Influence of ionization energy change on valence band offset in organic *p-n* junction

Kouki Akaike,[1,a] Kaname Kanai,[2] Yukio Ouchi,[1] and Kazuhiko Seki[1]

[1]*Department of Chemistry, Graduate School of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8602, Japan*
[2]*Research Core for Interdisciplinary Sciences, Okayama University, Tsushima-naka 3-1-1, Okayama 700-8530, Japan*

Valence band offsets at [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM)/metallophthalocyanine (MPc, M=Cu and Zn) interfaces have been investigated with ultraviolet photoelectron spectroscopy, which are organic *p-n* junctions in organic photovoltaics. The highest occupied molecular orbitals of MPcs rise toward the interface, while that of PCBM lowers. This behavior implies that the different energy band offsets from inorganic *p-n* junction are realized in organic *p-n* junction. The depletion layers were not observed at the interfaces. Such anomalous energy band offsets are attributed to the interfacial dipole and also ionization energy changes of MPcs and PCBM at the interface. © *2009 American Institute of Physics.* [doi:10.1063/1.3231926]

Organic photovoltaics (OPVs) have been extensively investigated as next class of photovoltaics due to their flexibility and lower cost. The power conversion efficiency (PCE) of both heteroplanar structure and bulk heterojunction devices has reached 5%–6%.[1–5] Greatly recent efforts have been paid to improve the values of PCE, e.g., the synthesis of C_{60}-derivatives,[6–9] the introduction of buffer layer between anode and active layer.[3,10] However, the device operation principle of OPVs is still elusive. The information of electronic structures at organic/electrodes and organic/organic (donor/acceptor) interfaces is highly desired to design high-performance OPVs because the energetics of the exciton and carriers at the interface are keys to understand the functions of OPVs. It is believed that the photoinduced electron transfer occurs at the donor/acceptor interface, so the energy band offsets at the interface should influence the efficiency of the processes. We can describe the charge separation processes in organic *p-n* junctions for OPVs by using the model of inorganic *p-n* junctions, in which the depletion layers are formed and an exciton is separated into hole and electron by the built-in potential. And then, hole and electron are effectively swept away to each electrode. On the other hand, the formation of the depletion layers is unexpected in organic *p-n* junctions, because organic semiconductors are usually used without the intentional doping. Therefore, the band profile in organic *p-n* junctions should be different from that in inorganic *p-n* junctions. Previously, some organic *p-n* junctions have been investigated by photoelectron spectroscopy,[11–14] but the further study is needed to fully understand the environment where the charge carriers are generated.[15]

In this letter, we investigated the valence band offsets at [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) [the molecular structure in Fig. 1(a)]/metallophthalocyanine (MPc) (M=Cu and Zn) interfaces with ultraviolet photoelectron spectroscopy (UPS). These interfaces are used for organic *p-n* junctions in several OPVs.[16,17] We observed the upward shift of the vacuum level (VL) and highest occupied molecu-

lar orbital (HOMO) peaks, which means that the depletion layers weren't recognized at the interfaces in contrast to inorganic *p-n* junction. We also found that the ionization energies of MPc and PCBM change at the interfaces, which attributes to such anomalous shifts of the HOMO peaks.

