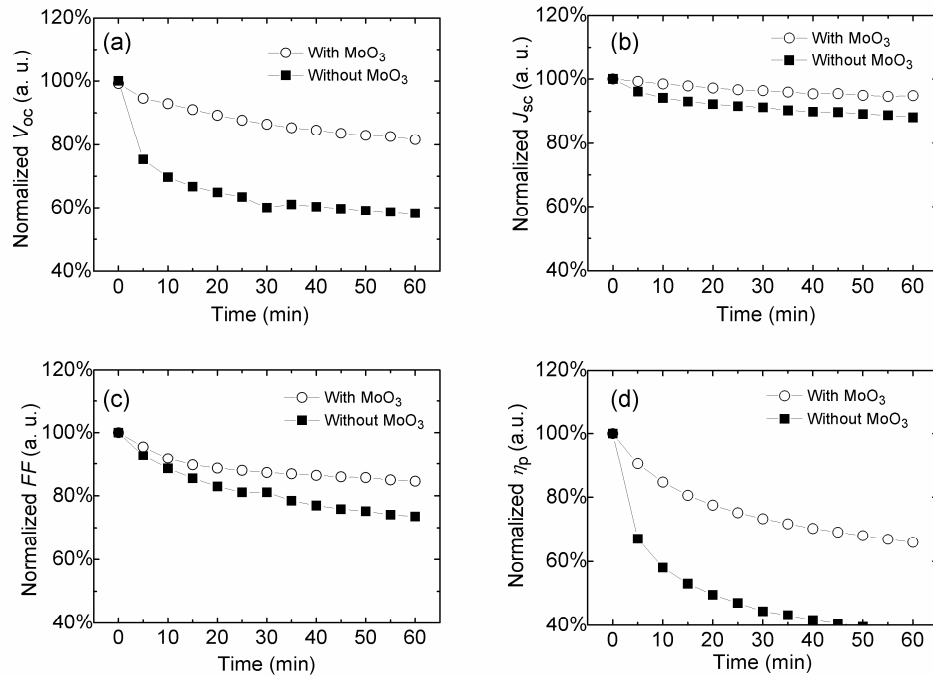
Figure 2b shows the  $\eta_p$  and  $J_{sc}$  as a function of the work function of the ITO/ $\text{MoO}_3$ . The  $\eta_p$  of the device with  $\text{MoO}_3$  layer increased from 1.24 % to 1.88% with increasing film thickness of  $\text{MoO}_3$ . On the other hand, the  $J_{sc}$  was independent of the film thickness of  $\text{MoO}_3$ . 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  $\eta_p$  is exclusively attributed to increase of  $V_{oc}$  by changing the film thickness of  $\text{MoO}_3$ . Since the enhancement of  $V_{oc}$  does not affect other device parameters, further improvement of  $\eta_p$  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  $\text{MoO}_3$  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/ $\text{MoO}_3$  anodes.

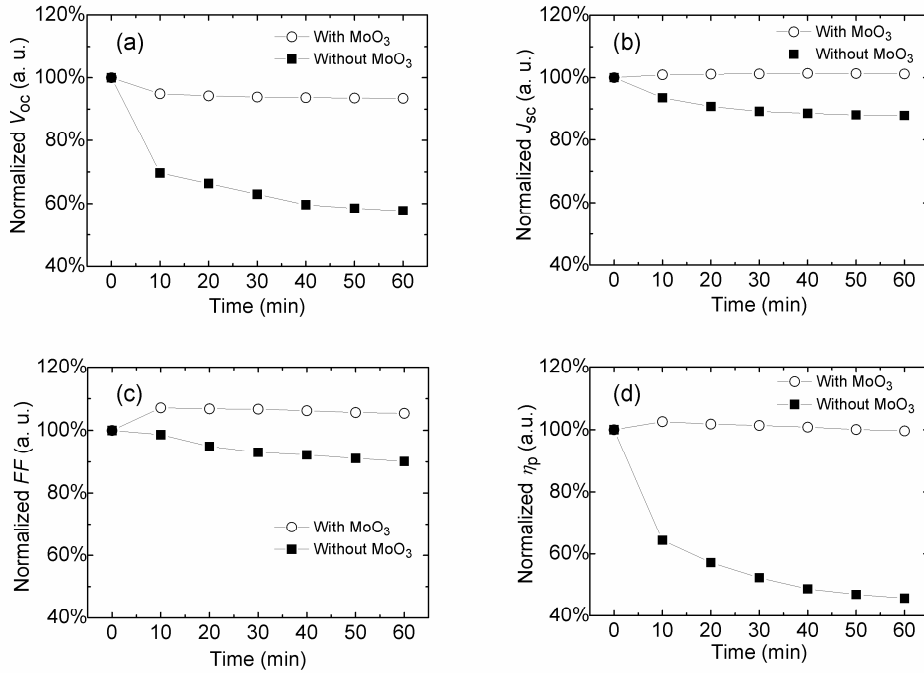
### Effect of MoO<sub>3</sub> buffer layer on device stability

