

Origin of the highest occupied band position in pentacene films from ultraviolet photoelectron spectroscopy: Hole stabilization versus band dispersion

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The electronic structure of pentacene/graphite, pentacene/Cu-phthalocyanine (CuPc)/graphite, and pentacene/SiO₂/Si(100) was studied by ultraviolet photoelectron spectroscopy as a function of the thickness of the pentacene film. We observed that the binding energy position of the highest occupied molecular orbital (HOMO) of pentacene becomes significantly lower on CuPc and SiO₂ surfaces than that on graphite. Furthermore, a splitting of the UPS band was observed only for the HOMO of thicker crystalline films on CuPc and SiO₂ surfaces, where the molecules are oriented with their long axis nearly perpendicular to the substrate surface. The splitting is ascribed to the intermolecular band dispersion, and the decrease in the threshold ionization energy on CuPc and SiO₂ surfaces originates from the HOMO-band dispersion as well as the increase in the relaxation/polarization energies, which may be caused by the better molecular packing structure with a nearly standing molecular orientation.

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I. INTRODUCTION

Organic optoelectronic devices usually comprise a structure of a hole transport layer, an electron transport layer, and several organic-metal and organic-organic interfaces.¹ The information on the electronic structure of these interfaces is essential in evaluating the performance of the devices and improving their characteristics by engineering interfaces for efficient carrier injection and transport. Energy-level alignment at organic-metal interfaces is dominated by charge exchange, chemical reaction, and/or interface electronic effects such as adsorbate-induced modification of the metal surface.² The formation of the interface dipole and the shift of the vacuum level (VL) are thus studied at these interfaces. The hole-injection barrier at organic-metal interfaces, which is defined as an energy difference between the Fermi level of the substrate (E_F^{sub}) and the highest occupied molecular orbital (HOMO), is determined by the metal work function (WF), the ionization potential (IP) of the molecule, and the interface dipole.^{2,3}

On the other hand, several groups have investigated organic-organic interfaces and found that the shift of the VL is generally small compared to that of organic-metal interfaces.¹ In some case, however, relatively large electrostatic dipole was observed, indicating that a significant charge transfer occurs through the interfaces.^{4,5} In relation to these works, Gao *et al.* demonstrated that the binding energy (E_B) of an organic electronic state can be tuned by p doping with acceptor molecules,⁶⁻⁹ and the control of the energy level at an organic-organic interface has become widely studied.¹⁰⁻¹³ Changes in the electronic structure near such organic-organic interfaces have generally been considered to originate from charge transfer through the interface,⁶⁻¹³ and the origin of the charge transfer has been discussed recently with the charge neutrality level existing near the interfaces.^{4,5} In contrast, Yamane *et al.* pointed out that a change in molecular orientation induces an electrostatic dipole in Cu-phthalocyanine (CuPc) thin films to affect the molecular en-

ergy level and VL.¹⁴ However, little is confirmed experimentally about the effects of molecular orientation/packing structure on electronic structures near organic-organic and organic-insulator interfaces. As a result, for example, there is a large variation in the reported mobility of pentacene in field-effect transistors (FETs).¹⁵⁻¹⁷

In the solid state, it is widely known that an energetic stabilization effect works on a photoionized molecule by the electronic polarization induced on its surrounding molecules.^{18,19} The stabilization energy stands for the electronic polarization energy (P_+) and a larger P_+ gives a smaller IP. Ellis *et al.* demonstrated that the IP of CuPc film depends on the film structure and growth mode on Au (001) substrate.²⁰ Recently, Amy *et al.* pointed out that P_+ is an important parameter that needs to be taken into account for device modeling, since it has a significant impact on charge-injection barriers.²¹ This also leads to a change in the mobility because of the variation of molecular packing structure, and could be an important origin of the large variation in the mobility of pentacene FETs.¹⁵⁻¹⁷ Furthermore, a HOMO-band broadening is expected for crystalline films due to the intermolecular band dispersion,^{22,23} which contributes to the lowering of the barrier height. Thus, we need to study systems where (i) molecular orientation is well defined and (ii) effective electron transfer through the interface is neglected in order to observe the effects of P_+ and the band dispersion on the charge-injection barrier or molecular energy levels near the interfaces.

