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# Energy level diagrams of C<sub>60</sub>/pentacene/Au and pentacene/C<sub>60</sub>/Au

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#### Abstract

The electronic structures of pentacene and  $C_{60}$  interfaces were investigated using ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS). The magnitudes of measured interface dipole were 0.11 eV and 0.07 eV for the  $C_{60}$  deposited on pentacene ( $C_{60}$ /pentacene) and the pentacene deposited on  $C_{60}$  (pentacene/ $C_{60}$ ), respectively. The obtained C 1s spectra on these samples show that no significant chemical bonds at the interface. The offsets of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) at the  $C_{60}$ -pentacene interface were 1.29 eV and 0.89 eV for  $C_{60}$ /pentacene/Au, while for pentacene/ $C_{60}$ /Au they were 1.5 eV and 1.1 eV. In this paper we present the complete energy level diagrams of  $C_{60}$ /pentacene/Au and pentacene/ $C_{60}$ /Au. © 2005 Elsevier B.V. All rights reserved.

Keywords: Pentacene; Fullerene; XPS; UPS; Interface dipole

## 1. Introduction

Organic thin film transistors (OTFTs) have attracted considerable attention since device properties comparable to those of hydrogenated amorphous silicon thin film transistors (a-Si:H TFTs) were reported in an organic semiconductor [1,2]. Previous studies have brought about many useful developments in materials and devices, allowing us to expect the potential application of organic semiconductors such as pentacene,  $C_{60}$ , and several other organic materials by replacing the traditional inorganic semiconductors in the near future [2–4].

There have been many recent attempts to fabricate the bipolar OTFTs adopting organic multilayer such as PTCDI- $C_{13}H_{27}$ /pentacene,  $\alpha$ -5T/PTCDI- $C_{13}H_{27}$ , and  $\alpha$ -6T/ $C_{60}$  [5–7]. Quite recently, Kuwahar et al. reported the bipolar OTFTs using  $C_{60}$ /pentacene multilayer [8]. The observed field effect mobility and threshold voltage were  $6.8 \times 10^{-2}$  cm<sup>2</sup>/Vs and -15 V in the p-channel operation and  $1.3 \times 10^{-3}$  cm<sup>2</sup>/Vs and 98 V in the n-channel operation; however, these values are inferior to those of the unipolar OTFTs reported previously [9,10]. The electrical properties of bipolar OTFTs must be further improved for

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0379-6779/\$ - see front matter © 2005 Elsevier B.V. All rights reserved. doi:10.1016/j.synthmet.2005.10.001 the meaningful device application. On the other hand, Yoo et al. reported interesting high efficient organic solar cells (OSCs) adopting  $C_{60}$ /pentacene [11]. A detailed understanding of the electronic states at the organic/organic interface is a prerequisite to further improving organic devices.

The electronic structures of organic/metal, organic/insulator, and organic/organic interfaces have been studied by several research groups [12–15]. In this paper we report the detailed electronic structures of the C<sub>60</sub> and pentacene multilayer system. The chemical reaction and charge transfer at the interface were investigated using X-ray photoelectron spectroscopy (XPS). The valence band electronic structure, work function, and ionization potential were examined via ultraviolet photoelectron spectroscopy (UPS). Information about interface dipole, band bending, and the offset of HOMO and LUMO level at each interface was obtained from the valence band and C 1s core level spectra. We have also studied the interface formation of pentacene/C<sub>60</sub>/Au and C<sub>60</sub>/pentacene/Au during the deposition process, and we present complete energy level diagrams of these.

## 2. Experimental

To investigate the interface formation and the resulting electronic structures, pentacene and  $C_{60}$  were evaporated on a sputter-cleaned Au (99.99%) plate step-by-step. The deposition

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rates for both pentacene and  $C_{60}$  were kept at 0.1 Å/s, and the layer thickness was monitored with a calibrated quartz thickness monitor. The background pressure of the preparation chamber was kept at  $1.4 \times 10^{-9}$  Torr during the film deposition. After completion of the desired layer, XPS and UPS spectra were obtained in a PHI 5700 spectrometer using monochromatic Al K $\alpha$  (1486.6 eV) and He I (21.2 eV) sources. Immediately after each layer deposition, the valence band (sample bias = -15 V), C 1s, and Au 4f spectra were collected for both pentacene and  $C_{60}$ . The base pressure of the analysis chamber was  $1 \times 10^{-10}$  Torr, and the energy scale for each spectrum was calibrated based on the Fermi level of clean Au.

