Electronic Structures of the Highest Occupied Molecular Orbital Bands of a Pentacene Ultrathin Film

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We report the energy dispersions of the highest occupied molecular orbitals (HOMO)-derived bands of a pentacene (Pn) thin film, whose in-plane structure resembles closely that of the *ab* plane of a low-density bulk Pn phase. Our present photoemission result indicates that the overlap of the π-orbitals of adjacent Pn molecules is larger than what was expected from theoretical calculations. Further, of the two HOMO-derived bands, the large dispersion width of the band with higher binding energy suggests that this one mainly contributes to the bandlike charge transport in a Pn crystal.

Organic molecules are promising materials to complement traditional silicon-based electronics, and have stimulated a great deal of interest for a variety of electronic applications [1–4]. Of the large number of organic molecules, pentacene (Pn) that is one of the prototypical conjugated organic molecules forming several polymorphic van der Waals crystals [5–7], has attracted much attention since it has been successfully used in organic thin film transistor with field effect mobility surpassing that of amorphous silicon [4]. At low temperature, the charge transport in Pn has been reported to have a bandlike nature [8,9]. The relatively large band dispersion observed along the *b* direction of Pn in the thin film phase [10] at room temperature suggests that the bandlike charge transport should play a major part at this temperature as well though charge carriers are scattered by lattice vibration [11]. A bandlike transport originates from an adequate overlap of the π-orbitals of adjacent molecules, and the overlap of the orbitals produces orbital-derived electronic bands whose dispersion behaviors correlate closely with the charge transport mechanism. Further, the relation between the contribution of the *coherent* bandlike transport and that of the *incoherent* hopping-related transport to the entire charge transport mechanism is still an outstanding issue in organic crystals. These mean that a proper understanding on the electronic band structures on the *ab* plane shown in Fig. 1 is an essential input to fully comprehend the charge transport mechanism of a Pn crystal. (Here we note that the π-orbitals are predicted to overlap adequately in the *ab* plane and to hardly overlap in the *c* direction.)

Clear widths of the two valence electronic bands derived from the highest occupied molecular orbital (HOMO) have been predicted theoretically [12–19] (the two HOMO-derived bands result from the presence of two nonequivalent Pn molecules in the unit cell as shown in Fig. 1). The predicted anisotropic dispersion of the two HOMO-derived

bands on the *ab* plane [13–19] suggests that there is a preferential charge transport direction in the Pn crystal. However, although this suggestion is important to improve the performance of Pn-based electronic applications, there is no experimental observation on the two-dimensional band structure on the *ab* plane so far. Moreover, since the dispersion width obtained experimentally in Ref. [10] suggests the widths obtained theoretically to be underestimated, an experimental observation of the electronic structure is indispensable to comprehend the electronic properties of Pn correctly. One of the main reasons for the lack of the experimental observation is that a thin single crystal, which allows to measure the two-dimensional electronic structure on the *ab* plane, was difficult to produce. Recently, a single crystal Pn thin film with its *ab* plane parallel to the surface and having a surface area larger than 200 μm^2, whose value is large enough for photoemission measurements, has been reported to grow on a Bi(001) surface [20,21]. This *ideal Pn film* makes possible to measure the band structures of the HOMO on the *ab* plane using angle-resolved photoelectron spectroscopy (ARPES).
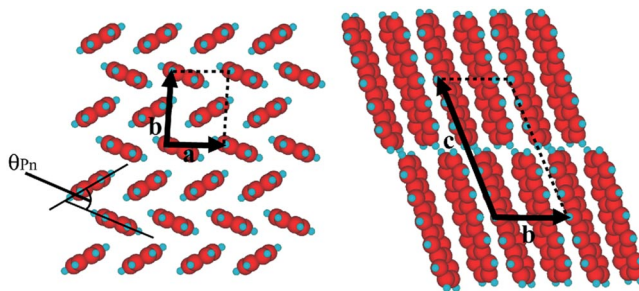

FIG. 1 (color online). The *ab* plane and *bc* plane of a Pn crystal. θ_{Pn} is the angle between the molecular planes of the two inequivalent molecules in the unit cell (the herringbone angle).

