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Degradation of interface between boron subphthalocyanine chloride and fullerene

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ABSTRACT

Apart from external environmental factors, we herein show with ultra-violet photoemission spectroscopy (UPS) studies that degradation in organic photovoltaic (OPV) devices can also be caused by internal deterioration of the donor/acceptor interface. Albeit with impressive initial open circuit voltage (Voc), boron subphthalocyanine chloride (SubPc)/fullerene (C₆₀) device shows a fast Voc decay upon operation. UPS results show that the energy offset between the highest occupied molecular orbit (HOMO) of SubPc and the lowest unoccupied molecular orbit (LUMO) of C₆₀ is reduced from 1.66 to 1.45 eV after aging in ultra-high vacuum (UHV) condition. This result is consistent with the change in built-in voltage of the corresponding device upon operation. The related charge interaction and degradation mechanism in the SubPc/C₆₀ device are discussed.

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1. Introduction

OPV device is of much recent interest as a low-cost and lightweight renewable energy conversion technology [1–3]. Despite recent advances made in enhancement of power conversion efficiencies (PCE), much improvement on device lifetime and operational stabilities are still needed before wide commercial applications [4,5]. Deterioration of organic and/or metal layers by external gases is often considered as a major cause for the short lifetime [6–9]. On the other hand, degradation in device performance is still obvious in devices with proper encapsulation or housed in inert environments [10–14]. These suggest that there are additional intrinsic degradation causes within the device.

Recently, we report the detrimental effects of indium doped oxide (ITO) substrate to adjacent organic materials [12,15]. Reactive oxygen species generated on ITO surface during routine UV-ozone treatment can gradually degrade its neighboring organic layer leading to shift in the organic layer's Fermi level away from its HOMO [12]. This is accompanied with decreases in carrier concentration and thus charge-transporting ability. While electronic properties of organic donor/acceptor heterojunction play a key role in controlling

the device efficiency, there are so far few studies on how ITO substrate affects electronic structures and stabilities of donor/acceptor heterojunctions [5].

In this work, we performed an interfacial study on the effects of UV-ozone treated ITO substrate to the SubPc/C₆₀ heterojunction. In particular, effects on the energy offset between the HOMO of SubPc and the LUMO of C₆₀, would be studied. This is the first direct demonstration on how evolution in electronic structures of a donor/acceptor junction leading to Voc degradation in the corresponding device.

2. Experimental

Device fabrication: Patterned ITO glass substrates with a sheet resistance of 30 Ω/sq were cleaned with Decon 90, rinsed in deionized water, then dried in an oven, and finally treated in an ultraviolet-ozone chamber. The device with a structure of ITO/SubPc (15 nm)/C₆₀ (44 nm)/BPhen (8 nm)/Al (80 nm) were fabricated via thermal evaporation. The deposition rates were monitored using quartz oscillating crystals and controlled at 0.1–0.2 nm/s for both organic and metal layers. After deposition of the organic layers, Al cathode was deposited through a shadow mask that defines an active device area of 0.12 cm². All devices were immediately encapsulated after fabrication. Current density–voltage (J–V) characteristics were measured with a programmable Keithley model 237 power source. Photocurrent was

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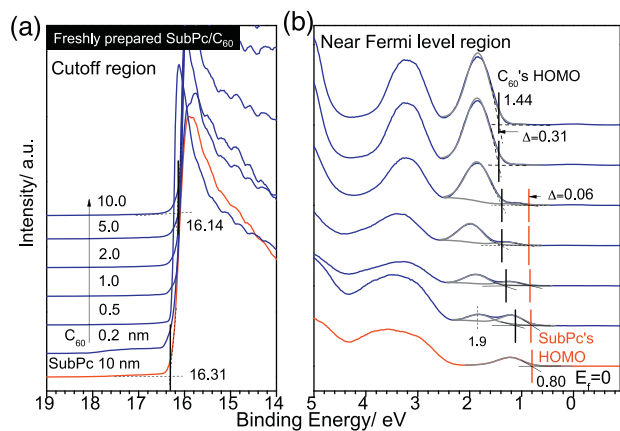


Fig. 1. Evolution of UPS He I spectra of cleaned SubPc/C₆₀ heterojunction in (a) secondary cutoff energy region; and (b) near Fermi level region. Incremental deposition of C₆₀ is on cleaned ITO/SubPc substrate. All unit marked in the figures are in unit of eV.

measured in the dark and under illumination with an Oriel 150 W solar simulator with an AM 1.5G (AM: air mass, G: global) filter at an intensity of 100 mW/cm². External quantum efficiency (EQE) spectra were measured using a Newport IQE 200 system [12].

Photoemission studies: UPS experiments were carried out in a VG ESCALAB 220i-XL surface analysis system with a base vacuum better than 10⁻⁹ Torr [12]. SubPc and C₆₀ films are in situ prepared in a deposition chamber connected to the ESCALAB system. Deposited films were transferred to the analysis chamber for UPS/X-ray photoemission studies (XPS) measurements or UHV aging without breaking vacuum. UPS spectra were fitted with Gaussian–Lorentzian functions after Shirley background subtraction. The HOMO onset positions of SubPc and C₆₀ were determined by linear extrapolation.