### 3. Results and discussion

The UPS spectra collected during the step-by-step layer deposition of the C<sub>60</sub>/pentacene/Au appear in Figs. 1 and 2. The spectra collection was performed in normal emission geometry with a 30° incidence photon angle. Fig. 1 shows the observed spectra near the HOMO region as a function of binding energy. The initial spectral feature of Au becomes weaker, and transforming into that of pentacene as pentacene deposition on the



Fig. 1. The UPS spectra near the HOMO region collected during the step-bystep layer deposition of  $C_{60}$ /pentacene/Au. Each spectrum is shown as a function of binding energy that was calibrated with respect to the Fermi level of the Au layer.



Fig. 2. The UPS spectra near the high binding energy cutoff region collected in situ during the step-by-step layer deposition of  $C_{60}$ /pentacene/Au, where each spectrum was obtained on the sample with indicated thickness of pentacene and  $C_{60}$  layer on clean Au surface.

clean Au surface proceeds. Due to the strong valence band signal of the Au layer, it is difficult to identify the HOMO level of the pentacene at the early stage of the deposition, but, it was recognizable after an approximately 0.8-nm-thick pentacene layer was deposited. The clear observation and energy level identification of the pentacene HOMO level was possible for the sample with pentacene layer more than 50 nm thick. The location of HOMO onset of pentacene was 0.96 eV lower than the Fermi level of Au, as indicated; this corresponds to the hole injection barrier between Au and the pentacene layer [16]. A similar spectral experiment was performed for the C<sub>60</sub> layer deposited on pentacene (102.4 nm)/Au. The recognizable HOMO level of the  $C_{\rm 60}$ appeared after the 0.8-nm-thick C<sub>60</sub> layer deposition. From the sample with a thick  $C_{60}$  layer, we determined that the HOMO onset of the C<sub>60</sub> layer was lay at 2 eV below the Fermi level of Au.

The vacuum level of the pentacene and  $C_{60}$  was determined through linear extrapolation of the UPS spectra near the high binding energy cutoff region. To obtain a clear signal near the high binding energy cutoff region, the sample was biased at -15 V, and the UPS spectrum was taken. Fig. 2 shows the obtained UPS spectra near the high binding energy cutoff region as a function of the binding energy relative to the Fermi level of the Au layer. During the step-by-step deposition of the sam-

ple, each spectrum was collected in situ on the sample with indicated layer thickness of pentacene and C<sub>60</sub> on a clean Au surface. The gradual shift of the high binding energy cutoff of C<sub>60</sub>/pentacene/Au is clear during the deposition. The high binding energy cutoff of the clean Au surface is located at 16.03 eV, and the work function of Au is determined to be 5.2 eV. Even with the small amount of pentacene (0.2 nm) layer deposition, there is a large shift of the high binding energy cutoff toward high binding energy. The shift of high binding energy cutoff was measured by 1.16 eV after enough coverage of the pentacene (102.4 nm) on Au was achieved, which corresponds to the total vacuum level shift between pentacene and Au. The cut off energy shift indicates that an interfacial dipole exists at the pentacene-Au interface. The electron redistribution from Au to pentacene occurred at the interface as the pentacene was deposited on Au, causing interface dipole and resulting in the vacuum level change. On the other hand, the high binding energy cutoff was moved backward as soon as the C<sub>60</sub> deposition on the pentacene layer began. The total shift of the high binding energy cutoff was saturated at 0.36 eV from the cutoff of pentacene after the deposition of a  $C_{60}$  layer above a certain value. The observed result indicates that another dipole layer exists at the  $C_{60}$ -pentacene interface, causing the vacuum level shift of C<sub>60</sub> toward the low binding energy side. The electron redistribution from pentacene to  $C_{60}$  occurred at the  $C_{60}$ -pentacene interface, induced interface dipole, and caused the vacuum level change [17].

The C 1s spectra obtained on the same sample with a monochromatic X-ray source appear in Fig. 3. There was no carbon contamination at the initial Au surface. It can be seen that the C 1s core level peak becomes larger and moves toward the high binding energy as the thickness of pentacene layer on Au increases. The total amount of the C 1s peak shift was 0.4 eV after enough coverage of the pentacene (102.4 nm) was achieved. The lack of significant profile change of the C 1s peak implies the absence of chemical bonds at the pentacene and Au interface, meaning that the magnitude of band bending at the interface is 0.4 eV.

