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Description	

## Independent control of open-circuit voltage of organic solar cells by changing film thickness of MoO<sub>3</sub> buffer layer

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The authors report the systematic control of  $V_{oc}$  as a function of the film thickness of molybdenum trioxide (MoO<sub>3</sub>) 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<sub>3</sub> film is increased from 0 to 50 nm in the device structure of indium-tin-oxide (ITO)/MoO<sub>3</sub> ( $x$  nm)/tetraphenylporphine (10 nm)/C<sub>60</sub> (40 nm)/bathocuproine (10 nm)/Ag (100 nm). The values between  $V_{oc}$  and the ionization potential ( $I_p$ ) of MoO<sub>3</sub> ( $x$  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. [DOI: 10.1063/1.2949321]

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 ( $\eta_p$ ) of 1%,<sup>1</sup> research has been focused on enhancing the efficiency of these cells by developing active materials and device structures.<sup>2-6</sup> The  $\eta_p$  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  $\eta_p$  approaching to 5% due to a drastic increase in  $J_{sc}$ .<sup>7</sup> 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  $\eta_p$ . 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  $\eta_p$ , 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.<sup>8-10</sup> Recently, Mutolo *et al.* reported on a double-heterojunction solar cells composed of boron subphthalocyanine chloride (HOMO level=5.6 eV) and C<sub>60</sub> (LUMO level=4.5 eV). In comparison to that of Cu-phthalocyanine (CuPc) (HOMO level=5.2 eV) and C<sub>60</sub>, the  $V_{oc}$  increased to 0.98 V.<sup>11</sup> 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<sub>60</sub> (LUMO=4.5 eV).<sup>6</sup> 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  $\eta_p$  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.<sup>8-10</sup> In the polymer organic solar cell, the increase in  $V_{oc}$  has been observed when varying the work function of the cathode electrode<sup>8,9</sup> or anode electrode.<sup>10</sup> 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.<sup>8,9</sup> 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.<sup>8,9</sup>

Here, we report the increase in  $V_{oc}$  by inserting of MoO<sub>3</sub> layer on ITO substrate to improve built-in potential. By using tetraphenylporphine (H<sub>2</sub>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<sub>60</sub> layer and the HOMO (5.5 eV) of H<sub>2</sub>TPP layer. Importantly, the enhancement in  $V_{oc}$  was achieved without decreasing the  $J_{sc}$  and FF and the  $\eta_p$  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  $\Omega$ /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<sub>3</sub> (0, 1, 5, 10, 20, and 50 nm)/H<sub>2</sub>TPP (10 nm)/C<sub>60</sub> (40 nm)/bathocuproine (BCP) (10 nm)/Ag (100 nm). Where H<sub>2</sub>TPP is used as *p*-type layer, C<sub>60</sub> is used as *n*-type layer, and BCP is used as an exciton blocking layer. H<sub>2</sub>TPP (99.0%) and C<sub>60</sub> (99.5%) were purchased from Aldrich and MTR, Ltd., respectively.

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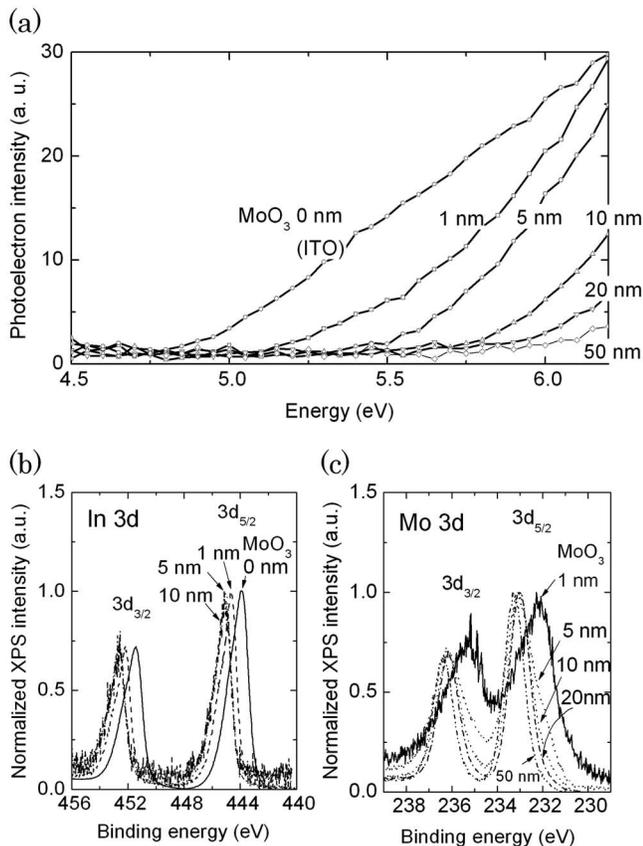