In this work, ultraviolet photoelectron spectroscopy (UPS) measurements were performed for three kinds of pentacene films: the first is pentacene on graphite [system (I)], and the second is a pentacene overlayer on well-oriented CuPc thin films, grown on graphite [system (II)]. On graphite, CuPc forms a well-oriented film with a flat-lying molecular orientation by weak van der Waals interaction.^{14,24-26} We observed that the hole-injection barrier at the pentacene/CuPc interface is significantly smaller than that at the pentacene/graphite interface. The observed difference be-

tween the HOMO-band positions of the pentacene layer in these two systems originates from the different IPs, which are caused by the difference in pentacene packing structure in these systems. We then studied the third system, pentacene on a SiO₂/Si(100) substrate, which is used in a pentacene FET device [system (III)], and discussed the electronic structure. We observed a splitting of the HOMO band, which may originate from the intermolecular energy band dispersion, for pentacene(thick)/CuPc/HOPG and pentacene(thick)/SiO₂/Si(100) systems.

II. EXPERIMENT

He I UPS spectra were measured using an apparatus described elsewhere.²⁷ The total instrumental energy resolution of the present measurements was set to be less than 60 meV as measured from the Fermi edge of an evaporated Au film. The sample was biased at -5.0 V so that the secondary-electron cutoff of the spectrum gives the VL. A highly oriented pyrolytic graphite (HOPG/ZYA grade) substrate was cleaved in air just before loading into the sample-preparation chamber ($\sim 10^{-8}$ Pa), and cleaned by *in situ* heating at typically 620 K for 15 h.

In system (I), the purified pentacene²⁸ was carefully evaporated onto the HOPG substrate at a substrate temperature of 295 K. In system (II), we first deposited a 1.6-nm-thick CuPc film on the HOPG substrate with purified CuPc,²⁴ and annealed the system at 420 K for 2 h to obtain a uniform film where the molecules orient with their planes parallel to the substrate surface.²⁶ Next, pentacene was evaporated onto the oriented CuPc film at a substrate temperature of 295 K. The deposition amount and deposition rate (0.05–0.1 nm/min) were measured with a quartz microbalance. For system (III), the SiO₂ substrate was prepared in three steps: (1) the oxidized film on a Si(100) wafer is removed with HF, (2) the Si wafer is oxidized in H₂O₂(30%)+H₂SO₄(99.99%) (3:1), and (3) the oxidized wafer is cleaned by UV/O₃ treatment just prior to loading into the UHV preparation chamber. The SiO₂ substrate was then heated *in situ* in the UHV preparation chamber at 473 K for 15 h. The x-ray photoemission spectroscopy (XPS) spectra of the SiO₂/Si(100) surface showed only a small trace of the C1s signal. No charging effects were detected throughout the measurements. The pentacene was deposited on the SiO₂ substrate kept at 295 K. The preparation method for system (III) is basically similar to that for the pentacene FET device.^{29–32} No annealing was performed for all pentacene films.

For all systems, we repeatedly conducted deposition and UPS measurement. All UPS spectra were measured at 295 K with *p*-polarized He I radiation. The angle between the incident photons and the detected photoelectrons is fixed to 45° with an acceptance angle of $\pm 12^\circ$. The spectra are measured at a photoelectron take-off angle of 0° (normal emission). For all spectra, E_B refers to (E_F^{sub}).

