The effect of ZnO surface conditions on the electronic structure of the ZnO/CuPc interface

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The interfacial electronic structures of zinc oxide (ZnO)/copper-phthalocyanine (CuPc) were investigated by *in situ* x-ray and ultraviolet photoelectron spectroscopy (UPS) to determine the effects of air contamination on the ZnO substrate. UPS spectra showed that the 0.2 eV of the interface dipole is generated at the interface of the air exposed ZnO/CuPc while the interface of the annealed ZnO/CuPc generated -0.2 eV. In both cases, no band bending was observed. On the other hand, band bending at 0.3 eV and an interface dipole of 0.2 eV were observed at the interface of the sputter cleaned ZnO/CuPc. The energy offset between the conduction band maximum of ZnO and the highest occupied molecular orbital of CuPc was determined to be 0.6–0.7 eV for the contaminated ZnO interface while the offset was 1.0 eV for the cleaned ZnO interface. Contaminating moisture has little effect on the offset while the charge transfer was blocked and the offset was decreased in the presence of hydrocarbons. © *2011 American Institute of Physics.* [doi:10.1063/1.3555440]

In recent years, organic photovoltaic (OPV) devices have attracted considerable attention due to their low cost, ease of fabrication, and their flexibility.[1] Many research groups have reported on attempts to improve their performances in terms of efficiency and stability. In particular, to overcome the weakness of organic materials, which include short exciton diffusion length and air instability, organic-inorganic hybrid structures are generally considered to be promising applications.[2] In this respect, zinc oxide (ZnO) is the most widely used inorganic semiconductor in this type of hybrid device because of its high transparency, nontoxicity, the ease of fabrication of thin films and nanostructure properties. In addition, ZnO/organic hybrid photovoltaic devices with inverted structures show a more stable performance in air than other organic-only devices.[3]

However, this hybrid device is usually contaminated at the organic/inorganic interface, as the result of the *ex situ* process associated with the different deposition methods between ZnO and the organic material. The presence of this contaminant may lead to interfacial states and the development of a tunneling barrier.[4] Although some concerns exist regarding this type of hybrid device due to the *ex situ* process used, a detailed understanding of the interfacial electronic structure with organic molecules in hybrid applications of ZnO is not available while the electronic structure and chemical bonding of organic molecules with single crystalline ZnO particles has been investigated.[5] A number of studies regarding the preparation of OPVs using copper-phthalocyanine (CuPc) haves been reported because of the appropriate band gap and desirable absorption properties of CuPc.

In this letter, we report on a study of the electronic structure and energy level alignments of the ZnO/CuPc interface using x-ray and ultraviolet photoemission spectroscopy (XPS and UPS) during the stepwise deposition of CuPc on each ZnO films. The samples were then exposed to air, postannealed after air exposure, and cleaned by Ar$^+$ sputtering. This permitted us to investigate the blocking of charge transfer at the ZnO/CuPc interface, as the result of carbon contamination.

100 nm thick ZnO films were deposited on indium tin oxide (ITO) coated glass substrates using a radio frequency sputtering method with a power of 150 W. The ZnO film showed a (0001) preferred orientation and the properties of the films characterized, as described in a previous paper.[6] We prepared various types of ZnO films and the surface was exposed to a laboratory ambient, annealed in an analysis chamber for 30 min at 300 °C, and cleaned by sputtering using Ar$^+$ ions for 3 min. In the *in situ* measurements, the CuPc (Sigma-Aldrich Co.) was thermally deposited in a deposition chamber that was directly connected to the analysis chamber. We collected photoemission spectra after each deposition step of CuPc, where the CuPc was deposited in steps of 0.2, 0.5, 1.0, 2.0, 5.0, 10.0, and 20.0 nm on each ZnO substrate. The analysis chamber was equipped with a hemispherical electron energy analyzer (PHI 5700 spectrometer), a monochromatic x-ray source (Al $K\alpha$, 1486.6 eV) and an unfiltered UV (He I, 21.2 eV) source. A sample bias of -15 V was applied to measure the work function of the sample. The energy scale of the spectra shown was calibrated with the Fermi level of the sputter cleaned Au substrate.

