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

Satoru Nakagoshi, Eiji Itoh

Department of Electrical and Electronic Engineering, Shinshu University
4-17-1 Wakasato Nagano Nagano 380-8553, Japan
Phone: +81-26-269-5227 E-mail: eitoh@shinshu-u.ac.jp

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 $\Delta E$ 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 MoO$_3$, V$_2$O$_5$, WO$_3$, and NiOx have been demonstrated as alternative effective buffer layers of PEDOT-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 (H$_2$TPP) in ITO/interfacial layer/ H$_2$TPP/C$_{60}$/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 (F$_{40}$CuPc) and tetrafluoro-tetracyanoquinodimethane (F$_{4}$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 enerdiagrams of the materials used in this study. After patterning the ITO (2nm in width), we have prepared a known multilayered structure based on ITO/interfacial layer/ H$_2$TPP/ C$_{60}$ (50nm)/ BCP (10nm)/Al(100nm). The oxide layer (NiO and MoO$_3$), F$_{40}$CuPc, F$_{4}$-TCNQ, H$_2$TPP, C$_{60}$, and BCP have been deposited by evaporation technique in a vacuum of $\sim$3×10$^{-4}$Pa. The deposition rates of MoO$_3$, Ni, H$_2$TPP, C$_{60}$, BCP, and Al were 0.05, 0.2, 0.1, 0.1, 0.1, and 1nm/s, respectively. A TCPP monolayer was adsorbed onto ITO electrode by immersing the TCPP solution (0.05mM ethanol solution) at room temperature for 1 hour before the evaporation of organic layers. Finally, 2-mm-wide, ca. 100-nm-thick Al electrodes were evaporated on the organic layers in a different vacuum chamber after brief exposure to air. The effective area is 4mm$^2$.

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.

![Chemical structures and enerdiagrams of materials](image)

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 H$_2$TPP (15nm)/ C$_{60}$ (50nm) multilayered devices with and without the buffer layer. Table 1 summarizes the $J_{SC}$, $V_{OC}$, fill factor (FF), and $t_p$ for H$_2$TPP (15nm)/ C$_{60}$ (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$_3$ 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 $\Delta$WF from 0.7 to 1eV across the film. However, $J_{SC}$ decreases from...
-1.77 to -1.37 mA/cm² for the devices upon MoOₓ probably due to the series resistance between ITO and MoOₓ. 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 future.

Figure 3 shows the J-V characteristics for H_{2}TPP (15nm)/ C_{60} (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 F_{16}CuPc, V_{OC} and FF become 0.45V and 0.45, respectively. Probably, charge carriers generate at the interface by insertion of F_{16}CuPc. However, V_{OC} and FF decreases with the insertion of the thickness of F_{16}CuPc. It is noted here that FF increases by insertion of very thin F_{16}CuPc 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 F_{16}CuPc or the dipole layer formed at the F_{16}CuPc/H_{2}TPP stack. On the other hand, V_{OC} increases to 0.81V with the insertion of extremely thin F_{16}-TCNQ having a stronger acceptor property. Since F_{16}-TCNQ is very thin, it becomes career doping to H_{2}TPP after the desposition of H_{2}TPP 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/ H_{2}TPP/ C_{60}/ BCP/ Al structures. The insertion of transition metal oxide enhance the charge injection at the ITO/ donor interface and markedly increase V_{OC} 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 F_{16}CuPc and F_{16}-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, V_{OC} decreases with the increment of F_{16}CuPc probably due to the insufficient electron affinity of F_{16}CuPc. On the other hand, F_{16}-TCNQ increases the V_{OC} value probably due to the stronger electron affinity compared with F_{16}CuPc. The detail will be discussed during the conference.

### Acknowledgement

This work was partly supported by Grant-in-Aid for Scientific Research (No. 22360123) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

### References