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Description	



Control of open-circuit voltage in organic photovoltaic cells by inserting an ultrathin metal-phthalocyanine layer

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The authors develop organic photovoltaic cells with multicharge separation (MCS) interfaces by inserting a very thin layer of metal phthalocyanine. The devices with MCS interface allow one to control short-circuit current density (J_{sc}) and open-circuit voltage (V_{oc}) . The power conversion efficiency (η_p) of the device with MCS interface (Cu-phthalocyanine/C₆₀ and pentacene/C₆₀) is enhanced compared with that of the device with single charge separation interface (pentacene/C₆₀). The enhancement of η_p is attributable to the increase in V_{oc} with maintaining the J_{sc} . By using Zn-phthalocyanine, which possesses longer excited lifetime compared with Cu-phthalocyanine, both J_{sc} and V_{oc} have been improved simultaneously and the η_p reaches 2.04%. © 2007 American Institute of Physics. [DOI: 10.1063/1.2775085]

In recent years, attention has been drawn toward solar energy conversion to develop inexpensive renewable energy sources. New concepts and approaches for production of efficient and low-cost organic solar cells have been desired for further development and application. So far, the power conversion efficiency (η_p) has steadily improved through the use of new materials and device structures.^{1–14} In particular, great effort has been made for the enhancement of short-circuit current density (J_{sc}). An approach to increase the J_{sc} is the use of molecules with high carrier mobilities.^{4,7} One of the representative materials is pentacene, and the photovoltaic cells using pentacene as the *p*-type layer attains high η_p values.⁴ The other one is the use of bulk heterojunctions (e.g., the composite of *p*-type and *n*-type materials) as an active layer in both polymer and small molecule-based solar cells.^{8–10,12,13}

In the bulk heterojunction cells, the distance that an exciton must travel from its generation site to charge-separation (CS) interface is reduced by the formation of interpenetrating network of *p*-type and *n*-type materials. This leads to a higher $J_{\rm sc}$ owing to the enhanced exciton diffusion length.¹³ Thus, the formation of the proper interpenetrating network in an active layer is a key for the improvement of $J_{\rm sc}$, which governs the final conversion efficiency 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 open-circuit voltage ($V_{\rm oc}$) due to the formation of an interpenetrating network. In other words, for further improvement of η_p , it is essential to enhance $V_{\rm oc}$, with maintaining the corresponding $J_{\rm sc}$.

Here, we demonstrate photovoltaic cell composed of multicharge-separation (MCS) interfaces in the active layer for the improvement of η_p (Fig. 1). Pentacene and phthalocyanines, Cu-phthalocyanine (CuPc) or Zn-phthalocyanine (ZnPc), are employed as the *p*-type molecules to form *p*-*n* junction with *n*-type of C₆₀. The highest occupied molecular orbital (HOMO) levels of those *p*-type materials are 5.0 eV

(pentacene)¹⁵ and 5.1 eV (CuPc and ZnPc).¹⁵ By inserting thin layer of phthalocyanines at the CS interface between pentacene/C₆₀, we obtain enhanced η_p and V_{oc} in accordance with the increased energy difference between the lowest unoccupied molecular orbital (LUMO) level of the *n*-type material and the HOMO level of the *p*-type material.^{16,17} Importantly, when 2-nm-thick CuPc was replaced with ZnPc, J_{sc} increase further in addition to the enhancement of V_{oc} .

Devices were fabricated on a glass substrate coated with an indium-tin-oxide (ITO) electrode. The thickness of ITO was 150 nm and the sheet resistance was 8.2 V/sq. Devices consisted of pentacene as *p*-type layer with high hole mobility, CuPc as a *p*-type material with large HOMO level, C₆₀ as *n*-type layer, and bathocuproine (BCP) as an exciton blocking layer. Pentacene and C₆₀ were purchased from Aldrich and MTR, Ltd., respectively. Pentacene and C₆₀ were sublimed in our laboratory before use. High purity materials of CuPc and BCP were provided by Nippon Steel Chemical Co., Ltd. and were used without further purification. All organic layers were deposited onto the ITO substrate by vacuum evaporation using Knudsen cells under 10^{-6} Torr.

