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ABSTRACT

The alignment of organic layer and metal layer energy levels within organic semiconductor devices is critical for efficient charge injection/collection at the electrodes. The electronic structure at the interface is usually examined using ultraviolet photoelectron spectroscopy (UPS) as the film thickness of the organic layer is built up incrementally (bottom-up method). As such, the morphology and crystallinity of the films that are examined using this technique may be different from the films used in actual devices because these properties are sensitive to the way in which the films are prepared. We have prepared [6]phenacene thin films with standing and lying molecular orientations on naturally oxidized silicon (SiO_2) and highly oriented pyrolytic graphite (HOPG) surfaces, respectively. UPS measurements were performed on films that were incrementally decreased in thickness using gas cluster ion beam (GCIB) sputtering (top-down method). The spectral shapes and ionization energies of the films that were formed using the bottom-up and top-down methods were similar. Importantly, the characteristic features of a monolayer on the HOPG substrate were also observed when a thick film (i.e., not built up in layers using the bottom-up method) was thinned down by GCIB sputtering. We have shown that UPS combined with GCIB sputtering is a useful technique for examining the energy level alignment of interfaces within films that are fabricated using conditions similar to those used for real devices.

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The energy level alignment of organic/electrode and organic/organic interfaces has a significant influence on the performance of organic semiconductor devices, including organic light emitting diodes (OLEDs), organic solar cells (OSCs), and organic thin-film transistors (OTFTs). For example, the efficiency of carrier injection/collection is affected by the energy barrier at the interface between the electrode and the organic layer.[1–3] The barriers for holes and electrons are determined by the energy difference between the Fermi level of the electrode and the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) level of the organic layer, respectively. The energy difference between the HOMO level of donor-type organic semiconductors and the LUMO level of acceptor-type organic semiconductors governs the open circuit voltage of an OSC.[4] Therefore, the importance of understanding and controlling the energy level alignment at the interfaces within devices (metal/organic, organic/organic) has been the subject of much investigation for the last two decades.[5–9]

Usually, ultraviolet photoelectron spectroscopy (UPS) is used to evaluate the energy level of an interface because it is a high resolution measurement, it does not cause damage, and it exhibits high surface sensitivity. Using this technique, interface energy levels are commonly evaluated by repeated vacuum deposition of small amounts of an organic material (usually several tenths of nanometers in thickness) and performing the UPS measurements after each deposition (bottom-up method).[5] A deposition rate of 0.01 nm s^{-1} or less is commonly used to ensure precise control over the film thickness. However, this technique forms films in an interrupted fashion, which is different from the formation of thicker films (hundreds of nanometers) used in real devices that are formed in one deposition. Additionally, to increase the efficiency of device manufacturing, the

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deposition rate is typically a few nanometers per second, which is much higher than that used in the bottom-up analysis. As the morphology, crystallinity, and molecular orientation of organic films can be highly sensitive to the fabrication conditions used, the film structures that are formed using the bottom-up method may not be representative of those in real devices.

Therefore, it is desirable to prepare organic films using the same conditions that are used to prepare films in devices and conduct the thickness-dependent UPS measurements by reducing the thickness of an organic film via sputtering (top-down method). However, common sputtering methods that use atomic ions (e.g., Ar^{+}) cause serious damage to organic molecules. It was recently shown that an argon-gas cluster ion-beam (Ar-GCIB) that was applied to a molecular layer did not destroy its molecular structure.[10–14] GCIB sputtering, in combination with X-ray photoelectron spectroscopy (XPS)[15,16] and time-of-flight secondary ion mass spectrometry (TOF-SIMS)[17–19] has been used to analyze the chemical state depth profiles or the composition of organic films.

