

Relationship between the work function of the hole collection electrode and the temperature dependence of open-circuit voltage in multi layered organic solar cells

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1. Introduction

Organic semiconductors are considered as a potential candidate for fabricating the low-cost, flexible and efficient photovoltaic devices (OPVs). The power conversion efficiency (η_p) of solar cells depends on the open-circuit voltage (V_{OC}), the short-circuit current density (J_{SC}), and the fill factor (FF), and they are still need of improvement for practical applications. 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 (HJs) interface, the relatively low gap donor materials with large ionization potential (IP) is preferred for the application of organic solar cells. However, larger IP value may increase the hole injection barrier height at the electrode/ donor interface.[1-3] 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. Since the work-function difference ΔWF forms the built-in potential or internal electric field across the film, the upper limit of V_{OC} would be attributed to the lower part of ΔWF and ΔE in the multi-layered devices.[4] Therefore, the use of large work-function electrode materials or the hole injection /extraction buffer layer is supposed to be important. Recently, transition-metal oxides such as MoO_3 , V_2O_5 , WO_3 , and NiO_x have been demonstrated as alternative effective buffer layers of PEDOT-PSS acidic buffer layer for organic solar cell applications since they can increase the work-function of electrode. It is also noted here that the defect states and the tail states, which may depend on the temperature, also reduce the V_{OC} and J_{SC} due to the trapped carrier and bimolecular recombination process. [5-7]

In this study, we have investigated the temperature dependence of photovoltaic properties in ITO/(buffer layer)/donor/ fullerene (C_{60})/ bathocuproine (BCP)/ Al structures in order to estimate the limitation factor of V_{OC} in the multilayered devices. Here, we have used the various donor materials in order to change the IP value systematically. We have then investigated the correlation between V_{OC} , IP, ΔWF and temperatures between 40 and 350K.

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/ Donor/ C_{60} (50nm)/ BCP (10nm)/ Al(100nm). The oxide layer (NiO), Donor, C_{60} , and BCP have been deposited by evaporation technique in a vacuum of $\sim 3 \times 10^{-4}$ Pa. The organic layers were deposited on 10nm-thick-NiO after oxidizing the 5 nm-thick Ni metal layer at 300°C for 30min in air since it was difficult to deposit NiO layer directly by heat-resistive evaporation technique and the work function of NiO is extremely sensitive to the degree of oxidation.

Here, we chose a series of donor materials as a function of IP of donor materials; (small IP) poly(3-hexylthiophene) (P3HT), Copper phthalocyanine (CuPc), (Bis[N-(1-naphthyl)-N-phenyl]benzidine) (α -NPD), 5,10,15,20 -

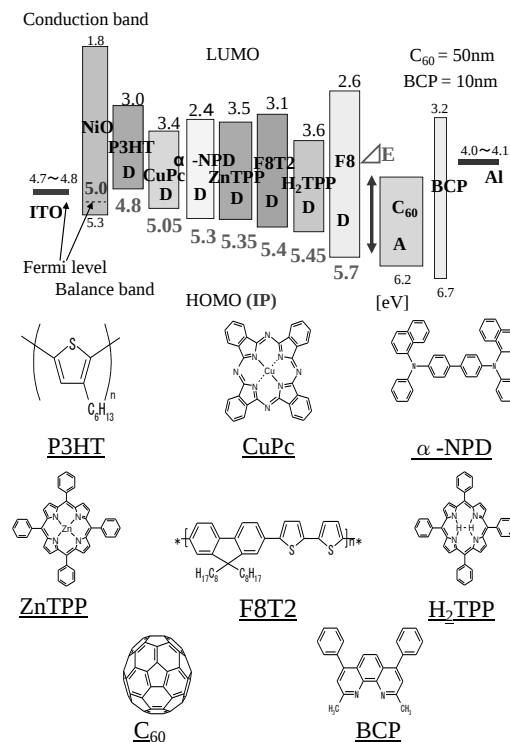


Fig 1 Chemical structure and energy diagrams of materials which used this study

Tetraphenyl-21H,23H-porphyrin zinc (ZnTPP), Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-bithiophene] (F8T2), 5,10,15,20-tetraphenylporphyrin (H₂TPP), and poly(9,9-dioctylfluorene) (F8) (large IP). C₆₀ and BCP are used as an n-type layer and an exciton-blocking buffer layer, respectively. The deposition rates of Ni, C₆₀, BCP, and Al were 0.2, 0.1, 0.1, and 1nm/s, respectively. 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.

