Improvement of hole injection characteristics in multilayered organic photovoltaic devices by the insertion of organic interfacial layer

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1. Introduction

Organic semiconductors are considered as a potential candidate for fabricating low-cost, flexible, and efficient photovoltaic devices (OPVs), and the increment of the open circuit voltage V_{OC} and short-circuit photocurrent density J_{SC} is major subject for the improvement of the efficiency of OPVs. Since the upper limit of the V_{OC} is considered as the energy difference between the lowest unoccupied molecular orbital (LUMO) level of acceptor (n-type) and the highest occupied molecular orbital (HOMO) of donor (p-type) level ΔE at the heterojunction interface, the relatively low gap donor materials with large ionization potential (IP) is preferred for the application of organic solar cells.[1,2] However, larger IP value may increase the hole injection barrier height at the electrode/ donor interface. One of the strategies to improve the efficiency of organic solar cells with a given set of organic semiconductor materials is to insert an interfacial buffer layer between active layers and electrodes, such as poly(styrene sulfonic acid) (PEDOT-PSS), a self-assembled monolayer (SAM), and transparent oxide materials. [2,3] Recently, transition-metal oxides such as MoO₃, V₂O₅, WO₃, and NiOx have been demonstrated as alternative effective buffer layers of PE-DOT-PSS for organic solar cell applications since they can increase the work-function of electrode [4,5] or form the charge-transfer (CT) complex. Here, the CT complex is also preferable way to improve the electrical properties since the CT complex can generate the charge carriers in donor materials at the vicinity of interface.

In this study, we have investigated the effect of the insertion of the interfacial layers inserted between the ITO electrode and porphyrin based donor materials (metal-free tetra- phenyl porphyrin (H₂TPP) in ITO/ interfacial layer/ H₂TPP/ C₆₀/ BCP/ Al multilayered heterojunction structures. Especially, we have focused on the 3 types of organic interfacial layers, porphyrin based SAM (Tetrakis (4-carboxyphenyl) porphyrin (TCPP)) as a hole injection buffer layer, fluorinated copper phthalocyanine (F₁₆CuPc) and tetrafluoro- tetracyanoquinodimethane (F₄-TCNQ) as a strong acceptor in order to form the CT complex at the ITO/ donor interface.[6,7]

2. Experimental

All devices were fabricated on 150-nm thick ITO-coated glass substrates. Figure 1 shows the chemical structures and energy diagrams of the materials used in this study. After patterning the ITO (2mm in width), we have prepared a known multilayered structure based on ITO/ interfacial layer/ $H_2TPP/$ C₆₀ (50nm)/ BCP (10nm)/

Al(100nm). The oxide layer (NiO and MoO_X), F_{16} CuPc, F_4 -TCNQ, H_2 TPP, C_{60} , and BCP have been deposited by evaporation technique in a vacuum of ~3×10⁻⁴Pa. The deposition rates of MoO_X, Ni, H₂TPP, C_{60} , BCP, and Al were 0.05, 0.2, 0.1, 0.1, 0.1, and 1nm/s, respectively. A TCPP monolayer was adsorbed onto ITO electrode by immersing the TCPP solution (0.05mM ethanol solution) at room temperature for 1 hour before the evaporation of organic layers. Finally, 2-mm-wide, ca. 100-nm-thick Al electrodes were evaporated on the organic layers in a different vacuum chamber after brief exposure to air. The effective area is 4mm².

Photovoltaic properties were measured in a grove box filled with argon and under global 1 sun AM 1.5 simulated solar simulator (SAN-EI Electric XES-40S1). All samples were illuminated through the ITO electrodes.



Fig. 1. The chemical structures and enerdiagrams of materials used in this study.

3. Result and discussion

Figure 2. shows the J-V characteristics for H₂TPP (15nm)/ C₆₀ (50nm) multilayered devices with and without the buffer layer. Table 1 summarizes the J_{SC}, V_{OC}, fill factor (FF), and η_P for H₂TPP (15nm)/ C₆₀ (50nm) multilayered devices with and without the buffer layer. In the case of device without the buffer layer, V_{OC} becomes 0.61V, whereas it increases to 0.95 and 0.88V for the devices upon the oxide film (MoO_X and NiO), respectively. The insertion of transition metal oxide enhance the charge injection at the anode and increase V_{OC} due to the increment of Δ WF from 0.7 to 1eV across the film. However, J_{SC} decreases from

-1.77 to -1.37mA/cm² for the devices upon MoO_X probably due to the series resistance between ITO and MoO_X. In the case of the device with TCPP as a buffer layer, V_{OC} increases to 0.75V. Therefore the insertion of TCPP organic buffer layer is an effective way to improve the photovoltaic properties. And the V_{OC} and the efficiency will be improved by optimizing the surface treatment of ITO surface in the near furure.