Figure 1 shows (a) the valance band region of UPS spectra, (b) the position for secondary electron (SE) cutoff shift for the interface between CuPc and air exposed ZnO, and (c) XPS spectra of oxygen and carbon at the air exposed ZnO

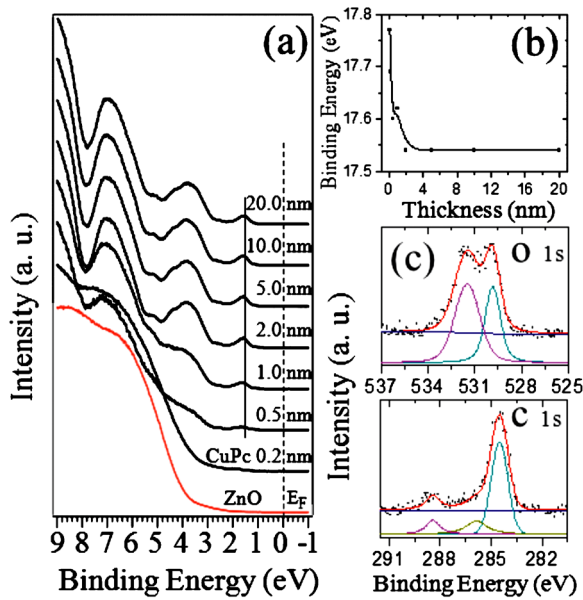a)Author to whom correspondence should be addressed. Electronic mail: mh.cho@yonsei.ac.kr.

FIG. 1. (Color online) (a) Valance band region of UPS spectra and (b) SE cutoff position shift in CuPc deposited on air exposed ZnO film. (c) The O 1s and C 1s XPS spectra for air contaminated ZnO surface.

FIG. 3. (Color online) (a) Valance band region of UPS spectra and (b) SE cutoff position shift in CuPc deposited on a sputter cleaned ZnO film. (c) O 1s and C 1s XPS spectra for sputter cleaned ZnO surface. 0.2 eV of interface dipole with 0.3 eV of bend banding was observed with a clean surface.

surface. All spectra were normalized to permit the effect of interface state to be clearly compared. The top spectrum in Fig. 1(a) shows that the characteristic emission features of CuPc in the valence region emerge in the CuPc sample that was grown on an air exposed ZnO film. The highest occupied molecular orbital (HOMO) onset of the CuPc is 1.2 eV from the Fermi level and a peak shift was not observed in either the XPS or UPS spectra during the deposition sequence, as indicated by the vertical line in the spectrum. This result implies the absence of band bending at the interface. The SE cutoff position shifts toward low binding energies and the shifts become saturated when the CuPc reaches a thickness of 2 nm, as shown in Fig. 1(b). This total shift of 0.2 eV can be attributed to the interface dipole (eD) because band bending does not occur. The XPS spectra in Fig. 1(c)
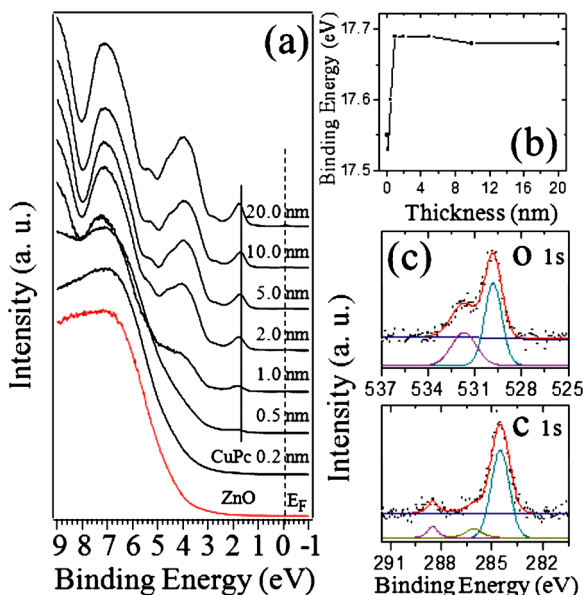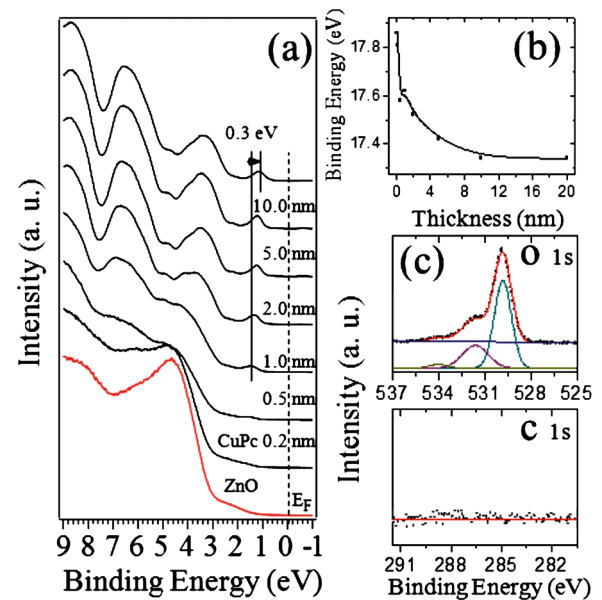
show that a quantity of water and hydrocarbon were absorbed on the air exposed ZnO surface. The O 1s peaks at 529.8 and 531.6 eV are assigned to oxygen atoms in a fully oxidized stoichiometric surrounding and to hydroxyl groups or intermediate states between O^{2-} and dissociated oxygen (O^{1-}), respectively.[7]