III. RESULTS AND DISCUSSION

Figure 1 shows the He I UPS spectra of the pentacene/HOPG system [system (I)] as a function of the deposition

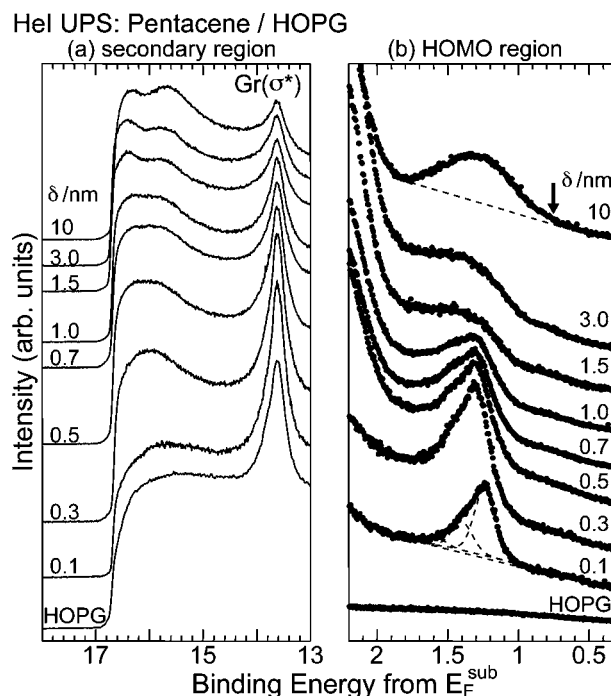


FIG. 1. He I UPS spectra of pentacene/HOPG system as function of deposition amount of pentacene (δ) in secondary region (a) and HOMO region (b). The films are not annealed. All of the spectra are measured at 295 K with a -5 V bias applied to the sample to observe the vacuum level. The E_B scale refers to E_F^{sub} .

amount of pentacene (δ) in the secondary-cutoff region (a) and the HOMO region (b). In Fig. 1(a), the VL hardly shifts (~ 0.01 eV) with increasing δ . In the substrate spectrum, a sharp peak at $E_B = 13.6$ eV, which originates from the σ^* conduction band of HOPG [Gr(σ^*)], is clearly observed, and the intensity decreases with the deposition of pentacene. In Fig. 1(b), for the 0.1-nm-thick film, the onset of the HOMO band is located at $E_B = 1.0$ eV, and the HOMO band consists of at least three components with the same energy separation of 160 meV. This fine structure in the HOMO band originates from the HOMO-hole/vibration coupling.^{27,28} These results indicate that the 0.1-nm film consists of small domains of well-ordered flat-lying molecules on HOPG.^{27,28} The HOMO band becomes gradually broader with increasing δ up to $\delta \approx 3$ nm, and the HOMO peak shifts to the higher- E_B side. The broadening of the HOMO band indicates that the pentacene multiplayer film consists of randomly oriented molecules on the HOPG. Furthermore, in the 10-nm-thick film ($\delta = 10$ nm), the onset of the HOMO band appears at about $E_B = 0.7$ eV (indicated by arrow). The IP of pentacene can be determined directly from the energy difference between HOMO and the onset of the secondary electron cutoff. Sato *et al.* demonstrated that the threshold IP of a pentacene film depends on its crystalline structure.³³ In system (I), for example, we obtained the threshold IP to be about 5.45 eV for $\delta \sim 3$ nm film, whereas 5.15 eV for $\delta = 10$ nm film, in good agreement with the reported value for amorphous-phase pentacene film where the molecules aggregate randomly.³³ The fact that the threshold IP of $\delta = 10$ nm film is smaller than that of thinner films suggests that a thicker film

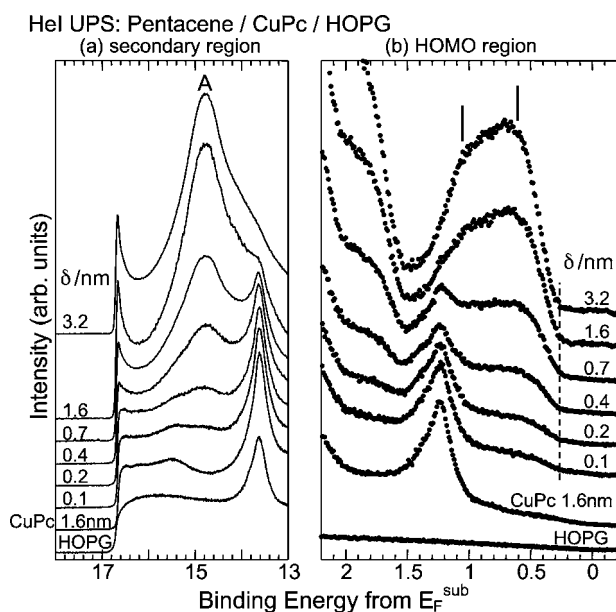


FIG. 2. He I UPS spectra of pentacene/CuPc/HOPG system as function of deposition amount of pentacene overlayer (δ) in secondary region (a) and HOMO region (b). The films are not annealed except for the CuPc film. All of the spectra are measured at 295 K with a -5 V bias applied to the sample to observe the vacuum level. The E_B scale refers to E_F^{sub} .