FIG. 1. (a) Ultraviolet photoemission spectra as a function of the film thickness of MoO<sub>3</sub> layer (0, 1, 5, 10, 20, and 50 nm) on ITO substrate. (b) XPS spectra of indium 3d as a function of the film thickness of MoO<sub>3</sub> (0, 1, 5, and 10 nm) on ITO substrate. (c) XPS spectra of molybdenum 3d as a function of the film thickness of MoO<sub>3</sub> (1, 5, 10, 20, and 50 nm) on ITO substrate.

H<sub>2</sub>TPP (Fig. 3) and C<sub>60</sub> 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<sub>3</sub> layers were evaporated by resistive heating and all organic layers were deposited onto the ITO substrate by vacuum evaporation using Knudsen cells under 10<sup>-6</sup> Torr. The ionization potential ( $I_p$ ) of MoO<sub>3</sub> ( $x$  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<sub>3</sub>. The  $I_p$  of MoO<sub>3</sub> ( $x$  nm) on ITO substrate increased from  $4.92 \pm 0.02$  to  $5.92 \pm 0.02$  eV with increasing film thickness of MoO<sub>3</sub> from 0 to 50 nm. This means that built-in potential formed between ITO/MoO<sub>3</sub> anode and Ag cathode ( $\phi_{Ag} = 4.26$  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<sub>3</sub>, we measured the binding energy of indium (In) 3d and molybdenum (Mo) 3d as a function of the film thickness of MoO<sub>3</sub> ( $x=0, 1, 5, 10, 20,$  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<sub>5/2</sub> shifted from 444 to 445 eV with increasing film thickness of MoO<sub>3</sub> from 0 to 10 nm. The shift of In 3d<sub>5/2</sub> to higher binding energy suggests that the electron transfer takes place from indium atom to MoO<sub>3</sub> layer. In contrast, the peaks of Mo 3d<sub>5/2</sub> and 3d<sub>3/2</sub> of the 1 nm thick MoO<sub>3</sub> film on the ITO showed broad spectra centered at

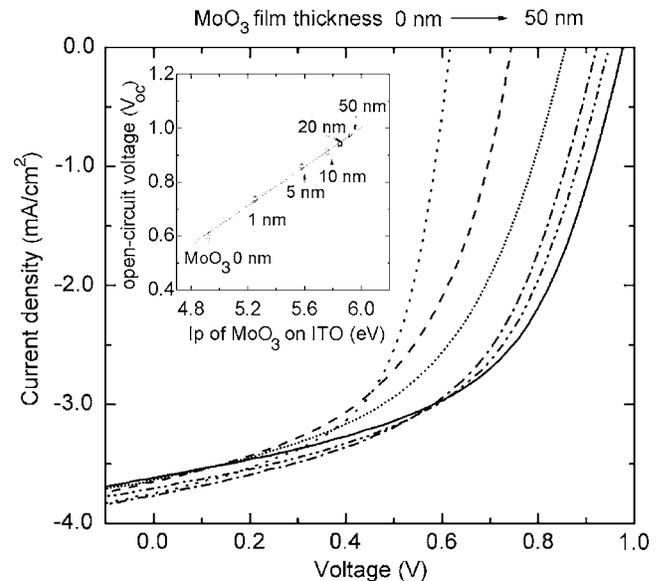


FIG. 2. Current density-voltage characteristics of ITO/H<sub>2</sub>TPP (10 nm)/C<sub>60</sub> (40 nm)/BCP (10 nm)/Ag (100 nm) under simulated AM1.5 solar illumination (100 mW/cm<sup>2</sup>). Inset:  $V_{oc}$  vs  $I_p$  as a function of the film thickness of MoO<sub>3</sub> (0, 1, 5, 10, 20, and 50 nm).

