PHYSICAL REVIEW B **68**, 033102 (2003)

Intermolecular energy-band dispersion in PTCDA multilayers

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(Received 26 August 2002; published 18 July 2003)

The electronic structure of a well-oriented perylene-3,4,9,10-tetracarboxylic acid-dianhydride multilayer prepared on MoS_2 single crystal surface were studied by angle-resolved ultraviolet photoemission spectroscopy using synchrotron radiation. From the photon energy dependence of normal emission spectra, we observed an intermolecular energy-band dispersion of about 0.2 eV for the highest occupied molecular orbital (HOMO) band of single π character. The observed energy-band dispersion showed a cosine curve, which originates from the intermolecular π-π interaction. Analyses using the tight-binding model gave that the transfer integral of about 0.05 eV for the π-π interaction, the effective mass of HOMO hole $m_h^* = 5.28 m_0$, and the hole mobility $\mu_h > 3.8\ \mathrm{cm}^2/\mathrm{V\,s}$. This is the first observation of the intermolecular energy-band dispersion of a conventional single-component organic semiconductor only with the weak intermolecular van der Waals interaction.

DOI: 10.1103/PhysRevB.68.033102 PACS number(s): 72.80.Le, 73.20.At, 79.60.−i

I. INTRODUCTION

Angle-resolved ultraviolet photoemission spectroscopy using synchrotron radiation (SR-ARUPS) is a powerful technique for direct measurements of the energy-band structures which is a fundamental basis for the understanding of electronic and optical properties of solids.[1,2] There are many reports on the observation of the intramolecular energy-band dispersion originating from the repeating units in a molecule.[3–12] These samples have the sufficiently wide bandwidth (~5 eV) for measuring the dispersion relation due to the intramolecular interaction originating from the covalent chemical bonds in a molecule. Some experimental works have been reported on the intermolecular energy-band dispersion for the families of organic charge transfer salts, such as dicyanoquinonediimide (DCNQI)-metal complex[13] and tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ).[14,15] In a single-component organic molecular film, on the other hand, the energy-band dispersion was observed only for two systems, C_{60} monolayer on GeS(001) (Ref. 16) and bis(1,2,5-thiadiazolo)-*p*-quinobis(1,3-dithiole) (BTQBT) multilayer[17] so far. The bandwidth of the highest occupied molecular orbital (HOMO) band is about 0.5 eV for DCNQI metal complex,[13] 0.75 eV for TTF-TCNQ,[14,15] 0.4 eV for C_{60} monolayer[16] and 0.4 eV for BTQBT multilayer.[17] Among these samples, BTQBT molecule have the sufficiently wide bandwidth for measuring the dispersion relation due to the increasing of the intermolecular interaction by the existence of the chalcogen atoms. For usual single-component organic semiconductors, however, the observation of the energy-band dispersion is in general difficult, because of the small bandwidth due to weak intermolecular van der Waals (vdW) interaction, and a difficulty of preparing well-oriented samples required for SR-ARUPS measurements.

It was reported that the archetypal organic semiconductor, perylene-3,4,9,10-tetracarboxylic acid-dianhydride (PTCDA), molecules orient with the molecular plane parallel to MoS_2 surface from monolayer to multilayer with high stability.[18–20] Therefore, the strong intermolecular π-π interaction due to their packing structure can be expected. In this paper, we report on the intermolecular energy-band dispersion of about 0.2 eV originating from the intermolecular π-π interaction for a well-oriented PTCDA multilayer, leading to an evaluation of the effective mass of the HOMO-hole, the hole mobility and the quantitative intermolecular π-π interaction (transfer integral) from SR-ARUPS measurements.

II. EXPERIMENT

SR-ARUPS measurements were performed at the beam line BL8B2 of the ultraviolet synchrotron radiation (UVSOR) facility at the Institute for Molecular Science. SR-ARUPS spectra were measured by using a newly constructed VG-ARUPS10 system with a multi-channel detector. The monochromatic synchrotron radiation was obtained by a plane-grating monochromator.[21] The energy resolution was 150 meV as measured from the width of Fermi edge of gold, and the acceptance angle of the photoelectron was ±0.8°.