In this Letter, we provide the dispersions of the HOMO-derived bands of a 1 monolayer (ML) Pn film grown on a Bi(001) surface along the three symmetrical directions of the *ab* plane. Two HOMO-derived bands, which could not be separated in the former studies, were clearly observed in the ARPES spectra. Of these two bands, the one with higher binding energy (E_B) shows dispersion in all the three directions, while the one with lower E_B hardly disperses. Our present result indicates that the overlap of the π-orbitals of adjacent Pn molecules is larger than what was expected from theoretical calculations, and the observed dispersions suggest that the higher E_B HOMO-derived band mainly contributes to the bandlike charge transport mechanism of a Pn crystal. Note that the band structure on the *ab* plane of a Pn monolayer is reported to strongly resemble that of a three-dimensional Pn crystal [14], and thus the present result would represent the electronic structure on a *ab* plane of the Pn crystal as well.

Photoemission spectra were obtained using an angle-resolved photoelectron spectrometer and an unpolarized He Iα radiation light. The total energy resolution was ~35 meV, and the angular resolution was $\pm0.1°$. The Bi(001) surface was prepared by depositing Bi onto a clean Si(111)-(7 × 7) surface [22] that was obtained by annealing an *n*-type (*P*-doped, 3 Ω cm) Si(111) wafer at 1520 K by direct resistive heating. After depositing Bi at 300 K, the sample was annealed at 380 K to improve the morphology of the Bi(001) film as suggested in Ref. [20]. We checked the quality of the Bi(001) surface by the observations of sharp spots in reflection-high energy electron diffraction (RHEED) and of quantum well states [23] in ARPES. Pn was purified by three-cycle sublimation in an Ar gas stream of 13 Pa, and deposited onto the well-ordered Bi film at a rate of approximately 2.5 Å/min.

Figure 2(a) shows the secondary electron cutoffs measured at different Pn deposition time. The work function of the Bi(001) surface obtained by the cutoff in the lowest spectrum, 4.32 eV, is in good agreement with the value reported for Bi in the literature [24–26]. As the deposition time increases, the work function becomes small and saturates at a time of 6 min. Taking the deposition rate of Pn into account, a time of 6 min indicates that the work function has been saturated when the Pn film thickness is ~15 Å, i.e., a thickness that corresponds to a coverage of 1 ML when the Pn molecules have their long molecular axes almost perpendicular to the surface (standing up orientation). By considering the saturated work function of Pn films, 3.91 eV, and the binding energy (E_B) at which the HOMO of Pn rises up, ~0.85 eV [see Fig. 3(a)], we obtain a threshold ionization potential of 4.76 eV. This value is in good agreement with the value reported for Pn films that are composed of standing molecules [27,28]. Further, the constant work function at Pn coverages higher than 1 ML indicates that there is no charge transfer at the Pn-Bi interface, and we therefore conclude that the inter-
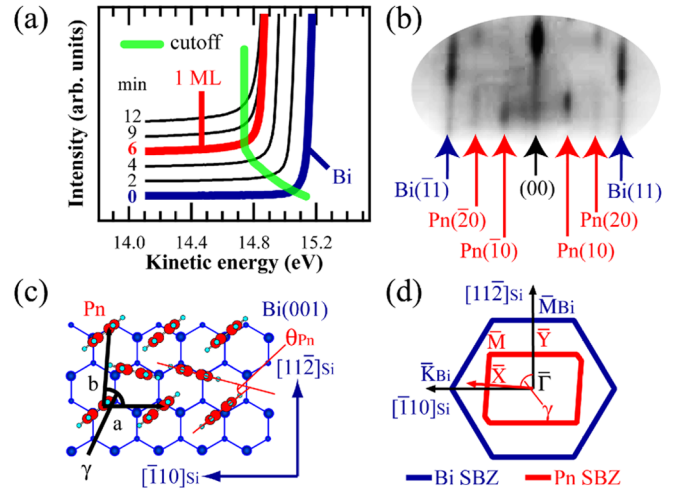