All organic materials were purchased from Aldrich. CuPc and ZnPc films of 8.5 and 10 nm, respectively, were prepared on indium tin oxide (ITO) in the preparation chamber (base pressure $<1\times10^{-7}$ Pa) by thermal evaporation. And then, PCBM was vacuum-deposited on MPcs films. Prior to the depositions, ITO substrate was solvent-cleaned and treated in UV-ozone. The UPS measurements were
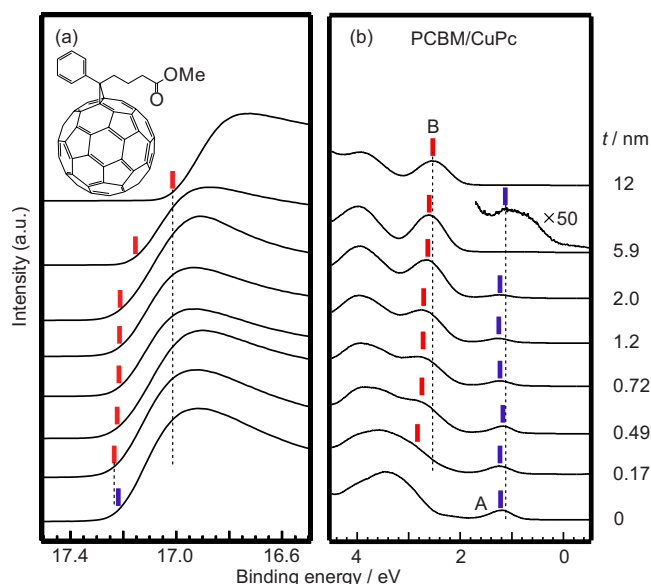

FIG. 1. (Color online) The thickness (*t*) dependence of the UPS spectra for PCBM/CuPc interface in the secondary electron cutoff region (a) and the HOMO region (b) are shown. The ticks in (a) indicate the spectral cutoffs. The peaks labeled by A and B in (b) indicate the HOMO-derived peaks of CuPc and PCBM, respectively. The dashed lines in (a) and (b) are the guides to eyes to recognize the energy shifts of the VL and HOMO peaks. The shoulder structure of the peak A at *t*=5.9 nm is ascribed to the satellite of the C_{60} HOMO peak, which is formed by He I β-line. The inset in (a) is the molecular structure of PCBM.

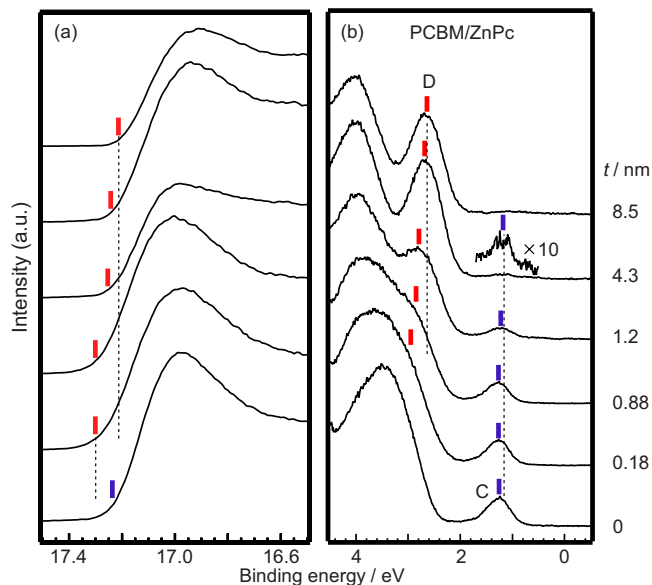a)Electronic mail: kakaike@mat.chem.nagoya-u.ac.jp.

FIG. 2. (Color online) The thickness (t) dependence of the UPS spectra for PCBM/ZnPc interface in the secondary electron cutoff region (a) and HOMO region (b) are shown. The ticks in (a) indicate the spectral cutoffs. The peaks labeled by C and D show the HOMO-derived peak of ZnPc and PCBM, respectively. The dashed lines in (a) and (b) are the guides to eyes to recognize the energy shifts of the VL and HOMO peaks.

FIG. 3. (Color online) (a) Ionization energies (I) of CuPc (squares) and PCBM (circles) at PCBM/CuPc interface, (b) I of ZnPc (triangles) and PCBM (circles) at PCBM/ZnPc interface as a function of PCBM thickness. The values of I for MPcs are plotted by dashed-line because of their ambiguity. The insets in (a) and (b) show the energy diagrams of the HOMOs of MPcs and PCBM at each interface.

performed in the analysis chamber (base pressure $<5 \times 10^{-8}$ Pa), using an electron spectrometer (Omicron spectrometer: EA125). He I resonance line (21.22 eV) was used as the excitation source for UPS measurements. The energies of VL were deduced using the secondary electron cutoffs of UPS spectra in normal emission with the sample biased by -5 V.