The incidence photon energy ($h\nu$) dependence was measured for 30-Å-thick PTCDA multilayer (~8 ML) at an

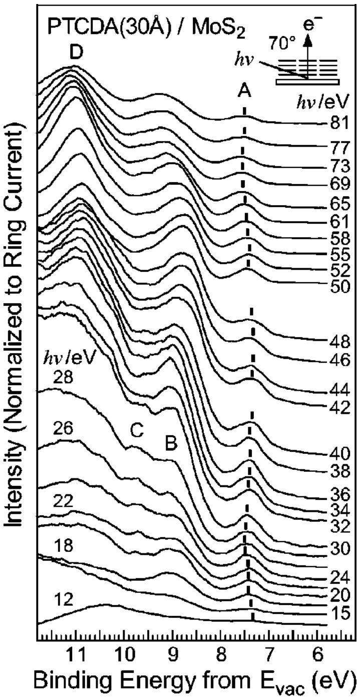

FIG. 1. Photon energy ($h\nu$) dependence of SR-ARUPS spectra along the surface normal for the 30-Å-thick PTCDA multilayer ($\sim$8 ML) prepared on the MoS_2 surface. The binding energy (E_B) scale refers to the vacuum level (E_{vac}).

electron take-off angle $\theta=0°$ (normal emission) and a photon incidence angle $\alpha=70°$. The $h\nu$ was tuned from 12 to 81 eV. In the present measurement, change of the PTCDA sample due to radiation damages was not observed.

A MoS_2 single crystal substrate was cleaved in the sample-preparation chamber ($\sim 10^{-10}$ Torr), and the quality of substrate surfaces was confirmed by SR-ARUPS and LEED measurements. The PTCDA sample, which was purified typically by three sublimation in a current of argon gas ($\sim$0.25 Torr), followed by two sublimation in a high vacuum of $\sim 10^{-5}$ Torr, was carefully evaporated onto the MoS_2 surfaces in the sample-preparation chamber. The film thickness and the deposition rate ($\sim$0.7 Å/min.) were measured with a quartz microbalance by assuming that the density of the film is similar to the single crystal (1.70 g/cm^3). The molecular orientation of the present PTCDA film was studied by LEED (Ref. 18) and the θ dependence of SR-ARUPS spectra.[19] From these, we confirmed that the PTCDA molecules orient with the molecular plane parallel to the MoS_2 surface.

III. RESULTS AND DISCUSSION

Figure 1 shows the $h\nu$ dependence of normal emission spectra for the well-oriented PTCDA multilayer, where the binding energy (E_B) is measured from the vacuum level (E_{vac}) and photoemission intensities are normalized to the ring current. In Fig. 1, band A, which is assigned to a single π character state distributed over the perylene core (π_P, HOMO),[19,20] is well separated from other valence bands. Other valence bands B, C, and D are assigned to some π_P states, n_O(C=O) states derived from oxygen $2p$, and some π_P and n_O states, respectively.[19,20] For the HOMO band, the continuous and significant change of the peak position and intensity are clearly seen with increasing $h\nu$. At $h\nu=12$ eV, the E_B of the HOMO peak is about 7.34 eV. With increasing $h\nu$, the HOMO band shifts to the higher E_B side, and turns back at $h\nu=26$ eV. Also, at $h\nu=44$ and 73 eV, the similar turn back of the peak exists. The total shift of the HOMO band is about 0.2 eV. For the origin of such a small E_B shift, one may consider the depth dependence of the relaxation energy of the HOMO hole as reported by Salaneck.[22] If this is the case, the HOMO band must shift to the higher E_B side with increasing $h\nu$ until $h\nu=20$ eV, then turn back and keep the shift to the lower E_B side, since the depth dependence of the relaxation energy of the HOMO hole depends on the kinetic energy (E_K) dependence of the photoelectron mean-free-pass in organic solids which has a minimum at $E_K\sim 15$ eV.[22,23] In the present measurements, however, the observed E_B shift was periodic and the E_B shift of the HOMO band was not observed in the θ dependence of the spectra.[19] By considering these results, we attribute the E_B shift of the band to the intermolecular energy-band dispersion. On the other hand, bands B, C, and D also show changes in peak positions and intensities depending on $h\nu$. They can be originate from the $h\nu$ dependence of photoionization cross section of various electronic states as well as the energy-band dispersion. Therefore, we will not discuss these in the present paper.

