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Electron affinity of pentacene thin film studied by radiation-damage free inverse photoemission spectroscopy

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The electron affinity of pentacene thin films has been evaluated during the last decades, but it is still under controversial due to varieties of film quality and radiation damages of the films introduced during inverse photoemission spectroscopy (IPES) experiment together with insufficient energy resolution of the instruments. We employed the near-ultraviolet IPES with a better energy resolution $0.27 \sim 0.32$ eV and using lower energy electron beams ($0\,\text{eV} \leq \text{Ei} \leq 4.9\,\text{eV}$) to study the unoccupied states of pentacene thin film. Due to a large mean-free-path of the electron in this energy region, the threshold electron affinity of the bulk of pentacene film was precisely determined to be 2.70 ± 0.03 eV. Using the threshold ionization energy of 4.90 ± 0.05 eV determined by ultraviolet photoemission spectroscopy, the band-gap energy of the pentacene film is obtained to be 2.20 ± 0.06 eV. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4821445]

Organic electronic devices, such as organic field effect transistor (OFET),[1–4] organic light emitting diodes (OLED),[5–7] and organic photovoltaic cell (OPV),[8–10] have developed rapidly in recent years, which have clearly shown their unique advantages in low cost, light weight, flexible properties, and so on. To improve the performance of organic devices, mechanisms of charge transfer/transport and charge separation have been widely investigated. These studies need accurate information on the electronic structure responsible to the processes. In general, however, it is not easy to reveal the electronic structure not only at substrate-molecule interfaces but also of the molecular film itself because the ionization energy (IE) and electron affinity (EA) of the film depend on the molecular orientation, crystal structure, and packing density.[11,12]

Pentacene is a typical organic material applied for OFET because of its high hole mobility.[1,3] The band-gap energy between highest-occupied and lowest-unoccupied molecular orbital (HOMO and LUMO) states of pentacene has been studied extensively during the last decades, but it is still under controversy. Different values have been reported with various methods, for instance, 2.8 eV when considering charge-transfer exction,[13] 2.2 eV[14] and 2.25 eV[15] by using photoconductivity measurement, 1.82 eV[16] from the optical absorption, and 2.2 eV from theoretical calculation.[17] However, there are very few reports on the band-gap energy determined accurately by ultraviolet photoemission spectroscopy (UPS) and inverse photoemission spectroscopy (IPES), because of limited number of reports on the EA value determined with IPES experiments. IPES has drawbacks in investigating organic materials due to its poor energy resolution and serious radiation damage of the target organic film introduced by the electron impact.

Based on the above background, recently Yoshida[18] developed the near-ultraviolet IPES (NUV-IPES) with which the unoccupied states of organic materials can be precisely examined at a higher energy resolution without damaging the samples.[18] In this study, we investigated the unoccupied states of pentacene thin film to measure precisely the EA with NUV-IPES and discussed the HOMO-LUMO band-gap energy by using the IE determined with UPS.

The NUV-IPES instrument is a homemade isochromat mode IPES. It consists of an Erdman-Zipf electron gun (E-gun), a focus lens for effective collection of the emitted photons, and a bandpass photon detector. The E-gun uses a barium-oxide (BaO) coated disc cathode, which was chosen for its low operating temperature of $T = 1150$ K aiming to minimize the thermal spread of electron velocities and avoid emission of excess stray light in the NUV region. The photon detector consists of a changeable optical bandpass filter (Semrock, Inc.) and a photomultiplier tube (R585, Hamamatsu Photonics). The wavelength of the bandpass filter is in the range of 254–335 nm with the corresponding photon energy $h\nu$ from 3.71 to 4.89 eV, which makes it possible to use lower kinetic energy electron beam for radiation-damage free IPES measurements of organic thin films. The optical lens and photon detector with the changeable bandpass filter were placed outside the vacuum chamber, while the E-gun was in the vacuum chamber. The details of the equipment were described elsewhere.[18]