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<sub>3</sub> films. The shift of the MoO<sub>3</sub> peaks agrees well with the electron transfer to MoO<sub>3</sub> layer. We have analyzed the Mo 3d<sub>5/2</sub> spectra by a peak deconvolution. (Fig. S1 in supplemental information)<sup>12</sup> In the all samples, the Mo 3d<sub>5/2</sub> 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<sup>5+</sup> (electron transferred state) and Mo<sup>6+</sup> (neutral state) of MoO<sub>3</sub>.<sup>13</sup> Since the peak area of the electron transferred state decreased with increasing film thickness of MoO<sub>3</sub>, (Fig. S2 in supplemental information)<sup>12</sup> the electron transfer takes place only at an interface between MoO<sub>3</sub> and ITO.

Figure 2 shows the current density-voltage ( $J$ - $V$ ) characteristics as a function of the film thickness of MoO<sub>3</sub>. The  $V_{oc}$  drastically increased from 0.57 to 0.97 V as the MoO<sub>3</sub> 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<sub>60</sub> layer and the HOMO (5.50 eV) of H<sub>2</sub>TPP layer. The linear relationship between  $I_p$  of ITO/MoO<sub>3</sub> ( $x$  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<sub>3</sub> and Ag.

Recently, Shrotriya *et al.* reported that the insertion of MoO<sub>3</sub> on ITO leads to the increase in  $V_{oc}$  of polymer-based solar cells.<sup>14</sup> However, the  $V_{oc}$  did not increase while the film thickness of MoO<sub>3</sub> 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<sub>60</sub> derivative layer and the HOMO (4.9 eV) of P3HT layer. The independence of  $V_{oc}$  on the thickness of MoO<sub>3</sub> was ascribed to the Fermi level pinning due to the electron transfer between MoO<sub>3</sub> and P3HT.<sup>14</sup> To check occurrence of the electron transfer from H<sub>2</sub>TPP to MoO<sub>3</sub> in our device, we measured the UV/visible/near-infrared (UV-VIS-NIR) absorption spec-

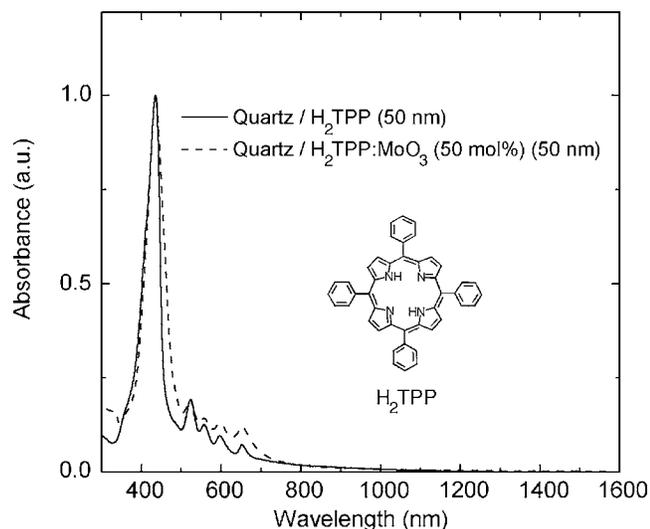


FIG. 3. Normalized UV-VIS-NIR absorption spectra of the films of H<sub>2</sub>TTP (50 nm) and a composite of H<sub>2</sub>TTP and MoO<sub>3</sub> (1:1 by mol) (50 nm) on quartz substrates. The chemical structure of H<sub>2</sub>TTP was shown in this figure.