The device structure used in this study is ITO/pentacene (50 nm)/CuPc $(x \text{ nm})/\text{C}_{60}$ (40 nm)/BCP (10 nm)/Ag(100 nm), which is fabricated by vapor deposition method (Fig. 1). The thickness of the CuPc layer is varied from 0 to 10 nm. Figure 1 shows schematic representations of MCS interfaces and the corresponding atomic force microscopy (AFM) images of surface morphologies of CuPc (x nm)/pentacene (50 nm). In the case of pentacene surface with no CuPc layer [Fig. 1(a)], we observe rough surfaces originated from the crystal growth of pentacene, whereas the image of CuPc (6 nm)/pentacene (50 nm) film becomes relatively flat [Fig. 1(c)], as indicated by root mean square (rms) factors. This may suggest that the surface roughness of pentacene layer on ITO is buried by CuPc layer as increasing the film thickness of CuPc. The increase in the CuPc layer is also confirmed by the absorption spectra. Comparing the absorption spectra of ITO/pentacene (50 nm)/CuPc $(0,2, \text{ and } 6 \text{ nm})/C_{60}$ (40 nm)/BCP (10 nm), the absorption intensity of CuPc layer clearly increases (see supplemental information 1).

91, 083518-1

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FIG. 1. (Color online) Illustration of the device structure with multicharge separation interface. The model of multicharge separation interface and atomic force microscope (AFM) images of the surface of (a) pentacene (50 nm), (b) CuPc (2 nm)/pentacene (50 nm) and (c) CuPc (6 nm)/ pentacene (50 nm) on ITO substrate.

Figures 2(a) and 2(b) show the current density-voltage (J-V) characteristics and values of J_{sc} and V_{oc} as a function of the thickness of CuPc layer under the illumination of AM1.5 (100 mW/cm²) simulated solar light. We observe increase of V_{oc} from 0.38 to 0.47 V by inserting thin layer of CuPc. The change of V_{oc} corresponds to the larger HOMO level of CuPc (5.1 eV) compared with pentacene (5.0 eV)[Fig. 2(c)]. Whereas, the J_{sc} exhibits plateau in the 0–2 nm range and then it decreased at thicker than 3 nm. Figure 2(d) shows η_p relative to the CuPc layer thickness. The maximum η_p attains 1.97% in ITO/pentacene (50 nm)/CuPc $(2 \text{ nm})/C_{60}$ (40 nm)/BCP (10 nm)/Ag (100 nm), which is higher than that of the device without CuPc layer.¹⁸ The J_{sc} decreases in the 3–6 nm range. Both V_{oc} and J_{sc} are approximately unchanged in the 6-10 nm range of CuPc layer. At this thickness range, pentacene layer may be completely covered by CuPc layer. The change of $V_{\rm oc}$ and $J_{\rm sc}$ as a function of CuPc thickness can be ascribed to the change of charge separation interface from pentacene/ C_{60} to CuPc/ C_{60} .



The transition of the dominant charge separation interface was confirmed by the photocurrent action spectra, as shown in Fig. 3(a). The device without CuPc layer exhibits a broad maximum at 440 nm due to the absorption of C_{60} , whereas two peaks at 590 and 670 nm are attributed to pentacene. It is obvious that the interface at pentacene/ C_{60} is responsible to charge separation in this device. By inserting 2-3 nm of CuPc layer, additional increase in external quantum efficiency (η_{EOE}) was observed in 700–800 nm regions accompanied with the slight decrease of the $\eta_{\rm EOE}$ at 590 and 670 nm. According to the absorption spectra of CuPc [Fig. 3(b)], the additional response in 700–800 nm is the contribution of CuPc layer. This suggests that charge separation also occurs at $CuPc/C_{60}$ and the coexistence of two charge separation interfaces, pentacene/C₆₀ and CuPc/C₆₀. The enhancement of $V_{\rm oc}$ can be attributed to the enhanced energy difference between HOMO of p-type material and LUMO of *n*-type material.^{16,17} Based on these results, the enhancement of η_p is attributed to the MCS interfaces where

FIG. 2. (Color online) (a) *J*-*V* characteristics of ITO/pentacene (50 nm)/ CuPc (*x* nm)/C₆₀ (40 nm)/BCP (10 nm)/Ag (100 nm) under simulated AM1.5 solar illumination, where the thicknesses of CuPc layer are 0, 2, and 6 nm. CuPc layer was replaced with 2-nm-thick ZnPc. (b) J_{sc} and V_{oc} as a function of the thickness of CuPc. (c) Energy diagram of the device used in this study. (d) η_P as a function of the film thickness of CuPc. Open square shows η_P of the device with 2-nm-thick ZnPc.