In order to eliminate the effect of adsorbed water on the surface, the air exposed ZnO film was annealed at a relatively low temperature of 300 °C for 30 min in a analysis chamber, because the structural transformation of ZnO occurs at higher temperature of 450 °C.[8] The chemical state of the annealed ZnO surface was examined using XPS. A comparison of XPS O 1s spectra of an air exposed ZnO film with that of an annealed film, confirmed that adsorbed water was removed, as evidenced by the fact that the peak at 531.6 eV was drastically decreased at the annealing temperature of 300 °C. On the other hand, the same intensity of the C 1s spectra in the air-exposed film before and after the annealing treatment indicates that hydrocarbons are not desorbed from air exposed ZnO surface. After the annealing treatment of ZnO, we investigated the energy state in detail using UPS, as shown in Fig. 2(a). The HOMO onset of CuPc was constant at 1.4 eV during the deposition and the electron affinity (χ) of ZnO was measured at 4.3 eV. Moreover, the SE cutoff position shift in (b) was 0.2 eV toward higher binding energy, which is opposite that for the dipole of the air exposed ZnO/CuPc interface. Therefore, a −0.2 eV interface dipole without band bending is formed at just the hydrocarbon terminated surface.

After Ar$^+$ sputtering for 3 min, we investigated the ZnO surface using XPS, as shown in Fig. 3(c). The C 1s peak was not observed on the ZnO surface cleaned by Ar$^+$ sputtering. On the other hand, the O 1s peak in the XPS spectrum after the cleaning process was not significantly different from that of the annealed film, as shown in Fig. 2(c). The change in UPS spectrum of the cleaned ZnO surface provides more important information, as shown in the O 2p

FIG. 2. (Color online) (a) Valance band region of UPS spectra and (b) SE cutoff position shift in CuPc deposited on a postannealed ZnO film. (c) O 1s and C 1s XPS spectra for a postannealed ZnO surface.
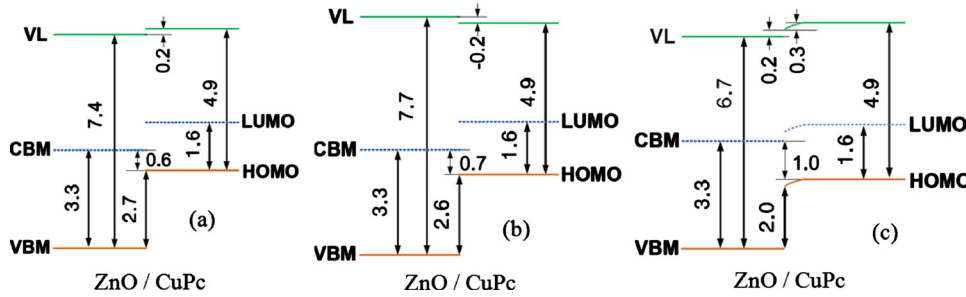
FIG. 4. (Color online) Energy level diagram of ZnO/CuPc for (a) air contaminated ZnO, (b) postannealed ZnO, and (c) sputter cleaned ZnO. The energy offset between CVM of ZnO and LUMO of CuPc which affect Voc are (a) 0.6 eV, (b) 0.7 eV, and (c) 1.0 eV.