involves larger- P_+ parts than a thinner film. Ozaki also demonstrated that pentacene molecules lie flat on the HOPG surface in the monolayer but they become gradually inclined with increasing δ at a substrate temperature of 123 K.³⁴ From these evidences, we may consider that the increase in P_+ for thicker films is related to the increase in molecular packing density when molecules become inclined (standing orientation).

Figure 2 shows the UPS spectra of the pentacene/CuPc/HOPG system [system (II)] as a function of the incremental deposition of the pentacene overlayer in the secondary-cutoff region (a) and the HOMO region (b). In Fig. 2(a), the VL shifts hardly (~ 0.02 eV) with increasing δ as in system (I). On the other hand, a new feature A at about $E_B=15$ eV (about 2 eV lower E_B from VL) appears in the secondary region and the intensity increases with δ as discussed in detail later. In Fig. 2(b), the HOMO band of CuPc is located at about $E_B=1.25$ eV with a very narrow band width (FWHM $= \sim 200$ meV) and the shift in the VL is very small, clearly demonstrating that the annealed 1.6-nm CuPc film consists of several uniform layers where the molecules orient with their planes parallel to the substrate surface, and the substrate is fully covered by the molecules.¹⁴ When pentacene is deposited on this CuPc film, a very broad HOMO band of the pentacene overlayer appears with the onset of about $E_B=0.26$ eV independent of δ . Note that the observed onset of the HOMO band of pentacene is located at an E_B position significantly lower than that of system (I). Another important evidence for system (II) is that the HOMO band of CuPc does not shift independent of the pentacene deposition. Thus, we can conclude that (i) the film structure of the underlying CuPc film remains unchanged upon pentacene deposition,

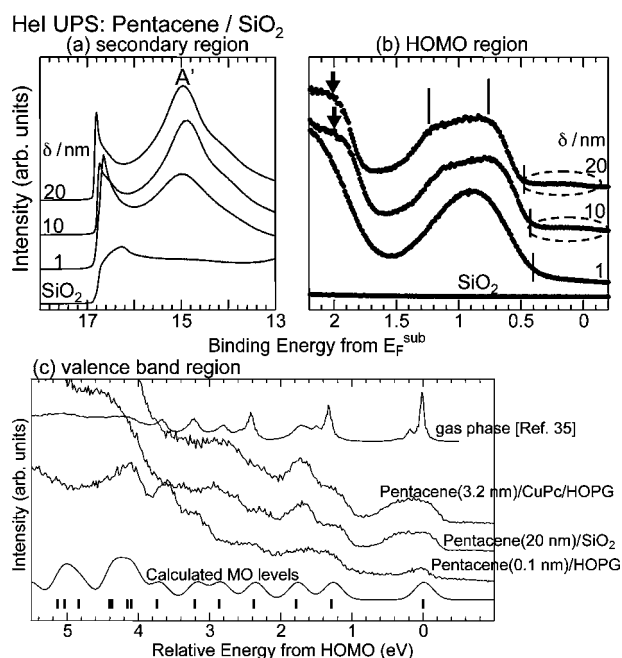


FIG. 3. He I UPS spectra of pentacene/SiO₂/Si(100) system as function of deposition amount of pentacene (δ) in secondary region (a) and HOMO region (b). The films are not annealed. All of the spectra are measured at 295 K with a -5 V bias applied to the sample to observe the vacuum level. The E_B scale refers to E_F^{sub} . Panel (c): The wide valence band region of pentacene/HOPG, pentacene/CuPc/HOPG and pentacene/SiO₂/Si(100) systems, compared with that of the gas-phase spectrum (Ref. 35). The energy is relative to the HOMO peak. MO energies calculated by a DFT (B3LYP/6-31G^{**}) method are also shown.