GCIB has also been used in conjunction with UPS for the analysis of the valence electronic structure of organic films.[20,21] Yun *et al.* examined pentacene thin films on poly (3,4-ethylenedioxythiophene) polymerized with poly-(4-styrenesulfonate) (PEDOT:PSS) and on polycrystalline Au.[22,23] They carefully examined the shape of the valence band spectra and the ionization energies (IEs) and concluded that any sample damage caused by the GCIB sputtering was negligible. Furthermore, the electronic structures of the interfaces (pentacene/PEDOT:PSS and pentacene/Au) were compared using both the bottom-up and top-down methods. Unfortunately, the surface of both PEDOT:PSS and polycrystalline Au is rough. Well-defined, initial monolayers could not be prepared on these surfaces using either the bottom-up or the top-down methods, which resulted in amorphous or disordered structures in the upper organic layers. The energy levels of pentacene thin films are dependent on their orientation because pentacene has a large molecular quadrupole moment. Films with standing or lying orientation have IEs of 4.9 eV and 5.5 eV, respectively.[24] The IEs that Yun *et al.* reported ($\sim$5.0 $\pm$ 0.1 eV) indicated that the pentacene films were close to the standing orientation but disordered. Thus, the influence of the GCIB sputtering on the crystallinity and the orientation of the pentacene molecules could not be determined.

We have examined the dependence of the valence electronic structure on molecular orientation and how this can be used as a method to probe molecular orientation. The influence of GCIB sputtering was examined by initially performing UPS analysis on a film that had it thickness increased incrementally (i.e., bottom-up method) and then analyzing the same film using the top-down method.

[6]phenacene was used for the organic material, shown in Fig. 1. [n]phenacenes, in which *n* benzene rings are fused in a zigzag form, have attracted attention in recent years for use as high mobility materials in OTFT.[25–29] [n]phenacenes have wider energy gaps and higher IEs than [n]acenes (e.g., pentacene), which results in greater chemical stability. Stable driving of OTFTs has been realized under ambient conditions. The mobility of [6]phenacene in an OTFT was reported to be 7.4 $cm^2\ V^{-1}\ s^{-1}$, which suggested that the film was highly crystalline with very little amorphous regions.[30] Furthermore, [6]phenacene possesses a permanent quadrupole moment[31] that is larger than that of pentacene, which results in a large difference in energy levels depending on its molecular orientation. Therefore, the molecular orientation of a [6]phenacene film should be well-defined, and if its orientation is changed by the GCIB, it should be easily detected using UPS.

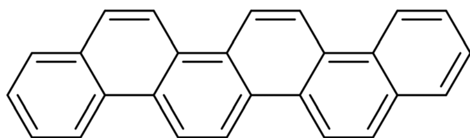

FIG. 1. Molecular structure of [6]phenacene.

The molecular orientation was controlled by the use of specific substrates, as described in the litrature.[24,32–35] Native oxide Si substrate (SiO_2) and an HOPG (highly oriented pyrolytic graphite: ZYA grade) substrate were used. The SiO_2 substrate was cleaned with pure water and then acetone for 5 min each. The surface of the HOPG substrate was cleaned by annealing for 16 h at 670 K using an infrared heater under an ultrahigh vacuum (9×10^{-7} Pa). Sublimation grade [6]phenacene was deposited on the substrates by resistance-heating under vacuum to form the films. The rate of deposition was 0.1 nm s^{-1}, the substrate was at ambient temperature during deposition, and the pressure within the deposition chamber was 8×10^{-7} Pa. The film thickness was monitored with a quartz crystal microbalance.

The films were transferred to a separate vacuum chamber for the UPS analysis without exposing the sample to the atmosphere. UPS measurements were performed using a VersaProbe II system (ULVAC-PHI) with He Iα resonance line (21.22 eV) radiation at ambient temperature and at a base pressure of 3×10^{-8} Pa. The total energy resolution was 100 meV, which was determined by the width of the Fermi level of the Au film. A photoelectron detection angle of 0°, normal to the sample surface, was used, and a bias voltage of −5 V was applied to the sample to collect the secondary electrons. The vacuum level was obtained from the cut-off of the secondary electrons.

The GCIB sputtering was performed with a GCIB-gun (ULVAC-PHI model 06–2500) that was attached to the measurement chamber. The cluster size was set to 2500, the acceleration voltage was set to 2.5 kV, the ion current was 8 nA, and the raster size was 10 $\times$ 10 mm. Under these conditions, the energy per Ar atom corresponded to 1 eV, which was likely why there was negligible damage to the molecules. The sputtering rate of the [6]phenacene thin film was approximately 0.3 nm min^{-1} as determined by dividing the initial film thickness by the sputtering time required for the [6]phenacene peak in the UPS measurement to disappear.

The bottom-up method involved repeated deposition/UPS measurement steps until the film was 10 nm thick. The same films were then analyzed using the top-down method, which involved repeated GCIB sputtering/UPS measurements.