After depositing pentacene on Au, we deposited C<sub>60</sub> stepby-step on the pentacene layer. As Fig. 3 shows, the gradual change of the spectral feature in the C 1s spectrum was clear as the thickness of C<sub>60</sub> layer increased. To investigate the C<sub>60</sub>/pentacene interface in detail, we fitted the C 1s spectra with two peaks corresponding to the carbon bonds in the pentacene and C<sub>60</sub> molecules, respectively. Fig. 4 shows the result for each C 1s spectrum obtained from the sample with pentacene (102.4 nm),  $C_{60}$  (0.8 nm)/pentacene (102.4 nm),  $C_{60}$  (1.6 nm)/pentacene (102.4 nm),  $C_{60}$  (3.2 nm)/pentacene (102.4 nm), and C<sub>60</sub> (51.2 nm)/pentacene (102.4 nm), respectively. The C 1s peak of the pentacene shifted slightly right after the deposition of  $C_{60}$ , moving by 0.5 eV toward the low binding energy after enough coverage of C<sub>60</sub> was achieved. This means that the charge redistribution occurred from pentacene to  $C_{60}$  at the pentacene region. On the other hand, the C 1s peak of the  $C_{60}$  emerged at the beginning of  $C_{60}$  layer growth. The peak shift reached 0.2 eV toward the low binding energy side for  $C_{60}$  (51.2 nm)/pentacene/Au. As a result, we know that the



Fig. 3. XPS spectra of the C 1s core levels obtained on the same sample used in UPS experiment.

band bending occurred at both sides of the pentacene (0.5 eV)and  $C_{60}$  (0.25 eV) interface [14]. The band bending fades out as distance from the interface increases for both pentacene and  $C_{60}$ . We also checked the core level spectra of Au by XPS and found no significant changes in the peak shape (not shown). The peak position of Au 4f was not changed with the deposition of pentacene and  $C_{60}$  onto the Au surface. Therefore, we concluded that the Au surface remained chemically intact by the organic overlayers, and resulting in no band bending in the Au region.

The exact amount of interface dipole, HOMO, and LUMO offset can be calculated by comparing the core level spectra and the valence band spectra of each deposition layer [14]. The total shift of HOMO ( $\Delta$ HOMO) consists of the HOMO offset ( $\Delta H_{cutoff}$ ) and the total band bending shift ( $V_{b}$ (tot)), as given by Eq. (1).

$$\Delta H_{\rm cutoff} = \Delta \rm HOMO - V_{\rm b}(\rm tot) \tag{1}$$

Because UPS and XPS only allow measurements of the occupied molecular orbitals, the LUMO offset ( $\Delta L_{cutoff}$ ) can be determined after considering the band gap of each layer, as shown in Eq. (2), where  $E_g$ (substrate) indicates the band gap of the substrate and  $E_g$ (layer) is the band gap of the deposited layer on the substrate. Here, we used the previously reported band gap values of 2.2 eV for pentacene and 2.6 eV for C<sub>60</sub> [18,19].

$$\Delta L_{\text{cutoff}} = \Delta H_{\text{cutoff}} - [E_{\text{g}}(\text{layer}) - E_{\text{g}}(\text{substrate})]$$
(2)



Fig. 4. Fitting results for each of C 1s spectrum obtained from the sample with pentacene (102.4 nm),  $C_{60}$  (0.8 nm)/pentacene (102.4 nm),  $C_{60}$  (1.6 nm)/pentacene (102.4 nm),  $C_{60}$  (3.2 nm)/pentacene (102.4 nm) and  $C_{60}$  (51.2 nm)/pentacene (102.4 nm), respectively.

The exact amount of interface dipole can now be obtained by subtracting the difference of the ionization energy of the deposited layer  $E_{ion}(layer)$  and that of the substrate  $E_{ion}(substrate)$  from  $\Delta H_{cutoff}$ , as shown in Eq. (3).

$$eD = \Delta H_{cutoff} - [E_{ion}(layer) - E_{ion}(substrate)]$$
(3)

As a result, we obtained 0.11 eV as the magnitude of the interface dipole between the pentacene and  $C_{60}$ . The LUMO offset was 0.89 eV, and the HOMO offset was 1.29 eV. The complete diagram of the electronic structure for  $C_{60}$ /pentacene/Au appears in Fig. 5.

We observed the electronic structure of the pentacene/ $C_{60}$ /Au film with a similar approach. The HOMO level of the  $C_{60}$  was recognizable from the sample with a 0.4-nm-thick  $C_{60}$  layer. After enough coverage of the  $C_{60}$  (25.6 nm) on Au was achieved, the HOMO onset of  $C_{60}$  was 1.7 eV away from the Fermi level of Au, indicating the magnitude of hole injection barrier from Au to  $C_{60}$ . The difference of high binding energy cutoff for  $C_{60}$  and Au was 0.54 eV. The HOMO level of the pentacene emerged after the deposition of 3.2-nm-thick pentacene on  $C_{60}$  (25.6 nm)/Au. The HOMO onset was located at 0.6 eV below the Fermi level of the Au, while the high binding energy cutoff of pentacene was shifted 0.33 eV toward the high binding energy for the thick pentacene layer deposition on  $C_{60}$  (25.6 nm)/Au.