FIG. 2 (color online). (a) Pn deposition time-dependent secondary electron cutoff measured with the sample biased at −15.0 V. (b) RHEED pattern of the 1 ML Pn film obtained with a 15 keV electron beam along the $[11\bar{2}]$ direction. (a) and (b) are obtained at room temperature. The adsorption sites of Pn on Bi(001) obtained by the RHEED pattern are displayed in (c). (d) Surface Brillouin zones (SBZs) of the Bi(001) surface and the Pn surface parallel to the *ab* plane. $\bar{K}_{Bi}$ and $\bar{M}_{Bi}$ are the symmetry point of the Bi(001) SBZ, and $\bar{X}$, $\bar{Y}$, and $\bar{M}$ are those of the Pn SBZ.

action between a Pn molecule and the Bi surface is considerably weak. This conclusion evidences the interaction between Pn and Bi proposed in the former studies [20,21].

Spots originating from both the 1 ML Pn film and the Bi(001) surface are observed in the RHEED image obtained at room temperature [Fig. 2(b)]. The unit cell parameters of the *ab* plane of the Pn film obtained from the RHEED spots ($a = 6.0 \pm 0.2$ Å, $b = 7.9$ Å, and $\gamma = 86 \pm 1°$) indicate that the present 1 ML Pn film has the same structure as that observed using STM, in which the parameters are reported to be $a = 6.170$ Å, $b = 7.871$ Å, and $\gamma = 86.33°$ [29]. The protrusions observed in the STM image of Ref. [21] suggest that the herringbone angle (θ_{Pn}) of the 1 ML Pn film on Bi(001) is $52 \pm 5°$. These value indicate that the structure of the 1 ML Pn film used in the present study is almost the same as the structure of the low-density bulk Pn phase ($a = 6.06$ Å, $b = 7.90$ Å, $\gamma = 85.8°$, and $\theta_{Pn} = 52.2°$) [5]. The intensities of the RHEED spots originating from the Pn film became weak a few hours after preparing the sample at room temperature even without irradiating the electron beam. Since this result means that Pn molecules mobile at room temperature and make the film disordered after a certain time, we have cooled down the sample to 140 K in order to make the Pn film more stable. The RHEED pattern observed at 140 K was the same as that observed at room temperature, and the intensities of the Pn originating RHEED spots hardly changed in the order of day at this low temperature. The same RHEED patterns means that there is no phase tran-
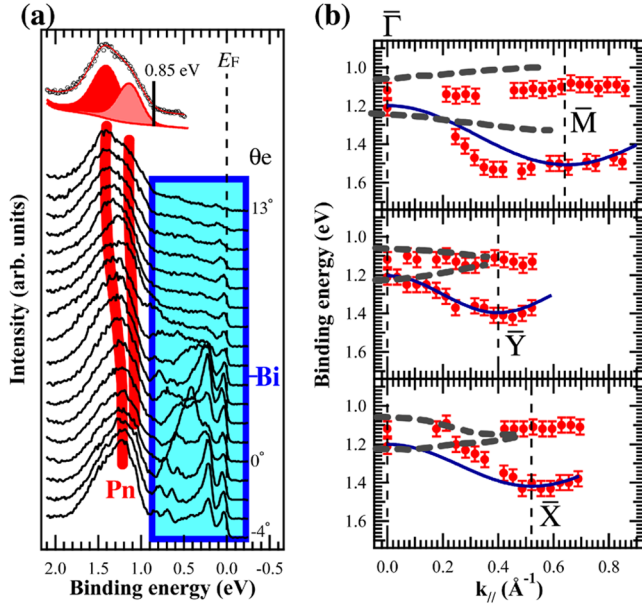
(a)

(b)