Figure 3 shows the changes of the  $J_{sc}$ , the  $V_{oc}$ , the  $FF$ , and the  $\eta_p$  for the OSCs with H<sub>2</sub>TPP as a function of light irradiation time. While the OSCs with no buffer layer were drastically degraded with operational time, inserting the MoO<sub>3</sub> between the ITO and the H<sub>2</sub>TPP suppressed the degradation. Although the  $\eta_p$  of the OSCs without the MoO<sub>3</sub> decreased to 37 % of its initial value after 60 min, the  $\eta_p$  of the OSC with the MoO<sub>3</sub> maintained 66 % of the initial value.

In addition to the H<sub>2</sub>TPP OSCs, we investigated the stability of the  $\alpha$ -NPD OSCs (Fig. 4). The  $\eta_p$  of the  $\alpha$ -NPD OSC with the MoO<sub>3</sub> maintained 100 % of the initial value, while the  $\alpha$ -NPD device without the MoO<sub>3</sub> decreased to 46 % of its initial value. In this device, we observed a slight increase in  $J_{sc}$ ,  $FF$ , and  $\eta_p$  of the OSCs with MoO<sub>3</sub> 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  $\alpha$ -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 MoO<sub>3</sub> layer markedly improved OSC stability, and suggests that the degradation of the OSCs mainly occurs at the ITO/ $p$ -type layer interfaces (*Vide infra*).

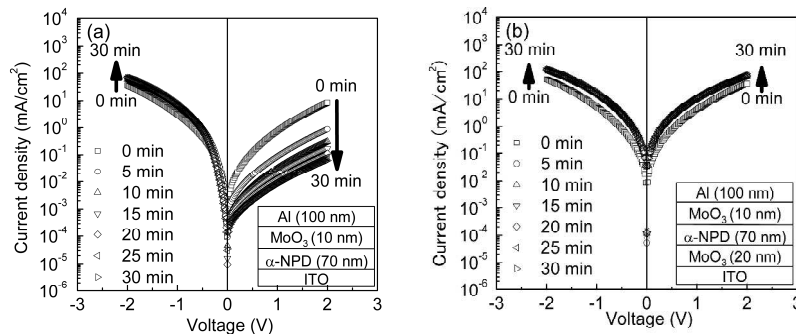


**Figure 3.** Changes of (a)  $V_{oc}$ , (b)  $J_{sc}$ , (c)  $FF$ , and (d)  $\eta_p$  for H<sub>2</sub>TPP OSCs with and without MoO<sub>3</sub> buffer layer under light irradiation.



**Figure 4.** Changes of (a)  $V_{oc}$ , (b)  $J_{sc}$ , (c)  $FF$ , and (d)  $\eta_p$  for  $\alpha$ -NPD OSCs with and without  $\text{MoO}_3$  buffer layer under light irradiation.

To get insights about the anode/ $\alpha$ -NPD interfacial degradation, we fabricated the hole-only  $\alpha$ -NPD devices. Figure 5 shows the changes of the  $J$ - $V$  characteristics of the hole-only devices during light irradiation. The hole-only  $\alpha$ -NPD device without the  $\text{MoO}_3$  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  $\text{MoO}_3$  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  $\alpha$ -NPD hole-only devices (a) without  $\text{MoO}_3$  and (b) with  $\text{MoO}_3$  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  $\alpha$ -NPD bulk layer, but is caused by an increase in hole injection barrier height between the ITO and the  $\alpha$ -NPD after light irradiation. In other words, the relative position of the HOMO level of the  $\alpha$ -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  $\alpha$ -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  $\text{MoO}_3$  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  $\text{MoO}_3$  film thickness, due to enhanced built-in potential with increasing  $\text{MoO}_3$  thickness. The highest  $V_{oc}$  (0.97 V) is consistent with the theoretical value estimated from the energy difference between the LUMO of  $\text{C}_{60}$  layer and the HOMO of  $\text{H}_2\text{TPP}$  layer. We have found that the OSC degradation occurs at the ITO and  $\alpha$ -NPD interface under light irradiation, and that the degradation can be prevented by inserting a  $\text{MoO}_3$  layer between ITO and the p-type layer. These findings would be beneficial for developing high performance organic solar cells.

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