Fig. 6 shows the fitting result for each C 1s spectrum obtained from the samples with  $C_{60}$  (25.6 nm), pentacene



Fig. 5. The complete energy level diagram of C<sub>60</sub>/pentacene/Au.

 $(0.8 \text{ nm})/C_{60}$  (25.6 nm), pentacene (1.6 nm)/C<sub>60</sub> (25.6 nm), pentacene (12.8 nm)/C<sub>60</sub> (25.6 nm), and pentacene (102.4 nm)/C<sub>60</sub> (25.6 nm). The C 1s peak of the C<sub>60</sub> was shifted 0.1 eV toward the low binding energy, and the C 1s peak of the pentacene was shifted 0.4 eV toward the high binding energy for pentacene (102.4 nm)/C<sub>60</sub>/Au. As a result, the band bending at the C<sub>60</sub>-



Fig. 6. Fitting result for each of C 1s spectrum obtained from the sample with  $C_{60}$  (25.6 nm), pentacene (0.8 nm)/ $C_{60}$  (25.6 nm), pentacene (1.6 nm)/ $C_{60}$  (25.6 nm), pentacene (12.8 nm)/ $C_{60}$  (25.6 nm) and pentacene (102.4 nm)/ $C_{60}$  (25.6 nm), respectively.



Fig. 7. The complete energy level diagram of pentacene/C<sub>60</sub>/Au.

pentacene interface was 0.1 eV for  $C_{60}$  and 0.5 eV for pentacene. The band bending in both sides diminishes as distance from the interface increases. From this calculation we obtained 0.07 eV as the magnitude of the interface dipole between the  $C_{60}$  and pentacene. The LUMO offset was 1.1 eV, and the HOMO offset was 1.5 eV, as Fig. 7 shows.

The comparison of energy level diagrams for  $C_{60}$ /pentacene/Au and pentacene/ $C_{60}$ /Au shows the asymmetric feature of their electronic properties. The HOMO and LUMO offsets at the pentacene- $C_{60}$  interface increased when the pentacene was deposited on the  $C_{60}$  layer. In other words, both the HOMO and LUMO offsets decreased by about 0.2 eV when the  $C_{60}$  was deposited on the pentacene layer, indicating a different amount of charge redistribution for  $C_{60}$ /pentacene and pentacene/ $C_{60}$ .

To compare the interface formation of the two cases, the attenuation of the C 1s spectrum originating from the bottom organic layer was examined as a function of top organic layer thick-



Fig. 8. The attenuation of C 1s spectrum as a function of top organic layer thickness. Open circles represent the C 1s spectrum of pentacene from  $C_{60}$ /pentacene/Au while closed circles do the C 1s spectrum of  $C_{60}$  from pentacene/C<sub>60</sub>/Au.

ness, as Fig. 8 shows. Open circles represent the C 1s spectrum of pentacene from  $C_{60}$ /pentacene/Au, and closed circles represent the C 1s spectrum of  $C_{60}$  from pentacene/ $C_{60}$ /Au. The C 1s spectrum of pentacene for  $C_{60}$ /pentacene/Au decays more rapidly than that of  $C_{60}$  for pentacene/ $C_{60}$ /Au, showing that the dense and uniform  $C_{60}$  overlayer formation occurs on the pentacene/Au rather than the pentacene overlayer on  $C_{60}$ /Au. The dense and uniform nature of the  $C_{60}$ -pentacene interface for  $C_{60}$ /pentacene/Au seems to enhance charge redistribution on the interface, resulting in better energy level alignment and supporting the smaller HOMO and LUMO offset and the larger interface dipole, as shown in the energy level diagram.

## 4. Conclusions

In conclusion, we obtained the complete energy level diagrams of C<sub>60</sub>/pentacene/Au and pentacene/C<sub>60</sub>/Au. We determined the magnitudes of the interface dipoles and band bendings occurring at the pentacene-C<sub>60</sub> interface. The measured HOMO and LUMO offsets at the C<sub>60</sub>-pentacene interface were 1.29 eV and 0.89 eV for C<sub>60</sub>/pentacene/Au, and they were 1.5 eV and 1.1 eV for pentacene/C<sub>60</sub>/Au. This shows the strong dependence of interface characteristics on the layering order in organic devices. The dense and uniform nature of the C<sub>60</sub>-pentacene interface for C<sub>60</sub>/pentacene/Au resulted in smaller HOMO and LUMO offsets and a larger interface dipole. The obtained results suggest that the device structure of C<sub>60</sub>/pentacene/Au is more favorable for the ambipolar OTFTs using C<sub>60</sub> and pentacene.

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