The energy-band dispersion of the HOMO band (A) can be determined using the simple tight-binding model with only nearest neighbor interactions as reported in the previous paper.[17] According to the tight-binding model and assuming the free-electron-like final states, the energy-band dispersion along the surface normal is given by

$$E_B(k_\perp)=E_B^0-2t\cos(a_\perp k_\perp), \tag{1}$$

$$k_\perp=[2m_e^*(h\nu-E_B-V_0)]^{1/2}/\hbar, \tag{2}$$

where E_B^0, t, $a_\perp$, $k_\perp$, m_e^*, and V_0 are the energy of the band center, the transfer integrals, the lattice spacing normal to the surface, the wave vector component of photoexcited electron along surface normal, the effective mass of the photoelectron in the final continuum state, and the average inner potential in the solid for the final free-electron-like parabola, respectively.

For the experimental determination of the energy-band dispersion, we need to determine the value of V_0. By assuming the direct inter-band transitions, a parabolic free-electron-like band in a constant V_0, and free electron mass m_0 for the final state, V_0 can be determined from the $h\nu$ dependence of the photoemission intensity[4,5,12] of the HOMO band as shown in Fig. 2. In the present system, the nearly free-electron-like final-state bands becomes flat at the Γ point due to the gap opening, and the occupied band is nearly flat due to their very small band dispersion. Therefore, we can expect a large joint density-of-state (DOS) for the direct transition leading to a maximum in the peak intensity when $h\nu$ matches the energy separation between these bands

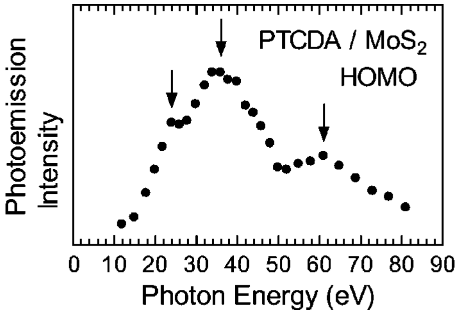

FIG. 2. Photon energy dependence of the photoemission intensity of the HOMO band (peak A in Fig. 1).

at the Γ point. Since the HOMO band dispersion is very small in comparison of the dispersion of final states, it can be considered that only the DOS of the nearly free-electron-like final-state bands dominate the three maxima in Fig. 2. As seen in Fig. 2, the maxima of the HOMO-band intensities are clearly seen at $h\nu = 24$, 36, and 61 eV. For these $h\nu$, the final-state-energies above the vacuum level (E^f) are $E^f = 16.5$, 28.6, and 53.5 eV for $h\nu = 24$, 36, and 61 eV, respectively. For these maxima in Fig. 2, we must also take into account the influence of the $h\nu$ dependence of the photoionization cross section. However, The E^f of the three maxima in Fig. 2 agree well with the energy positions of the high-DOS parts of the conduction bands estimated from the low-energy electron transmission spectrum.[24] Therefore, three maxima in Fig. 2 are considered to originate from the DOS of the final state. From these results, V_0 was determined to be -5.1 eV.

Figure 3 shows the best-fit energy-band dispersion curve along with the experimental results calculated by Eq. (2), in which $V_0 = -5.1$ eV. In this fitting, we used a least-squares fitting of the observed E_B positions to cosine curve in the tight-binding model.[17] From these fitting, the other parameters E_B^0, t, and $a_\perp$ were found to be 7.43, 0.05 eV, and 3.8 Å, respectively. The estimated lattice spacing of 3.8 Å is larger than the spacings of 3.22 and 3.25 Å between the molecular network sheets in α-PTCDA and β-PTCDA crystals, respectively.[25] In the present fitting, we assumed that $m_e^* = m_0$. When we use the parameter as $m_e^* > m_0$, the lattice constant can be obtained as $a_\perp < 3.8$ Å from tight-binding fitting. Another possible origin of this discrepancy might be different molecular packing structures between the films and crystals. We cannot give a definite origin of this difference at present. For further consideration about this problem, we need to measure the θ dependence of SR-ARUPS spectra for a single crystal.