tra of 50 nm thick films of H<sub>2</sub>TTP and a composite of H<sub>2</sub>TTP and MoO<sub>3</sub> (1:1 by mol) on quartz substrates using an absorption spectrometer (V-570 JASCO Co.). It has been reported that, in the case of composite films of  $\alpha$ -NPD and MoO<sub>3</sub>,<sup>15</sup> a broad absorption peak appeared at NIR region as a proof of an electron transfer from  $\alpha$ -NPD (HOMO = 5.02  $\pm$  0.02 eV) to high-work-function MoO<sub>3</sub>. On contrary, no additional absorption peak appeared at NIR region in the absorption spectrum of the composite film of H<sub>2</sub>TTP and MoO<sub>3</sub> (Fig. 3). From this result, we conclude that there is no Fermi level pinning take place between H<sub>2</sub>TTP to MoO<sub>3</sub>.

Figure 4 shows the  $\eta_p$  and  $J_{sc}$  as a function of the film

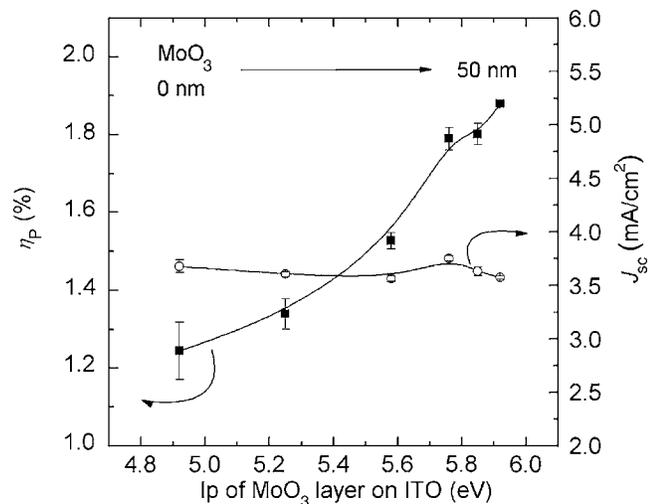


FIG. 4. The power conversion efficiency ( $\eta_p$ ) and the short-circuit current density ( $J_{sc}$ ) of the devices as a function of the film thickness of MoO<sub>3</sub> (0, 1, 5, 10, 20, and 50 nm).

thickness of MoO<sub>3</sub>. The  $\eta_p$  of the device with MoO<sub>3</sub> layer increased from 1.24% to 1.88% with increasing film thickness of MoO<sub>3</sub>. On the other hand, the  $J_{sc}$  was independent on the film thickness of MoO<sub>3</sub>. 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  $\eta_p$  is exclusively attributed to increase in  $V_{oc}$  by changing the film thickness of MoO<sub>3</sub>. Since the enhancement in  $V_{oc}$  does not affect to other device parameter, further improvement in  $\eta_p$  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<sub>3</sub>. The  $V_{oc}$  increased from 0.57 to 0.97 V as the MoO<sub>3</sub> film thickness due to the enhanced built-in potential with increasing MoO<sub>3</sub> thickness. The  $I_p$  of ITO/MoO<sub>3</sub> ( $x$  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<sub>60</sub> layer and the HOMO of H<sub>2</sub>TTP layer. The suppression of the Fermi level pinning between MoO<sub>3</sub> and H<sub>2</sub>TTP is responsible for the enhancement in  $V_{oc}$ . By choosing organic materials which do not form electron transfer state with MoO<sub>3</sub>, the systematic control of  $V_{oc}$  was realized together with the enhancement in the device performance of organic solar cells.

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- <sup>12</sup>See EPAPS No. E-APPLAB-92-074825 for a detailed analysis of XPS spectra of Mo3d as a function of the film thickness MoO<sub>3</sub> on ITO and summary of device characteristics of ITO/MoO<sub>3</sub> ( $x$  nm)/H<sub>2</sub>TTP (10 nm)/C<sub>60</sub> (40 nm)/BCP (10 nm)/Ag (100 nm). For more information on EPAPS, see <http://www.aip.org/pubservs/epaps.html>.
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