Indium tin oxide (ITO) substrates (10-nm ITO sputtered on a quartz plate) were commercially purchased (Geomatec. Co. Ltd), ultrasonically cleaned by acetone and ultra-pure water, and then treated in UV ozone. 10-nm-thick pentacene films were prepared by vacuum evaporation on the ITO substrates at the deposition rate of 0.5 nm/min in a separated UHV chamber and then introduced to the UHV measurement chamber of NUV-IPES. Note that exposing the film to 1 ATM air (nitrogen and oxygen) during the sample transfer to the measurement chamber results in only a shift of the Fermi level (E_F) in the band gap giving the IE of HOMO unchanged.[19,20] The same result can be expected for LUMO and EA.

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The Fermi level (E_F) of the IPES spectrum was determined by measuring a clean Ag substrate. The vacuum level (E_{vac}) was determined from the inflection point of the low-kinetic-energy cutoff of the electron transmission current spectrum for each IPES experiment. The energy resolution[21] of the spectra was measured as 0.29, 0.30, 0.32, and 0.27 eV for the bandpass filters with the center wavelength of 254, 280, 285, and 335 nm from the first derivative of the Fermi edge in the Ag IPES spectra.

The data acquisition time that is necessary to obtain radiation-damage free spectra was evaluated in advance by using typical organic molecules copper phthalocyanine (CuPc)[18] and diindenoperylene (DIP). No spectral change was found after 5 eV electron beam irradiation for 1 h at the electron-beam current around 1.0 μA. The present NUV-IPES measurement of the pentacene was carried out with the electron kinetic energy below 5 eV at the beam current of about 1.0 μA and each spectrum was recorded in an acquisition time less than 1 h. Actually, no remarkable change was observed for the spectra of the pentacene film at the present measurement conditions. We here mention that spectral changes due to radiation damage of the film were detected when 10 eV electron beam was used, which is in the typical electron beam energy range in the conventional IPES experiments.

Pentacene thin films prepared on ITO substrates consist of well-ordered molecules with standing orientation, and the IE of 10-nm thick thin film was measured with He I UPS as described in the supplementary material.[43]

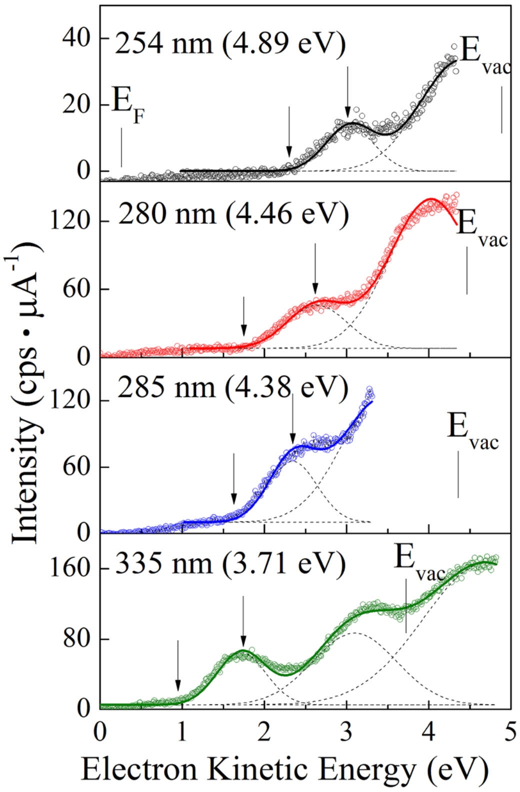

FIG. 1. NUV-IPES spectra of pentacene using four bandpass filters with different center energies. The vacuum level (E_{vac}) and Fermi levels (E_F) are shown by vertical bars. The work function is 4.63 eV for each spectrum. The onset and peak positions of LUMO are indicated by arrows. The energy resolution of the spectra was measured as 0.29, 0.30, 0.32, and 0.27 eV for the bandpass filters with the center wavelength of 254, 280, 285, and 335 nm.

