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Author(s)	Kinoshita, Yoshiki; Takenaka, Rie; Murata, Hideyuki
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Description	

Japan Advanced Institute of Science and Technology

Independent control of open-circuit voltage of organic solar cells by changing film thickness of MoO$_3$ buffer layer

Yoshiki Kinoshita, Rie Takenaka, and Hideyuki Murata[a)]

School of Materials Science, Japan Advanced Institute of Science and Technology, Ishikawa 923-1292, Japan

The authors report the systematic control of V_{oc} as a function of the film thickness of molybdenum trioxide (MoO$_3$) buffer layer in the organic solar cells. The open-circuit voltage (V_{oc}) increased from 0.57 to 0.97 V as the thickness of MoO$_3$ film is increased from 0 to 50 nm in the device structure of indium-tin-oxide (ITO)/MoO$_3$ (x nm)/tetraphenylporphine (10 nm)/C$_{60}$ (40 nm)/bathocuproine (10 nm)/Ag (100 nm). The values between V_{oc} and the ionization potential (I_p) of MoO$_3$ (x nm) on ITO exhibit linear relationship, where the I_p values change from 4.92 to 5.92 eV as they increase from 0 to 50 nm. The enhancement of V_{oc} was achieved without affecting short-circuit current density and fill factor. Consequently, the power conversion efficiency of the device increases from 1.24% to 1.88% primarily due to the increase in V_{oc}. © 2008 American Institute of Physics.
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In recent years attention has been drawn toward solar energy conversion to develop inexpensive renewable energy sources. Since Tang reported that the thin film organic solar cells based on a single donor-acceptor heterojunction exhibit a power conversion efficiency (η_P) of 1%,[1] research has been focused on enhancing the efficiency of these cells by developing active materials and device structures.[2–6] The η_P of the solar cells depend on the open-circuit voltage (V_{oc}), the short-circuit current density (J_{sc}), and the fill factor (FF). Recently, organic solar cell employing polymer-fullerene heterojunctions have been shown to have high η_P approaching to 5% due to a drastic increase in J_{sc}.[7] In this device, the formation of the proper interpenetrating network in an active layer is a key for the improvement in J_{sc}, which governs the η_p. However, in these composite cells, it is quite challenging to precisely control the formation of interpenetrating network by solely fabrication process such as annealing condition. Furthermore, there is no enhancement effect of V_{oc} due to the formation of interpenetrating network. In other words, for the further improvement in η_p, it is essential to enhance V_{oc}, while maintaining the corresponding J_{sc} and FF.

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.[8–10] Recently, Mutolo *et al.* reported on a double-heterojunction solar cells composed of boron subphthalocyanine chloride (HOMO level=5.6 eV) and C$_{60}$ (LUMO level=4.5 eV). In comparison to that of Cu-phthalocyanine (CuPc) (HOMO level=5.2 eV) and C$_{60}$, the V_{oc} increased to 0.98 V.[11] We have reported that the increase in V_{oc} by inserting thin layer of CuPc and Zn-phthalocyanine (ZnPc) with higher HOMO level (5.1 eV) at the interface of pentacene (HOMO=5.0 eV)/C$_{60}$ (LUMO=4.5 eV).[6] The V_{oc} was linearly increased from 0.38 to 0.47 V as a function of thickness of CuPc or ZnPc. However, the J_{sc} of the device decrease as increasing CuPc thickness at thicker than 2 nm. As

the results the overall η_p rather decreased at the maximum V_{oc}.

According to the metal-insulator-metal model, the V_{oc} depends on the difference of work function of electrodes.[8–10] In the polymer organic solar cell, the increase in V_{oc} has been observed when varying the work function of the cathode electrode[8,9] or anode electrode.[10] The increase in V_{oc} is attributed to enhancement in built-in potential generated by the difference of work function of electrodes. However, if the Fermi level pinning takes place at the interface between electrode and organic layer, increase in built-in potential cannot be observed.[8,9] In this case, the work function of the metal is pinned to the work function of the semiconductor (typically via surface states) by charge transfer of electrons between the metal and the semiconductor. As a result, the presence of surface charge will create a band bending, which leads to a reduction in the built-in potential in the bulk of the device.[8,9]

Here, we report the increase in V_{oc} by inserting of MoO$_3$ layer on ITO substrate to improve built-in potential. By using tetraphenylporphine (H$_2$TPP) as p-type material, the Fermi level pinning was suppressed and the V_{oc} effectively increased from 0.57 to 0.97 V. The obtained highest V_{oc} is consistent with the theoretical value estimated from the energy difference between the LUMO (4.5 eV) of C$_{60}$ layer and the HOMO (5.5 eV) of H$_2$TPP layer. Importantly, the enhancement in V_{oc} was achieved without decreasing the J_{sc} and FF and the η_p of the device linearly increased from 1.24% to 1.88% with V_{oc}.