and (ii) there is no serious charge exchange between pentacene and CuPc. The difference between observed E_B 's of the HOMO-band onsets of pentacene for system (I) and system (II) originates from the difference between the IPs of pentacene films. For system (II), the obtained threshold IP is 4.74 eV, being in good agreement with the reported value for the crystalline phase of pentacene film which is composed of standing molecules.³³ The IP of system (II) is smaller than that of system (I) for both the center and onset of the HOMO band. Thus, the P_+ of system (II) is larger than that of system (I), and the molecular packing density of system (II) is larger than that of system (I). Accordingly, we suppose that pentacene forms a crystalline film on CuPc with a standing molecular orientation. Furthermore, note that the HOMO band consists of at least two features for thicker films. This HOMO-band splitting is a key to the small threshold IP of this system. The origin of this splitting will be discussed later.

Figure 3 shows the He I UPS spectra of the pentacene/SiO₂ system as a function of δ in the secondary-cutoff region (a) and HOMO region (b). As seen in Fig. 3(a), feature A' appears at about $E_B=15$ eV (about 2 eV lower E_B from VL) in good correspondence with feature A in system (II). In Fig. 3(b), the onset of the HOMO band is located at about $E_B=0.4$ eV. The small feature near the E_F (surrounded by a dashed oval) is the HOMO-1 (indicated by arrow) excited by the He I β ($h\nu=23.08$ eV) satellite. From the energy

difference between the onset of the HOMO and the VL, the obtained threshold IP of this system is 4.77 eV, in good agreement with the value for system (II). Features A and A' in the secondary region of the crystalline film were reported in early papers, where the origin was explained by autoionization of molecular excitons.³⁵ However, the present results clearly show that the features considerably depend on the film structure. This structure-dependent characteristic indicates that the features originate from a high DOS of the conduction bands.³⁶ Consequently, it is confirmed that pentacene forms a crystalline film on CuPc and SiO₂. Recently, Oehzelt reported that major parts of the pentacene films grown on a polycrystalline Cu at ambient substrate temperature (below 330 K) have a (001) orientation of the thin-film crystal phase, where molecules are standing due to a lack of the large crystal domains in the substrate required to form a template suitable for initiating epitaxial growth.³⁷ Thus, the present films on CuPc and SiO₂ substrates have a similar (001) orientation.

It is important to note that the HOMO band consists of at least two features in the crystalline films as marked in Figs. 2(b) and 3(b). One may be tempted to consider that this originates from two molecular domains with different P_+ 's. To clarify the origin, the UPS spectra of the pentacene film on each substrate with the gas-phase spectrum are compared in Fig. 3(c) for the extended energy region.³⁸ The energy scale is relative to the HOMO peak. The molecular orbital (MO) energies calculated by a density functional theory (DFT) method are also shown, in which we used an unrestricted open-shell wave function (B3LYP/6-31G**). As seen in Fig. 3(c), HOMO-1 and HOMO-2 in all films do not show splitting as HOMO does, and correspond well to the gas-phase spectrum. This evidence suggests that the origin of the HOMO-band splitting is not the existence of the two domains with different P_+ 's in the film. We thus conclude that the observed HOMO band splitting originates mainly from energy band dispersion, which is attributable to from intermolecular π - π interaction in the crystalline domains of standing molecular orientation.^{21,22} The present results may give a band dispersion of ~ 0.5 eV, which is in good agreement with the theoretical value of about²³ 0.6 eV and may play an important role in providing a high carrier mobility in pentacene FETs.^{15-17,39} The center of the HOMO is located at a smaller E_B for the crystalline pentacene on CuPc and SiO₂. This can be explained by the larger P_+ in these films.