NUV-IPES spectra of pentacene films on ITO are shown in Fig. 1, where spectra measured with four bandpass filters with the center wavelength of 254 nm (4.89 eV), 280 nm (4.46 eV), 285 nm (4.38 eV), and 335 nm (3.71 eV) are displayed after the intensity is normalized by the incidence electron current and subtracting a constant background. The measurement was repeated for two times with each filter to make sure that there are negligible effects of radiation damages in the spectra. We observed no spectral change in the final spectrum with $h\nu = 335$ nm (highest energy resolution). E_{vac} and E_F positions in each spectrum are indicated by vertical bars, and the onset and peak positions of LUMO features are by arrows. Each of the four spectra shows essentially similar features as reported in the previous study.[22] The spectral features, including onsets and peaks of the unoccupied states, shift rigidly with the photon energy of the bandpass filter.

Note that there is a weak intensity (tail) below the LUMO onset. It is not from the ITO substrate since the conduction band of the substrate begins to appear at 1.7 eV above E_F.[23] We assume that this weak feature is due to light emission from high-density molecular excitons created by the intense electron beam. It is known that there are conduction band features in pentacene films (standing orientation) at ∼1.7 eV above E_{vac},[12] but the similarity of IPES features in Fig. 1 independent of the kinetic energy regions of

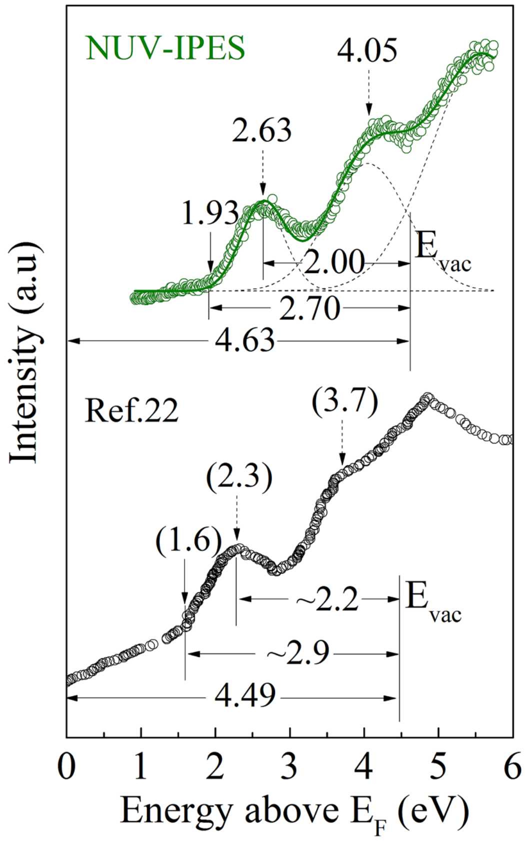

FIG. 2. NUV-IPES (green, 10-nm film on ITO) of pentacene compared with the reported conventional IPES result[22] (black, 7.5-nm film on Au). The E_{vac} is shown by vertical bar in each spectrum. The onset of LUMO is indicated by solid arrow, and peak positions of LUMO and 2nd unoccupied level are by dashed arrows. The values in brackets are estimated by the present authors.

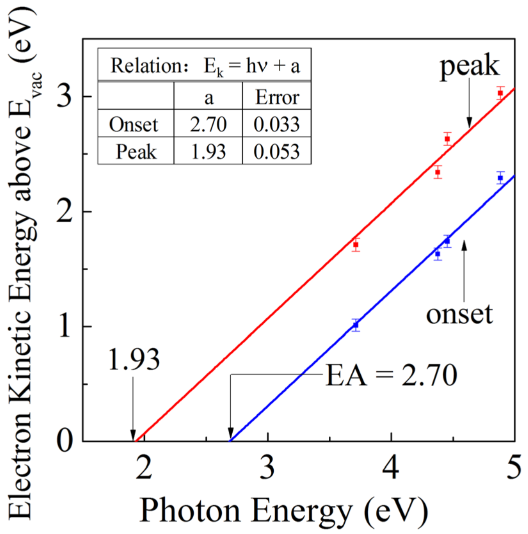

FIG. 3. The kinetic energies (E_k) of LUMO onset (blue) and peak (red) in Fig. 1 plotted as a function of the photon energy ($h\nu$). The energy resolution is shown with error bars. Fitting the LUMO onset energies to a linear function with unity slope ($E_k = h\nu + a$) gives the electron affinity (EA = 2.70 eV) of the pentacene film from the intercept (a in the inset table).

incidence electron beams indicates that the initial state effect in the spectra due to the conduction band features can be negligible.