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2-nm-thick phthalocyanine on pentacene layer exclusively increases V_{oc} with maintaining the corresponding J_{sc} . Increase in CuPc thickness more than 3 nm leads to decrease in the contribution of pentacene/C₆₀ interface. Finally, the device with 6-nm-thick CuPc layer no longer show the peaks ascribed to pentacene and appears two new peaks at 620 and 700 nm which correspond to the absorption peaks of CuPc. At this thickness, the charge separation interface is dominated by CuPc/C₆₀ interface.

To get more insights of the MCS interfaces, we have discussed the reason for a decrease in J_{sc} by insertion of CuPc layer thicker than 3 nm. Based on the theory for pn junction solar cells, decrease in J_{sc} can be attributed to the increase in R_s . However, we have confirmed that R_s remains constant even though the thickness of CuPc is thicker than 3 nm. (see supplemental information 2). Thus, in the device with thicker CuPc layers, J_{sc} would be limited by η_{EOE} , which is the product of the efficiencies of the following four steps: (1) exciton formation by photoabsorption (η_A), (2) exciton diffusion to the charge separation interface (η_{ED}), (3) exciton dissociation by charge transfer at the charge separation interface (η_{CT}) , and (4) the collection of free carrier at the electrodes ($\eta_{\rm CC}$). In the present devices, exciton dissociation at charge separation interface $\eta_{\rm CT}$, would be the key parameter for governing $J_{\rm sc}$. Because $\eta_{\rm A}$ should be improved rather than decreased as increasing the CuPc thickness, $\eta_{\rm ED}$ would be unchanged since the thickness of CuPc layer is always less than the exciton diffusion length of CuPc (10 nm) (Refs. 3 and 6) and $\eta_{\rm CC}$ should be always the same since electrode metal is unchanged.

Based on the discussion regarding $\eta_{\rm CT}$ we can interpret the difference of J_{sc} by inserting different metalphthalocyanine. We notice that the lifetime of singlet excited state of CuPc (6 ps) (Ref. 19) is three orders of magnitude shorter than that of pentacene (19 ns).²⁰ In this situation, $\eta_{\rm CT}$ at $CuPc/C_{60}$ interface should be reduced compared with the efficiency at pentacene/C₆₀ interface. On the other hand, if CuPc layer was replaced with ZnPc which possesses the same HOMO level but exhibits longer excited state lifetime (3.3 ns)²¹ the J_{sc} is expected to enhance in addition to the $V_{\rm oc}$. Indeed, by using ZnPc, we observe the increases in the $J_{\rm sc}$ from 8.02 to 8.75 mA/cm² as well as enhancement of $V_{\rm oc}$ (0.43 V). By comparing with the device without a thin layer of metal-phthalocyanine, both J_{sc} and V_{oc} have been improved simultaneously and the resulting η_p reaches 2.04%. Now, we have controlled both J_{sc} and V_{oc} in photovoltaic cells by taking advantages of the MCS interfaces.

FIG. 3. (a) η_{EQE} spectra as a function of the thickness of CuPc film. (b) Absorption spectra of the films of pentacene, CuPc and C₆₀. The film thickness of all samples are 50 nm.

 C_{60} and pentacene/ C_{60} . By inserting a very thin layer of phthalocyanine layer (~2 nm), we can increase V_{oc} without affecting J_{sc} . The maximum η_p attains 2.04% in ITO/ pentacene (50 nm)/ZnPc (2 nm)/ C_{60} (40 nm)/BCP (10 nm)/Ag (100 nm) and the enhancement is largely attributable to the MCS interfaces, where properties of molecules (e.g., lifetime of excited state) directly reflect to device performance. This approach will provide a device architecture for the development of efficient organic solar cells. In addition, since the device structure composed of MCS interfaces allows us to control V_{oc} , this device structure would provide a means for systematic investigation of the operation mechanism of organic solar cells.

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