We summarize the energy levels of pentacene and the expected film structure of each system in Fig. 4, where the gas-phase value is cited from the reported value.³⁸ The Fermi level of each substrate is also shown. It is generally not easy to discuss the true effects of crystalline structure and P_+ on the energy-level alignment for usual organic-based interface systems due to the complicated nature and mixed origins of the interface dipole.^{2,40,41} In our systems, on the other hand, there is a little interface dipole layer between pentacene and underlying materials (HOPG, CuPc, and SiO₂). Hence, one can say that, the observed difference in the HOMO- E_B position of pentacene in the present systems is caused by the difference in the IP of pentacene film that depends on molecular orientation/packing structure, which affects the intermolecular dispersion as well as P_+ .

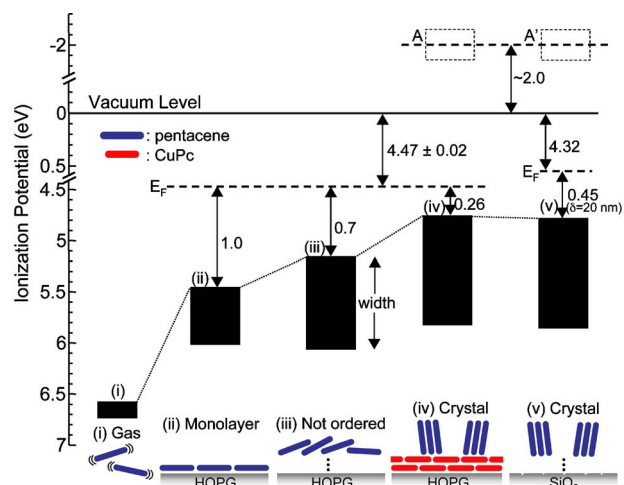


FIG. 4. (Color online) Schematic diagram of energy levels of various pentacene systems from vacuum level; (i) gas phase, (ii) monolayer film on HOPG, (iii) amorphous film on HOPG, (iv) crystalline film on CuPc/HOPG, and (v) crystalline film on SiO₂. The gas-phase value is cited from Ref. 35. The Fermi level of each system is also shown.

Schwieger *et al.* examined the effects of molecule-substrate interaction and the surface roughness of the underlying substrate on the growth of pentacene film by comparing the molecular orientation of pentacene on SiO₂ with that on GeS(001).⁴² If the interaction between pentacene and substrates is stronger than the pentacene-pentacene interaction, the adsorption of the pentacene occurs in a lying geometry. In addition, they suggested that surfaces that are rough on a molecular scale do not provide well-defined adsorption sites for pentacene and a standing molecular geometry can then be favored. The different molecular orientation in the present systems (I), (II), and (III) can also be understood in terms of a different interaction between pentacene and the underlying surfaces, since the intermolecular interaction of pentacene is nearly similar for all films. We here note from our experimental results that the interaction between pentacene and HOPG is stronger than pentacene-pentacene interaction in the first monolayer region even for the inert HOPG surface. It is reasonable to suppose that there are enough adsorption sites for pentacene to adsorb in a lying geometry on the HOPG surface, since the HOPG surface is atomically flat. In systems (II) and (III), on the other hand, the film growth is dominated by pentacene-pentacene interaction probably due to the surface roughness of the substrate in a molecular scale as on polycrystalline Cu.³⁷ Although CuPc molecules orient flat on the HOPG surface, it is likely that there are not enough adsorption sites for pentacene.

IV. CONCLUSION

In conclusion, we observed a large variation of about 0.7 eV in the threshold E_B of the HOMO of pentacene films depending on the substrate. The threshold E_B position of the HOMO of pentacene on CuPc and SiO₂ is much lower than that on HOPG. Furthermore, we found evidence of intermo-

lecular energy band dispersion in crystalline pentacene films on CuPc and SiO₂, which may play an important role in the hole-injection barrier and a high carrier mobility in pentacene FETs. The difference in the threshold positions of the HOMO band in these systems originates from the difference in the relaxation/polarization energies and the fairly large energy band dispersion, which are caused by the difference in molecular orientation/packing structure. The present results show that it is important to prepare a film with better

crystallinity to realize better electrical properties even for polycrystalline films.

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