Devices were fabricated on a glass substrate coated with indium-tin-oxide (ITO) electrode. The thickness of ITO was 150 nm and the sheet resistance was 8.2 Ω/sq. After solvent cleaning, the ITO substrates were treated with ultraviolet (UV) ozone for 30 min and then annealed at 150 °C for 10 min. The device structure is ITO/MoO$_3$ (0, 1, 5, 10, 20, and 50 nm)/H$_2$TPP (10 nm)/C$_{60}$ (40 nm)/bathocuproine (BCP) (10 nm)/Ag (100 nm). Where H$_2$TPP is used as p-type layer, C$_{60}$ is used as n-type layer, and BCP is used as an exciton blocking layer. H$_2$TPP (99.0%) and C$_{60}$ (99.5%) were purchased from Aldrich and MTR, Ltd., respectively.

[a)]Author to whom correspondence should be addressed. Electronic mail: murata-h@jaist.ac.jp.
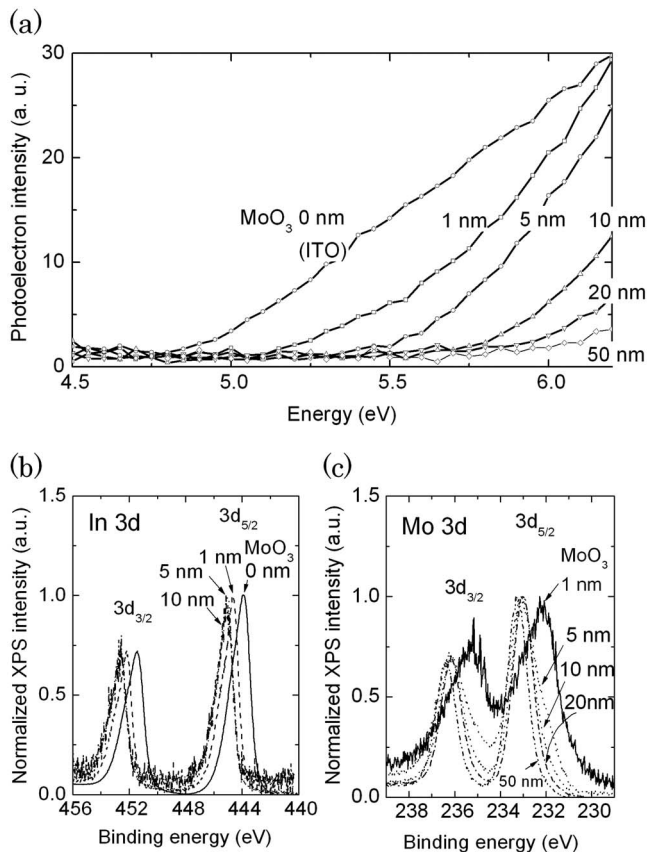
FIG. 1. (a) Ultraviolet photoemission spectra as a function of the film thickness of MoO_3 layer (0, 1, 5, 10, 20, and 50 nm) on ITO substrate. (b) XPS spectra of indium $3d$ as a function of the film thickness of MoO_3 (0, 1, 5, and 10 nm) on ITO substrate. (c) XPS spectra of molybdenum $3d$ as a function of the film thickness of MoO_3 (1, 5, 10, 20, and 50 nm) on ITO substrate.
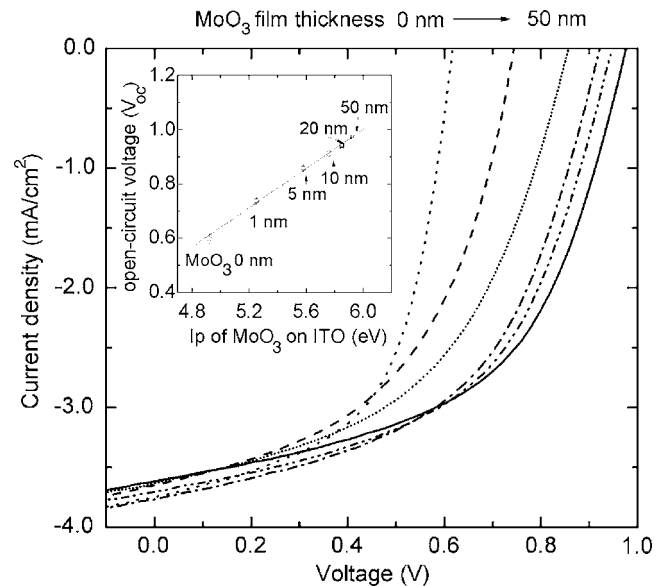