3. Results and discussions

Fig. 1 shows evolution of He I UPS spectra of the SubPc/C₆₀ junction with increasing C₆₀ film thickness. The bottom spectrum in Fig. 1 shows a spectrum from the pristine SubPc (10 nm) film deposited on an UV-ozone treated ITO anode substrate. From the cutoff at 16.31 eV (Fig. 1a), the work function of the SubPc film is

determined to be 4.89 eV. Upon C₆₀ deposition, the cutoff energy slightly shifts to 16.14 eV.

The onsets of the HOMO peaks in Fig. 1b are obtained by linear extrapolation of the UPS spectra near the lower binding energy (BE) region. The HOMO onset of SubPc is observed at 0.80 eV away from the Fermi level (E_f, defined as zero BE). Meanwhile, the HOMO signal from C₆₀ emerges at ~1.9 eV which is strongly tangled with that of SubPc. The UPS spectra at low BE region are therefore fitted with the Gaussian function after background subtraction. The fitted results are shown as gray lines in Fig. 1b. As the thickness of C₆₀ increases, its HOMO shows an energy shift of 0.31 eV toward the higher BE side. In contrast, the HOMO peak of SubPc shows negligible shift (~0.06 eV).

To study the influences of UV-ozone treated ITO on the band alignment at the SubPc/C₆₀ interface, the above experiment was repeated by depositing C₆₀ on ITO/SubPc substrates aged in UHV for different durations. Figs. 2a and b shows He I UPS spectra of 10 nm SubPc films aged for different durations in UHV. Upon timed aging, the cutoff energy of the UPS spectrum shifts toward the high BE side from 16.40 to 16.66 eV, while the HOMO edge shifts from 0.8 to 1.03 eV. Changes in the work function and HOMO level of SubPc are summarized in Fig. 2c. The freshly prepared SubPc film has a work function and a HOMO level of 4.8 and 0.8 eV respectively. As expected, these results are in agreement with those in Fig. 1 within experimental error. Upon aging, the work function and the HOMO level of SubPc downward shift to ~4.5 and ~1.0 eV, respectively. These results show that the organic film degrades on the UV-ozone treated ITO substrate. However, no measurable O signal in XPS can be found in the aged SubPc film. The degradation is mainly characterized by shifting of the E_f away from its HOMO, leading to reduction in mobile hole concentration in the resulting SubPc film. As a reference, the experiment is repeated by preparing CuPc on ITO substrate. The energy level of CuPc film changes as a function of aging time in the same condition is presented in Fig. 2c. The energy levels of CuPc have limited changes during aging. For reference, the valence properties of a freshly prepared and a 12-h UHV stored (without continuous measurement) SubPc films are also examined using UPS. Both the secondary energy cutoff and HOMO peak of SubPc film show negligible energy shift before and after UHV storage.

The experiment is continued by further depositing C₆₀ on the aged ITO/SubPc substrates with corresponding UPS spectra shown in Fig. 3. As the thickness of C₆₀ increases, both the spectra cutoff

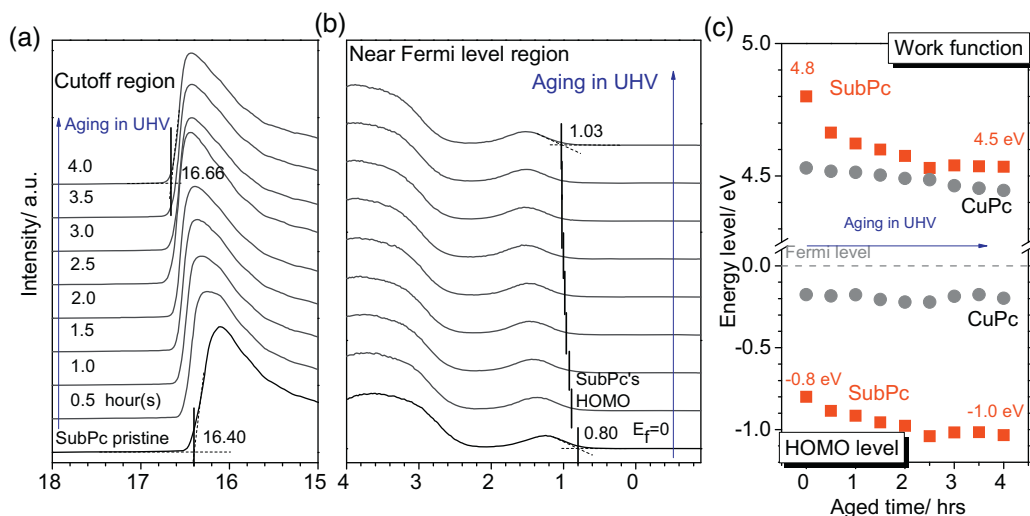


Fig. 2. UPS He I spectra of SubPc film prepared on UV-ozone treated ITO substrate as a function of time at (a) secondary cutoff energy region, and (b) near Fermi level region. All unit marked in the figures are in unit of eV. (c) Energy level of SubPc (solid square) and CuPc (solid circle) film changes as a function of aging time in UHV condition.

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