FIG. 3 (color online). (a) ARPES spectra of the Pn 1 ML on Bi(001) measured at 140 K along the $\bar{\Gamma}$-$\bar{Y}$ direction. The uppermost spectrum shows the decomposition of the Pn induced structure at $\theta_e = 13°$. (b) Band dispersions of the two HOMO-derived bands of the 1 ML Pn film adsorbed on Bi(001). The theoretical dispersions of the HOMO-derived bands reported in Ref. [19] are indicated by dashed lines. Solid curves are the dispersion obtained by analyzing the higher E_B HOMO-derived band using a simple tight-binding model.

sition within this temperature range for the Pn film used in the present study. Further, the RHEED patterns show that a single-domain Pn film was obtained, and thus the ARPES spectra can be analyzed without the ambiguity that would have otherwise been caused by contributions from the two other domains.

The ARPES spectra of a 1ML Pn film adsorbed on Bi(001) measured along the $\bar{\Gamma}$-$\bar{Y}$ direction at 140 K are shown in Fig. 3(a). Of the structures observed in the spectra, the intensities of those between $E_B = 0$ and 0.9 eV decrease at higher Pn coverages. This result indicates that these structures originate from the Bi(001) substrate. Moreover, the binding energies of the structures that originate from Bi and their relative intensities resemble closely to those observed on a clean Bi(001) surface [23]. The close resemblance supports the above-mentioned conclusion that the interaction between a Pn molecule and the Bi substrate is considerably weak.

The intensities of the structures observed between $E_B = 1.0$ and 1.8 eV increased at higher Pn coverages, i.e., in a E_B range where no strong feature has been observed on a Bi(001) clean surface. Taking this result into account and by considering that the E_B of the HOMO-1 is more than 1 eV higher than that of the HOMO [28], we conclude that the origins of these structures is derived from the HOMO of Pn. The HOMO-derived structure has a peak at $E_B \sim$

1.2 eV with an asymmetric line-shape at a photoelectron emission angle (θ_e) of $-4°$. This asymmetric line-shape results from hole-vibration coupling [30,31]. The line shape of the HOMO-derived structure becomes less asymmetric at $\theta_e = 0°$, and the peak position starts to shift to higher E_B at $\theta_e = 3°$. At $\theta_e = 7°$, the HOMO-derived structure clearly splits into two peaks, and at $\theta_e = 13°$, it shows a peak at $E_B \sim 1.4$ eV with a shoulder at $E_B \sim 1.1$ eV. These observations suggest the presence of two HOMO-derived bands. In order to confirm the presence of two bands, we have analyzed the spectra using Voigt functions and a polynomial background. The uppermost spectrum shows the decomposition of the Pn induced structure at $\theta_e = 13°$. The open circles are the experimental data, and the solid line overlapping the open circles is the fitting result that is obtained using the components shown below the spectrum. The thick lines overlapping the HOMO-related structures shows the dispersions of the two HOMO-derived bands obtained from the fitting results.

In order to show the overall dispersions of the HOMO-derived bands, the ARPES spectra are put into E_B-$k_\parallel$ diagrams, where $k_\parallel$ is the momentum parallel to the surface along the $\bar{\Gamma}$-$\bar{M}$, $\bar{\Gamma}$-$\bar{Y}$, and $\bar{\Gamma}$-$\bar{X}$ directions in Fig. 3(b). The dashed curves shown in Fig. 3(b) are the theoretical dispersions of the HOMO-derived bands of the low-density bulk Pn phase reported in Ref. [19]. (The dispersions of the HOMO-derived bands reported in Ref. [16] were almost the same as those in Ref. [19], though there is a difference of approximately 0.1 Å in the structural parameters used in the two calculations. This indicates that although the structural parameters are not exactly the same, our results would represent the electronic structure of the low-density bulk Pn phase.) Of the two experimental HOMO-derived bands, the dispersion behaviors of the experimental higher E_B band are completely different from those obtained theoretically, whereas the behaviors of the lower E_B band, which disperses slightly upward in the $\bar{\Gamma}$-$\bar{M}$ direction and hardly disperses in the two other directions, show agreements between experimental and theoretical results. The experimental higher E_B band disperses downward while the theoretical one disperses slightly upward in the $\bar{\Gamma}$-$\bar{Y}$ and the $\bar{\Gamma}$-$\bar{X}$ directions, and although both the experimental and theoretical higher E_B bands disperse downward in the $\bar{\Gamma}$-$\bar{M}$ direction, their dispersion widths are different. The dispersion widths of the experimental higher E_B band are 330 ± 40 meV, 210 ± 40 meV, and 220 ± 40 meV along the $\bar{\Gamma}$-$\bar{M}$, $\bar{\Gamma}$-$\bar{Y}$, and $\bar{\Gamma}$-$\bar{X}$ directions, respectively. These values show reasonable agreement with the width reported in a former experimental study [10]. Moreover, the maximum difference in binding energy between the higher E_B band and the lower E_B one, ~ 460 meV, is almost the same as the values reported for Pn films with standing up orientation on different substrates [28]. This similarity suggests that the large dispersion widths obtained in the present study are intrinsic in the 1 ML standing Pn film and do