FIG. 2. Current density-voltage characteristics of ITO/H_2TPP (10 nm)/C_{60} (40 nm)/BCP (10 nm)/Ag (100 nm) under simulated AM1.5 solar illumination (100 mW/cm^2). Inset: V_{oc} vs I_p as a function of the film thickness of MoO_3 (0, 1, 5, 10, 20, and 50 nm).

H_2TPP (Fig. 3) and C_{60} were sublimed in our laboratory before use. High purity material of BCP was provided by Nippon Steel Chemical Co., Ltd. and was used without further purification. MoO_3 layers were evaporated by resistive heating and all organic layers were deposited onto the ITO substrate by vacuum evaporation using Knudsen cells under 10^{-6} Torr. The ionization potential (I_p) of MoO_3 (x nm) on ITO substrate are measured by an ultraviolet photoelectron spectroscopy (AC-2, Riken Keiki Co.).

Figure 1(a) shows ultraviolet photoemission spectra as a function of the film thickness of MoO_3. The I_p of MoO_3 (x nm) on ITO substrate increased from 4.92 ± 0.02 to 5.92 ± 0.02 eV with increasing film thickness of MoO_3 from 0 to 50 nm. This means that built-in potential formed between ITO/MoO_3 anode and Ag cathode (ϕ_{Ag} =4.26 eV) (Ref. 9) would increase from 0.66 to 1.66 eV. To investigate the origin of the change in I_p with increasing film thickness of MoO_3, we measured the binding energy of indium (In) $3d$ and molybdenum (Mo) $3d$ as a function of the film thickness of MoO_3 ($x=0$, 1, 5, 10, 20, and 50 nm) on ITO with a x-ray photoelectron spectroscopy (XPS) (ULVAC PHI 5600). As shown in Figs. 1(b) and 1(c), the binding energy of In $3d_{5/2}$ shifted from 444 to 445 eV with increasing film thickness of MoO_3 from 0 to 10 nm. The shift of In $3d_{5/2}$ to higher binding energy suggests that the electron transfer takes place from indium atom to MoO_3 layer. In contrast, the peaks of Mo $3d_{5/2}$ and $3d_{3/2}$ of the 1 nm thick MoO_3 film on the ITO showed broad spectra centered at

232.0 and 235.1 eV. These peaks are located at lower binding energy compared with those peaks at 233.3 and 236.4 eV of the 50 nm thick MoO_3 films. The shift of the MoO_3 peaks agrees well with the electron transfer to MoO_3 layer. We have analyzed the Mo $3d_{5/2}$ spectra by a peak deconvolution. (Fig. S1 in supplemental information)[12] In the all samples, the Mo $3d_{5/2}$ peak was separated to two peaks at the binding energies of 231.9 and 233.0 eV. According to the earlier report, the peaks at 231.9 and 233.0 eV were assigned to Mo^{5+} (electron transferred state) and Mo^{6+} (neutral state) of MoO_3.[13] Since the peak area of the electron transferred state decreased with increasing film thickness of MoO_3, (Fig. S2 in supplemental information)[12] the electron transfer takes place only at an interface between MoO_3 and ITO.

Figure 2 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 to 0.97 V as the MoO_3 film thickness increases from 0 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 I_p 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.