The molecular orientation of [6]phenacene on SiO_2 has been examined previously using X-ray diffraction.[28] The diffraction pattern exhibited strong peaks (0 0 L), with values of L up to 5. The observation of 5th order diffraction was consistent with highly crystalline films. The molecules were oriented with their molecular long axis tilted 30° from the surface normal of the SiO_2 substrate. Although the atomic positions of [6]phenacene have not been determined yet, the molecules are believed to pack with a herringbone arrangement, which is analogous to the single crystal structure of [5]phenacene (picene).[36] Conversely, there are no reports on the molecular orientation of [6]phenacene on HOPG. However, planar aromatic molecules such as pentacene, copper phthalocyanine, and pentacenequinone all adopt a

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lying orientation on HOPG substrates.[37,38] As such, it is likely that the [6]phenacene molecule also adopts a lying orientation, which should be clear from the energy levels determined using UPS.

UPS spectra of [6]phenacene films on SiO_2 (varying film thickness) obtained from the bottom-up and top-down methods are shown in Fig. 2(a). The residual thickness that resulted from the top-down method was calculated from the sputtering rate. The spectra from the film prepared using the bottom-up method contained three peaks in the energy region that was examined. As the film thickness increased, the intensity of the peaks increased, particularly the peak centered at 8.4 eV. Furthermore, a shoulder appeared at 6 eV when the film thickness was 10 nm. The shapes of the spectra observed using the top-down method were nearly identical to those from the bottom-up method. The shoulder at 6 eV disappeared, and the intensity of the third peak (8.4 eV) decreased rapidly. The IEs that were obtained from the onset of the HOMO peak were approximately 5.6 eV and were almost independent of the film thickness and the film preparation method.

The UPS spectrum of [6]phenacene on HOPG that was obtained using the bottom-up method is shown in the lower panel of Fig. 2(b). The IE of this film was approximately 6.2 eV, which was ∼0.6 eV larger than the film on SiO_2. The difference in the energy levels was caused by different molecular orientations. The spectral line shapes of the film on the HOPG substrate were also completely different from those of the films on the SiO_2 substrate. Additionally, they were dependent on the film thickness. When the film thickness was less than 1 nm, the onset of the HOMO peak was steep, and sharp peaks were observed at 6.6 eV [vertical bars, Fig. 2(b)], 7.2 eV, and 8 eV. As the film thickness increased, the two low energy peaks broadened and merged into a single broad peak. This behavior can be attributed to band dispersion arising from the intermolecular electronic coupling.

A band calculation based on a predicted single crystal structure of [6]phenacene resulted in large valence band widths of approximately 0.5 eV within the herringbone layer (*ab*-plane), while a few smaller band widths (10 meV) occurred along the *c*-axis.[39] The fact that the first monolayer of [6]phenacene molecules was oriented lying flat on the HOPG surface may indicate that only small intermolecular electronic coupling occurred, while the herringbone arrangement in the multilayer may indicate that large intermolecular coupling occurred, and this resulted in the broadening of the spectral features. This extreme dependence on the thickness was not expected to occur in the films that were oriented in a standing fashion because the herringbone arrangement was already established in the monolayer.

The spectra of [6]phenacene on the HOPG substrate from the top-down analysis are shown in the upper panel of Fig. 2(b). The spectral line shapes from both methods were similar. The spectral features that were attributed to the monolayer were present in the spectra from both methods [top-down method (0.9 nm) and bottom-up method (0.2 nm)]. This indicated that the orientation of the first layer remained the same, even when the 10-nm-thick film was sputtered with GCIB. Therefore, it can be believed that the GCIB method did not affect the electronic state of the [6]phenacene thin film and effectively sputtered away the organic molecules without disturbing their orientation that resulted from weak interactions between the molecules. As such, GCIB appeared able to remove multiple layers of the thick organic film down to a monolayer film.