not result from an external effect such as Pn-substrate interaction. Since a larger dispersion width suggests a stronger intermolecular electronic coupling, we conclude that the π-π interaction between adjacent molecules is stronger than what was predicted theoretically.

Within a simple tight-binding approximation, in which the dispersion is given by $E_B = E_c - 2t\cos(2\pi k_\parallel/a^*)$, the charge transport is discussed [31,32] in terms of hole mobility that can be expressed as $\mu_h = e\tau/m_h > (e/m_h) \times (\hbar/W)$, and can be simplify as $\mu_h > 20(m_0/m_h)(300/T)$ in the case of $W > k_B T$ [33,34]. E_c, t, a^*, τ, m_h, m_0, and W are the energy of the band center, the transfer integrals, the wave number between two $\bar{\Gamma}$ points in the corresponding direction, the relaxation time due to scattering, the free electron mass, the effective mass of the hole, and the width of the higher E_B HOMO-derived band. As shown in Fig. 3(b), the calculated dispersion obtained by the above equation (solid curve) agrees well with the experimental one along the $\bar{\Gamma} - \bar{Y}$ direction. The agreement shows the validity of using the above approximation for the hole mobility, and leads to an estimation of $m_h = 1.26m_0$ and $\mu_h > 34.1$ cm^2/V s at 140 K, a mobility that is larger than those reported for a low-density bulk Pn phase in the literature but comparable to the value reported recently for the high-density bulk Pn phase [8]. In contrast to the agreement along the $\bar{\Gamma}$-$\bar{Y}$ direction, the calculated dispersions do not agree well with those obtained experimentally along the two other directions. The disagreement suggests that the wave function is no longer able to be expressed in terms of a set of localized states, and thus that the charge carriers are more delocalized in the $\bar{\Gamma}$-$\bar{M}$ and $\bar{\Gamma}$-$\bar{X}$ directions than in the $\bar{\Gamma}$-$\bar{Y}$ direction. This delocalization suggests a high carrier mobility, and we therefore conclude that the bandlike charge transport plays a role that is considerably large even in the low-density bulk Pn phase.

In conclusion, we have shown the dispersions of the two HOMO-derived bands of an ultrathin Pn film grown on Bi(001) along the three symmetrical directions of the ab plane. We have also provided evidences of the weak interaction between a Pn molecule and the Bi(001) surface that was expected in the literature [20,21]. Of the two HOMO-derived bands, the higher E_B one shows dispersion along the $\bar{\Gamma}$-$\bar{M}$, $\bar{\Gamma}$-$\bar{Y}$, and $\bar{\Gamma}$-$\bar{X}$ directions with widths of 330 ± 40 meV, 210 ± 40 meV, and 220 ± 40 meV, respectively, while the lower E_B one hardly disperses in all the three measured directions. Our present result indicates that the overlap of the π-orbitals of adjacent Pn molecules is larger than what was expected from theoretical calculations. Further, the dispersion behaviors of the two HOMO-derived bands suggests that the one with higher E_B mainly contributes to the bandlike charge transport, and that the hole mobility is considerably large.

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