state of Fig. 3(a). The χ of sputter cleaned ZnO (3.4 eV) is in good agreement with previous results for a Zn terminated ZnO surface (0001) because oxygen on the surface is preferentially removed by sputtering during the cleaning process.[9] The valence band maximum (VBM) of ZnO and the HOMO onset position appear at 3.0 eV and 0.7 eV from the Fermi level, respectively. During the subsequent deposition of CuPc on the sputtered ZnO surface, the HOMO onset position is shifted to lower binding energy by 0.3 eV. Moreover, only a rigid spectral shift by 0.3 eV in Cu $2p$, N $1s$, and C $1s$ is observed. The consistent shift values indicate that band bending of about 0.3 eV, is generated. Since the total SE cutoff position shift caused by contributions by both the eD and band bending toward a lower binding energy up to 0.5 eV, as shown in Fig. 3(b), the eD between sputtered ZnO and CuPc, 0.2 eV, can be calculated.

Combining all of spectral changes, we drew the band alignments between ZnO and CuPc, as shown in Fig. 4. The vacuum level of the ZnO film was obtained with a position of the SE cutoff and the VBM. We estimated the conduction band minimum (CBM) and the lowest unoccupied molecular orbital (LUMO) position from the reported energy gap of ZnO (3.3 eV) and CuPc (1.6 eV), respectively.[10,11] The χ for ZnO and an ionization energy of CuPc were determined to be 4.0 and 4.9 eV, which are consistent with previously reported values within the error margin of our measurements.[9,12] The band alignment between air exposed ZnO and CuPc in Fig. 4(a) is indicative of a typical staggered junction with a positive 0.2 eV for eD due to charge redistribution. (We defined the positive sign of eD as the direction of the electric field from ZnO to CuPc) The eD, in this case, is not accompanied by a charge transfer from p-type CuPc to n-type ZnO because band bending does not occur. Therefore, charge transfer across ZnO/organic interface can be achieved while that from CuPc to ZnO can be blocked by the presence of water or hydrocarbons that are absorbed during the air exposure of the ZnO surface.[13] Another important finding is that the energy offset between the CBM for ZnO and the HOMO for CuPc was determined to be 0.6 eV, which is believed to be proportional to the open circuit voltage of an organic solar cell.[14] After the annealing treatment, the charge transfer between ZnO and CuPc also is not sufficient to bend the electronic structure. The related band diagram is shown in Fig. 4(b). The energy offset between the CBM for ZnO and the HOMO for CuPc was 0.7 eV and this value was not affected by the annealing treatment, in spite of the opposite direction of eD. Band bending of CuPc was observed only at the cleaned ZnO surface as shown in Fig. 4(c). This band bending occurred due to the depletion region of the CuPc layer by charge transfer across the ZnO/CuPc interface. As a result of

eD and band bending, a larger energy offset (1.0 eV) between CBM of ZnO and HOMO of CuPc was formed in the case of the cleaned ZnO, compared to the contaminated ZnO.

The results reported herein, indicate that ZnO/CuPc hybrid structures have some promise for use in photovoltaic applications. The electronic structure of the clean ZnO/CuPc interface shows band bending of the typical p-n junction and electron transfer from CuPc as a donor to ZnO as an accepter in photovoltaic applications. In addition, the band offset between CBM of ZnO and HOMO of CuPc is sufficiently large to allow for efficient charge separation (1.0 eV). However, contamination of the ZnO surface by hydrocarbons can have a critical effect on band structure. The band offset was reduced from 1.0 to 0.7 eV and the charge transfer was significantly decreased in cases of such contamination. For the case of moisture, contaminating water lowed the χ of ZnO and eD at the interface while the band offset changed just 0.1 eV and the interfacial electronic structure was barely effected.

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