In Fig. 2, the present NUV-IPES spectrum (with $h\nu = 3.71$ eV) is compared with the IPES spectrum measured by Amy *et al.* for a 7.5-nm-thick pentacene film on a polycrystalline Au at an energy resolution of 0.45 eV.[22] Amy *et al.* carried out IPES measurements for pentacene films of different thicknesses, 2.5, 5, 7.5, and 10 nm,[22] where they found that the EA (as at the LUMO peak) decreases slightly with the thickness due to an decrease in the polarization energy, showing thickness dependent changes in the packing structure in the Au film. As clearly seen in Fig. 2, the NUV-IPES peak shape is much clearer and sharper. In Fig. 2, we estimated energies of the onset and peak positions of the features in Amy's IPES using their original figure,[22] since they did not report the exact values in Ref. 22. The work function estimated with Amy's IPES is 4.49 eV, which is smaller by 0.14 eV than the present value (4.63 eV). Furthermore, it is seen that Amy's spectral features are shifted by ~0.3 eV to the E_F in comparison with the NUV-IPES. The difference of the energy positions between the NUV-IPES and Amy's spectrum may be caused by difference of the packing structure of the films, the density of band gap states (DOGS),[19] and the different energy resolution of the two measurement systems. Exposure of the film to air, in the present NUV-IPES experiments, leads to only a shift of the E_F to the HOMO due to a tiny increase in the

TABLE I. The present EA and related reported energies [ionization energy (IE_{onset}), electron affinity (EA_{onset}), threshold HOMO-LUMO band-gap energy (ΔE_{HL}), transport gap (ΔE_{trans}), and optical band-gap (ΔE_{opt})] of pentacene (values in eV).

Sample	Substrate/comment	IE_{onset}	EA_{onset}	ΔE_{HL}	ΔE_{trans}	ΔE_{opt}	References
10 nm film	ITO	…	2.70	2.20	…	…	This work
7.5 nm film	Polycrystalline Au	5.1[a]	2.9[a]	2.2[a]	…	…	22
0.2 nm film	SnS_2	5.41	…	…	…	…	25
0.2 nm film	Au(111)	5.07	…	…	…	…	25
1 nm film	HOPG	4.74	…	…	…	…	26
1 nm film	ITO	4.74	…	…	…	…	26
10 nm film	ITO	4.90	…	…	…	…	43
20 nm film	ITO	4.90	…	…	…	…	27
3 nm film	HOPG	5.15	…	…	…	…	12
10 nm film	PEDT/PSS[e]	5.0	…	…	…	…	28
12 nm film	C_{60}	5.00	…	…	…	…	29
40 nm film	Au(111)	5.25	…	…	…	…	19
15 nm film	SiO_2	4.90	…	…	…	…	19
20 nm film	SiO_2	4.90	…	…	…	…	30
Single crystal	…	4.95	…	…	…	…	27
ML crystalline film[b]	Bi(001)	4.76	…	…	…	…	31
8 nm crystalline film[c]	Cu(110)	4.77	…	…	…	…	32
12 nm crystalline film[d]	HOPG	5.5	…	…	…	…	33
Gas phase	…	6.54–6.58	…	…	…	…	34,35
300 nm film	Ag/glass	…	…	…	2.8	…	13
0.6–3 μm film	Au film, photoconductivity	5.07	2.70–2.87	2.2	…	…	14
Single crystal	Photoconductivity	…	…	2.25	…	…	15
200 nm film	Al film	…	…	…	…	1.82	16
50–150 nm films	ITO and glass	…	…	…	…	1.80	36
Solution	…	…	…	…	…	2.13	37
Calculation	…	5.03	2.64	…	2.4	1.85	24
Calculation	…	4.8	2.6	2.2	…	…	17

[a] The values were estimated by the present authors from the original figure in Ref. 22.
[b] Monolayer crystalline film of standing molecules.
[c] Single crystalline multilayer film.
[d] Oriented polycrystalline thin film (long molecule axis parallel to the surface).
[e] poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate).