Figures 1(a) and 1(b) show the UPS spectra of PCBM/CuPc interface as a function of the thickness of PCBM (t) on CuPc film in the secondary electron cutoff and the HOMO regions, respectively. The secondary electron cutoff indicated by the ticks in Fig. 1(a) shifts toward lower binding energy (E_B) with increasing t to 12 nm by 0.20 eV, which means that the VL rises. We also noticed that the VL is lowered at $t=0.17$ nm by ~0.02 eV. On the other hand, the HOMO peaks of CuPc and PCBM labeled A and B in Fig. 1(b) shift toward lower E_B with increasing t by 0.11 and 0.38 eV, respectively. The similar trends are observed at PCBM/ZnPc interface. The secondary electron cutoff indicated by the ticks in Fig. 2(a) and HOMO peaks of ZnPc and PCBM indicated by C and D in Fig. 2(b) shift toward lower E_B by 0.06, 0.08, and 0.29 eV, respectively. The energies of VLs and HOMO peaks rise with increasing t like PCBM/CuPc interface, although the VL lowers at $t=0.18$ nm. Such upward shifts were also observed in core-level spectra by x-ray photoelectron spectroscopy (the data not shown). Similar trends were observed at other interfaces, C_{60}/CuPc,[11–13] C_{60}/pentacene,[14] and F_{16}CuPc/CuPc interfaces.[17] The observed band profiles at the PCBM/MPc interfaces are completely different from that in inorganic p-n junctions. In inorganic p-n junctions, the downward and upward band bending occur from p- and n-sides to the interface, respectively. The depletion layers are formed to align the Fermi levels. This means that the similar depletion layers cannot be recognized at PCBM/MPc interfaces. Therefore, the lowering of the VL at the early stage of PCBM deposition on MPc
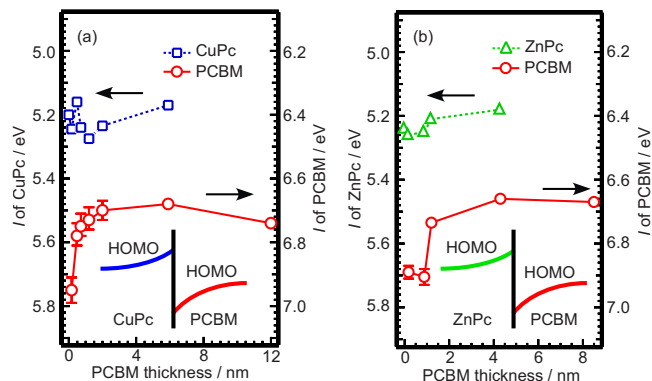
films can be ascribed to not the downward band bending like inorganic p-n junctions, but the shift of the secondary electron cutoff for PCBM toward higher E_B at the interfaces. The upward shifts in VL, HOMO, and core levels by PCBM deposition are attributed to the formation of interfacial dipole which can be caused by the electron transfer from MPcs to PCBM.[18,19] But the origins of the VL shift have been still unclear. According to the semiconductor physics, open circuit voltage (V_{oc}) of OPVs can be described to the built-in-potential, which is the energy width of the downward band bending across p-n junction due to the depletion layers. On the other hand, such energy shifts were not observed at the PCBM/MPcs interfaces as mentioned above. Therefore, we suggest that the origin of V_{oc} for the OPVs including PCBM/MPcs interfaces can't be simply understood using the model of inorganic p-n junction.