Fig.2. J-V characteristics of ITO / buffer layer / $H_2TPP(15nm)$ / $C_{60}(50nm)$ / BCP(10nm) / Al devices under AM1.5 illumination

Table 1. A summary of J_{SC} , V_{OC} , FF, and η_P of ITO / buffer layer / $H_2TPP(15nm) / C_{60}(50nm) / BCP(10nm) / Al devices$

Buffer layer	J_{sc} (mA/cm ²)	$V_{oc}(V)$	FF	η _P (%)
Without buffer layer	-1.66	0.61	0.34	0.35
MoO _X	-1.37	0.95	0.25	0.32
NiO	-1.53	0.88	0.37	0.51
ТСРР	-1.77	0.73	0.34	0.44



Fig.3. J-V characteristics of ITO / charge generation layer / $\rm H_2TPP(15nm)$ / $\rm C_{60}(50nm)$ / BCP(10nm) / Al devices under AM1.5 illumination

Table 2. A summary of $J_{SC},$ $V_{OC},$ FF, and $\eta_P~$ of ITO / charge generation layer / $H_2TPP(15nm)$ / $C_{60}(50nm)$ / BCP(10nm) / Al devices

Charge generation layer	J_{sc} (mA/cm ²)	$V_{oc}(V)$	FF	η _P (%)
F ₁₆ CuPc 1nm	-1.51	0.45	0.45	0.30
F ₁₆ CuPc 3nm	-1.72	0.4	0.44	0.30
F ₁₆ CuPc 5nm	-1.03	0.37	0.36	0.14
F ₁₆ CuPc 10nm	-0.62	0.34	0.30	0.063
F ₄ -TCNQ 0.4nm	-1.14	0.81	0.28	0.26

Figure 3 shows the J-V characteristics for H₂TPP (15nm)/ C₆₀ (50nm) multilayered devices with the charge generation layer. Table 2 summarizes the J_{SC}, V_{OC}, FF, and η_P for each device. In the case of device upon 1nm-thick F₁₆CuPc, V_{OC} and FF become 0.45V and 0.45, respectively. Probably, charge carriers generate at the interface by insertion of F₁₆CuPc. However, V_{OC}, and FF decreases with the insertion of the thickness of F₁₆CuPc. It is noted here that FF increases by insertion of very thin F₁₆CuPc layer compared with the device without interfacial layer. We therefore considered that the contact resistance was successfully improved by the formation of CT complex. And one reason for the decrement of V_{OC} is probably due to the low electron affinity of F₁₆CuPc or the dipole layer formed at the $F_{16}CuPc/H_2TPP$ stack. On the other hand, V_{OC} increases to 0.81V with the insertion of extremely thin F₄-TCNQ having a stronger acceptor property. Since F₄-TCNQ is very thin, it becomes career doping to H₂TPP after the desposition of H₂TPP donor layer. And the increment of the Work Function of doped H_2 TPP layer way cause the increment of V_{OC} like the device with buffer layer.

4. Conclusion

In this study, we have investigated the photovoltaic properties of multilayered devices consisting of ITO/ interfacial layer/ H2TPP/ C60/ BCP/ Al structures. The insertion of transition metal oxide enhance the charge injection at the ITO/ donor interface and markedly increase Voc due to the increment of ΔWF across the film. A same tendency was again obtained by the insertion of ultra-thin porphyrin based SAM (TCPP) film. We also investigated the effect of the insertion of strong acceptors such as F16CuPc and F₄-TCNQ between ITO and donor material. The value of FF increases by the insertion of F_{16} CuPc probably due to the generation of charge carriers at the interface. However, Voc decreases with the increment of F16CuPc thickness probably due to the insufficient electron affinity of F₁₆CuPc. On the other hand, F₄-TCNQ increases the V_{OC} value probably due to the stronger electron affinity compared with F₁₆CuPc. The detail will be discussed during the conference.

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