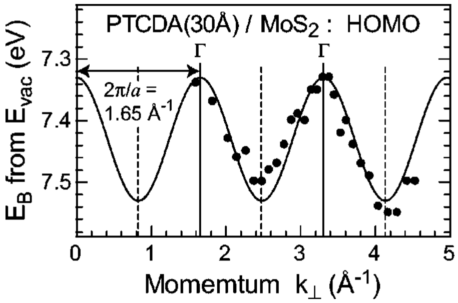

FIG. 3. The experimental dispersion for the HOMO band (filled circles) in the extended zone scheme and the best-fit curve (solid line) in the tight-binding model. In this figure, the first Brillouin zone extends over $\pm\pi/a$, and only for $k_\perp \geqslant 0$ are shown. The energy of the band center, the transfer integral, the lattice spacing normal to the surface and the inner potential are $E_B^0 = 7.43$ eV, $t = 0.05$ eV, $a_\perp = 3.8$ Å, and $V_0 = -5.1$ eV, respectively.

On the other hand, the lateral lattice constants for the PTCDA/MoS$_2$ system were found to be 13.8 and 21.2 Å from LEED measurements,[18] hence the reciprocal lattice constants in these directions are 0.23 and 0.15 Å^{-1}, respectively. In the present SR-ARUPS measurements, the acceptance angle of the photoelectron was $\pm 0.8°$. Therefore, the lateral wave-vector components of photoexcited electron along surface parallel ($k_\parallel$) were averaged for $k_\parallel = 0 \sim 0.02$ Å^{-1} when $h\nu = 12$ eV and for $k_\parallel = 0 \sim 0.06$ Å^{-1} when $h\nu = 81$ eV. That is, ~ 13 and $\sim 40\%$ of the lateral Brillouin zone are integrated at $h\nu = 12$ and 81 eV, respectively. If there is considerable tight-binding band dispersion along the lateral direction, the HOMO band must shift to the higher E_B side with increasing $h\nu$. However, we could not observe such a E_B shift but a periodic E_B shift. Thus, we consider that the main origin of the observed E_B shift is due to π-π interaction along surface normal than the lateral interaction.

As seen in Fig. 3, we succeeded to observe the HOMO-band dispersion of about 0.2 eV for the PTCDA multilayer along the surface normal. The observed HOMO-band dispersion originates from the intermolecular π-π interactions along the molecular plane normal. The transfer integral of the HOMO band for the PTCDA multilayer, $t_{\mathrm{PTCDA}} = 0.05$ eV, is smaller than that of the BTQBT multilayer, $t_{\mathrm{BTQBT}} = 0.09$ eV.[17] This relates to the difference of the intermolecular vdW interaction between PTCDA and BTQBT. Using the parameters which were obtained from the HOMO-band dispersion in Fig. 3, the effective mass of HOMO hole (m_h^*) is obtained to be $m_h^* = 5.28 m_0$. Thus, the hole mobility (μ_h) is approximately calculated as $\mu_h > 3.8$ cm^2/V s which can be approximately expressed as $\mu_h > 20 m_0 / m_h^*$ when $\tau > \hbar / k_B T$, where τ is the relaxation time due to scattering.[26] We believe that these parameters are important for discussing the electrical doping to PTCDA films and the molecular exciton dispersion which has the same order of the dispersion-width for the present HOMO-band dispersion.[27] This is the first observation of the intermolecular valence-band dispersion of a conventional single-component organic semiconductor only with the weak intermolecular vdW interaction.

ACKNOWLEDGMENTS

The authors thank to S. Tanaka, T. Mori, Y. Yabuuchi, and the staff of the UVSOR facility for their support in various ways. This work was supported by the Joint Studies Program of UVSOR facility of Institute for Molecular Science and by Grant-in-Aid for Creative Scientific Research from the Japan Society for the Promotion of Science (Grant No. 14GS0213).

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