We also noticed that the shifts of the HOMO peaks for PCBM are larger about 0.2 eV than those of the VLs. This indicates that the ionization energy (I) of PCBM changes because I is defined as energy difference between the HOMO and VL. Actually, I of PCBM at PCBM/CuPc interface is about 0.2 eV larger than that in thicker region (>2.0 nm), as shown by the circles in Fig. 3(a). The change of I for PCBM can be mainly attributed to the decrease of the polarization energies (P_+) between the interface and bulk regions. The estimation of P_+ is supposed to be deduced by adiabatic ionization energy. However, we used the vertical ionization energies deduced from E_B of the HOMO peaks for qualitative discussion, because it is difficult to recognize threshold of the HOMO peak for PCBM, especially at the interfaces. The value of P_+ is expected to be proportional to molecular polarizability and $N^{4/3}$, where N is the number density of molecules.[20,21] We suggest the possible mechanism of the change in I for PCBM in Figs. 4(a) and 4(b). Yang *et al.*[22] reported that the electron diffraction patterns were clearly observed for PCBM film grown under low-solvent evaporation rate. Since we carefully deposited PCBM on MPc films (approximately 0.1 nm/min.), PCBM film can exhibit the relatively ordered structure. However, the structure of PCBM film at the PCBM/MPc interfaces may be perturbed, leading a decrease in the number density of PCBM at the interface, compared with the bulk. Thus, we suppose that the number density of PCBM at the interfaces [N_1 in Fig. 4(a)] is smaller
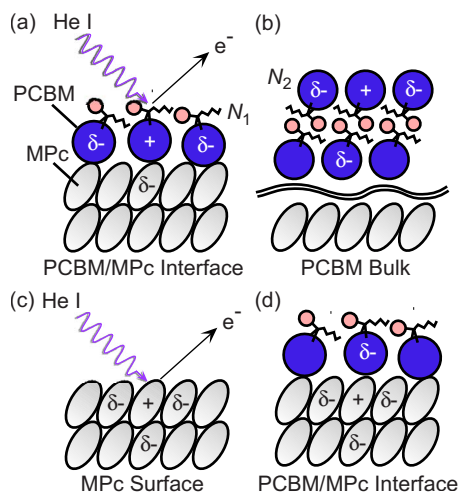
FIG. 4. (Color online) The possible mechanisms of ionization energy changes for PCBM (a) and (b) and MPcs (c) and (d). N_1 and N_2 in (a) and (b) represent the number densities of PCBM at the interfaces and bulk region, respectively.

than that in the bulk region [N_2 in Fig. 4(b)], which leads to a decrease of P_+ at the interfaces. This lowers the E_B of the HOMO for PCBM at the interfaces, which realizes the upward shift of the HOMO peak for PCBM.

We also estimated I for MPcs using the VL of neat MPc films and E_B of the HOMO peaks for MPcs. I of CuPc indicated by the squares in Fig. 3(a) slightly decreases until $t = 5.9$ nm at PCBM/CuPc. The similar decrease in I of ZnPc was observed at PCBM/ZnPc interface [the triangles in Fig. 3(b)]. At surface of the MPc films [Fig. 4(c)], the photohole caused by photoemission is stabilized by the polarization of surrounding MPc molecules. On the other hand, at PCBM/MPc interfaces [Fig. 4(d)], PCBM molecules contacting with the photoionized MPc take part in a stabilization of the photoionized MPc molecule. The polarization of PCBM increases the value of P_+ for MPc at the interface, which can lead the upward shift of the HOMOs for MPcs at the PCBM/MPc interfaces. Finally, it is noted that the photoionized state of the molecule corresponds to the state where one molecule accepts a hole. Therefore, the deduced valence band offset from the photoemission gives direct information about the transport across the interface.

In summary, we observed the upward shifts of the VL and HOMOs at the PCBM/MPc interfaces, which don't correspond with the band profiles of the typical *p-n* junctions. The interfacial dipole and ionization energy changes of MPcs and PCBM at the interfaces influence the valence band offsets, which leads to those anomalous energy shifts. The ob-

served results indicate that the polarization energy should be taken into account to determine the energies of the valence band offsets at organic donor/acceptor interfaces.

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