Electrical characterizations were performed in a vacuum chamber equipped with the cryostat at the temperatures between 40 and 350K with a source meter (ADCMT model 6241A) and global 1 sun AM1.5 solar simulator (SAN-EI Electric model XES-40S1). All devices were illuminated through ITO electrodes.

3. Results and Discussion

Figure 2 (a) shows the J-V curves in ITO/NiO/F8T2/C₆₀/BCP/Al HJs devices under white light illumination measured at various temperatures. As shown in Fig.2 (a), the J_{SC} increase with the increment of temperatures. And a classical diode like characteristics was successfully observed at the temperature above 250K. It is noted here that the slope of J-V curves in the vicinity of V_{OC} markedly decreases at the temperature below 200K, while the V_{OC} gradually increases with the decrement of temperatures. The reduction in J_{SC} and the conductivity at low temperatures is probably attributable to the reduced charge transport and charge injection across the thermally activate organic films. In contrast, V_{OC} value is almost fixed at constant value of about 0.6V in the F8T2/C₆₀ multilayered device without NiO. In our previous study, we reported the relationships between the IP value and the V_{OC} of multi-layered device with and without oxide buffer layers, and the V_{OC} is limited by work-function difference of Al and oxide layers. Since the ΔWF between Al and ITO electrodes is 0.6-0.7eV, the V_{OC} value might be pinned at 0.6V for all temperatures.

Figure 3 shows the temperature dependence of V_{OC} for several Donor/ C₆₀ multi-layers with and without NiO layers. The V_{OC} in ITO/NiO/CuPc/ C₆₀/ BCP/ Al device increases from 0.34 V (350 K) to 0.81 V (40K) with the decrement of temperatures. Although the temperature dependence of V_{OC} in the CuPc/ C₆₀ multilayered device without NiO is almost the same as the device with NiO for 200K, the V_{OC} is again pinned at ~0.6V at lower temperatures. Of interest is that the V_{OC} measured at 300K increases with the IP of donor layer in the device with NiO. However, the value of V_{OC} is again saturated at about 1.1V at the temperature below 150K probably due to the ΔWF limit. The larger work function material should be required for the higher V_{OC} at low temperatures.

4. Conclusions

In this study, we have investigated the photovoltaic properties of multi-layered organic photovoltaic devices consisting of ITO/(NiO)/Donor/C₆₀/BCP/Al structures. V_{OC}

increases with the decrement of temperature between 40K and 350K. The V_{OC} was pinned at ~0.6V for the device without buffer layer probably due to the insufficient work-function difference between ITO and Al electrodes. And the hole injection is also suppressed at ITO/donor interface in the device with large IP donor materials. We have therefore concluded that the insertion of buffer layer with large work-function or surface treatment of ITO electrode is very important for the improvement of V_{OC} and charge transport properties in the multi-layered organic solar cell applications. The detail of the temperature dependence will be discussed in the conference sessions.

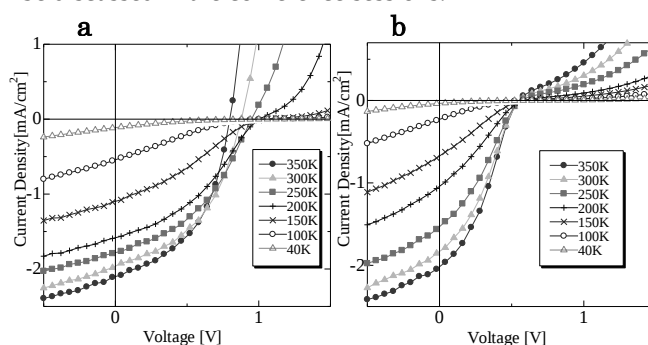


Fig.2 The J-V characteristics of multi-layered devices measured at the temperatures between 350K to 40K
(a) ITO/NiO/F8T2/C₆₀/BCP/Al device,
(b) ITO/F8T2/C₆₀/BCP/Al device

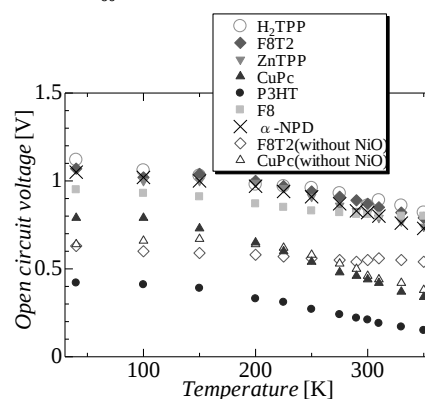


Fig.3 The temperature dependence of open circuit voltage in various multilayered devices

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