Recently, Shrotriya et al. reported that the insertion of MoO_3 on ITO leads to the increase in V_{oc} of polymer-based solar cells.[14] However, the V_{oc} did not increase while the film thickness of MoO_3 on ITO changed from 1 to 20 nm. Furthermore, the highest V_{oc} (0.6 V) of the device was only half of the maximum value that can be expected by the energy difference between the LUMO (3.7 eV) of C_{60} derivative layer and the HOMO (4.9 eV) of P3HT layer. The independence of V_{oc} on the thickness of MoO_3 was ascribed to the Fermi level pinning due to the electron transfer between MoO_3 and P3HT.[14] To check occurrence of the electron transfer from H_2TPP to MoO_3 in our device, we measured the UV/visible/near-infrared (UV-VIS-NIR) absorption spec-
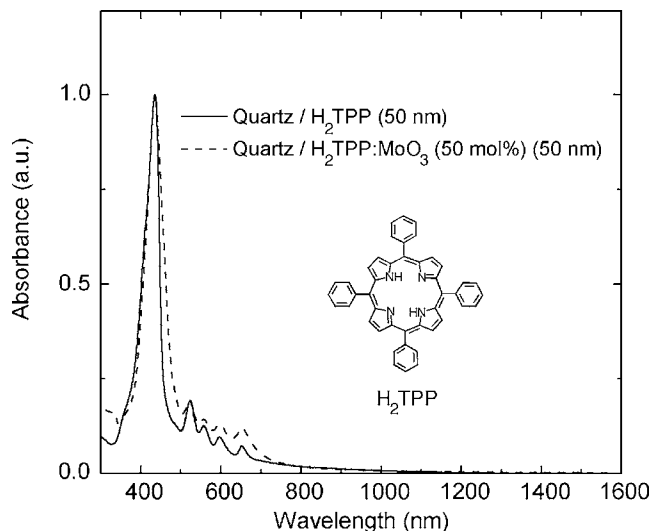
FIG. 3. Normalized UV-VIS-NIR absorption spectra of the films of H_2TTP (50 nm) and a composite of H_2TTP and MoO_3 (1:1 by mol) (50 nm) on quartz substrates. The chemical structure of H_2TTP was shown in this figure.

tra of 50 nm thick films of H_2TPP and a composite of H_2TPP and MoO_3 (1:1 by mol) on quartz substrates using a absorption spectrometer (V-570 JASCO Co.). It has been reported that, in the case of composite films of α-NPD and MoO_3,[15] a broad absorption peak appeared at NIR region as a proof of an electron transfer from α-NPD (HOMO $=5.02 \pm 0.02$ eV) to high-work-function MoO_3. On contrary, no additional absorption peak appeared at NIR region in the absorption spectrum of the composite film of H_2TPP and MoO_3 (Fig. 3). From this result, we conclude that there is no Fermi level pinning take place between H_2TPP to MoO_3.

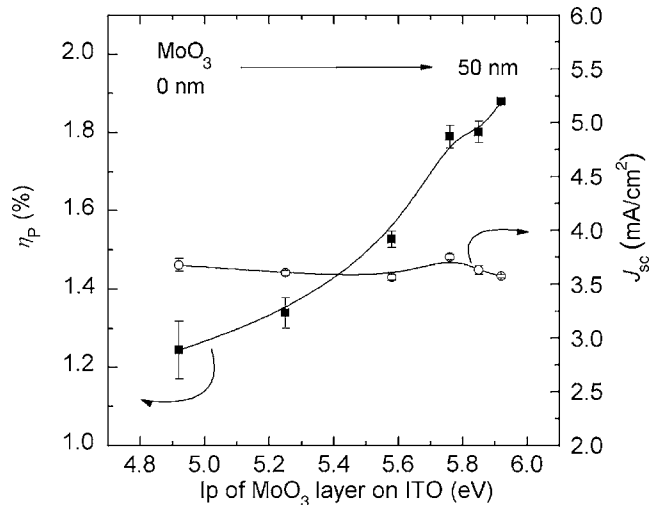Figure 4 shows the η_p and J_{sc} as a function of the film

FIG. 4. The power conversion efficiency (η_p) and the short-circuit current density (J_{sc}) of the devices as a function of the film thickness of MoO_3 (0, 1, 5, 10, 20, and 50 nm).

thickness of 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 on the film thickness of MoO_3. The FF of the device was also unchanged in the thickness range of 0 to 50 nm (supplemental Fig. S3 and Table S1). Thus, the enhancement in η_p is exclusively attributed to increase in V_{oc} by changing the film thickness of MoO_3. Since the enhancement in V_{oc} does not affect to other device parameter, further improvement in η_p may be achieved in the devices consisting bulkheterojunction interface.

In conclusion, we have investigated the change in V_{oc} as a function of the film thickness of MoO_3. The V_{oc} increased from 0.57 to 0.97 V as the MoO_3 film thickness due to the enhanced built-in potential with increasing MoO_3 thickness. The I_p of ITO/MoO_3 (x nm) and V_{oc} exhibit linear relationship and 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. The suppression of the Fermi level pinning between MoO_3 and H_2TPP is responsible for the enhancement in V_{oc}. By choosing organic materials which do not form electron transfer state with MoO_3, the systematic control of V_{oc} was realized together with the enhancement in the device performance of organic solar cells.

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