DOGS,[19] thus giving a larger LUMO onset energy in Fig. 2, while the EA keeps the value unchanged.

The kinetic energies (E_k) of four onsets and peaks of the LUMO observed in Fig. 1 are plotted against the detected photon energy ($h\nu$) in Fig. 3 to evaluate the EA and the LUMO position from the E_{vac} by the least-squares fitting of the relation $E_k = h\nu + a$ (a is constant, giving EA, etc.), where the peak positions of the LUMO are obtained by fitting the spectra with Gaussian curves. This procedure can effectively depress the systematic error existing in determining the threshold EA and the peak energy of the LUMO due to unexpected change in the electron kinetic energy at very low energy region. The resultant energy from E_{vac} to the LUMO onset (threshold EA) is 2.70 ± 0.03 eV, and to the peak position is 1.93 ± 0.05 eV. Bussolotti *et al.*[19] obtained the electron mean-free-path of pentacene thin films (λpen) to be $9\,\mathrm{nm} < \lambda\mathrm{pen} < 27\,\mathrm{nm}$ for electron kinetic energy region 3.8–4.4 eV, indicating that the present EA and the LUMO position are not those for the surface region but for the bulk region of the pentacene films.

In Table I, the present EA and related reported values of pentacene are summarized, including threshold EA by IPES,[22] photoconductivity and internal photoemission yield,[14] threshold IEs by UPS,[12,19,22,25–35,43] band-gap energies obtained by photoconduction[15] and estimated by optical absorption,[16,36,37] and calculated results.[17,24]

It is known that pentacene has 3 major different phases in solid state, thin film phase, bulk phase, and singly crystal phase.[38–41] Bulk and single crystal phases have a similar packing density, but thin film phase has a smaller density.[41] Although quantitative contributions of preparation conditions of the film on the packing structure, e.g., thin film and bulk phases, are still open questions, the phases can be judged from both the HOMO peak shape of UPS[41] and peak position of X-ray diffraction spectra.[42] For the present films, the bulk phase is estimated from the UPS data of pentacene films on ITO as discussed in supplementary meterial.[43] The IE of 10–20-nm pentacene films (bulk-phase structure) on ITO was determined as 4.90 ± 0.05 eV,[43] and 4.90 eV was also reported for 15-nm pentacene thin film (thin-film-phase structure) on SiO_2,[19] while 4.95 eV for the single crystal.[27] The IEs for the thin film phase[19] and the bulk phase[43] are thus considered to be the same in experimental accuracy.

In order to obtain the HOMO-LUMO gap, we use the threshold IE (4.90 ± 0.05 eV) determined by the present UPS experiment.[43] Hence, the band-gap energy of pentacene films is obtained to be 2.20 ± 0.06 eV, which is considered to be the value for the bulk region of the film (both of thin-film and bulk phases) within the experimental error.

In conclusion, the unoccupied states of pentacene were studied by NUV-IPES, which provides the electron affinity at higher energy resolution, without introducing radiation damages into the pentacene films. The threshold electron affinity was precisely measured to be 2.70 ± 0.03 eV. Using the threshold IE of 4.90 ± 0.05 eV determined by UPS, the band gap energy is obtained to be 2.20 ± 0.06 eV for the thin film. The accurate band gap energy will allow precise discussion on the energy level alignment and exciton binding energy, hence to reveal fundamental properties regarding charge injection, transport, and separation mechanisms.

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[43] See supplementary material at http://dx.doi.org/10.1063/1.4821445 for ionization energy of pentacene on ITO studied by ultraviolet photoemission spectroscopy.