If the molecular orientation was affected by the sputtering, charge-quadrupole interactions would cause the IE to fall between those of the lying and standing orientations. Therefore, as the value of the energy level was a sensitive parameter that indicated molecular orientation, we examined the dependence of the IE on film thickness, as shown in Fig. 3. The IE of the vertically orientated film on SiO_2, as determined using the bottom-up method, was almost unchanged as the film thickness increased from 1 nm (5.55 eV) to 10 nm (5.56 eV). This result

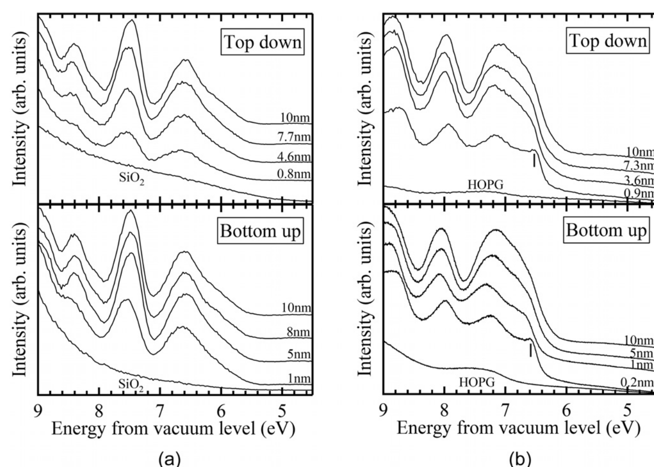

FIG. 2. UPS spectra of [6]phenacene on (a) a SiO_2 substrate and (b) a HOPG substrate obtained using the bottom-up method and the top-down method. Only part of the spectra obtained using the top-down method is shown.

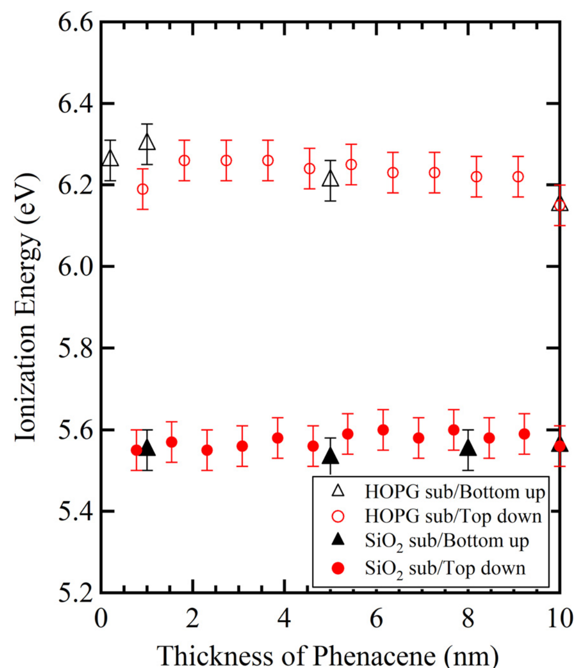

FIG. 3. Ionization energies of [6]phenacene thin films on SiO_2 and HOPG substrates as functions of film thickness, as determined using the bottom-up and top-down methods.

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strongly suggests that the vertical orientation was maintained throughout this film thickness range that was examined. The IEs, as determined using the top-down method, were almost identical to those obtained using the bottom-up method. Conversely, the bottom-up method showed that the IEs of the horizontally orientated film on the HOPG substrate began at 6.3 eV (film thickness <1 nm) and decreased to 6.15 eV (film thickness = 10 nm). The top-down method yielded IEs that were close to those determined using the bottom-up method. If the horizontal orientation of the molecules was disturbed by the GCIB sputtering, the IE must be reduced or a spectral component with a low IE should be observed, neither of which happened.

The fact that the IEs of the [6]phenacene thin films that were determined using the top-down and bottom-up methods were very similar indicated that the top-down method can be used to determine the original electronic state of a film, and it can also detect changes in the IE that are caused by slight changes in molecular orientation. Furthermore, it is possible to perform measurements along the depth of a film as small as a molecular layer by sufficiently decreasing the rate of GCIB sputtering.

In conclusion, we have examined the effects of GCIB sputtering on the electronic structure of [6]phenacene thin films. The UPS spectra of films with varying thicknesses on SiO_2 and HOPG substrates were compared using the bottom-up and top-down methods. The spectral line shapes and IEs from films with standing and flat molecular orientations, determined using the bottom-up and top-down methods, exhibited excellent agreement. Importantly, the details in the spectral line shapes observed in the course of the bottom-up measurements were closely reproduced by the top-down analysis using GCIB sputtering. Therefore, we believe that the top-down method described in this work represents an important way to evaluate the electronic states along the depth direction of organic films that are fabricated using conditions similar to those used for real devices.

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