Effect of adsorbed molecular ordering to the superconductivity of a 2D atomic layer crystal

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The effect of 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) adsorption to the physical properties of a two-dimensional (2D) atomic-layer superconductor (ALS) In/Si(111)-($\sqrt{7}\times\sqrt{3}$) has been studied by angle-resolved photoelectron spectroscopy, transport measurements and scanning tunneling microscopy. Hole doping from the adsorbed molecules has been reported to increase the T_c of this ALS, and the molecular spin to decrease it. Owing to its large electron affinity and its nonexistent spin state, the adsorption of PTCDA was expected to increase the T_c. However, the PTCDA adsorption dopes only a small amount of holes and causes a suppression in T_c with a sharp increase in the normal-state sheet resistance, followed by an insulating transition. Taking disordering of the arrangement of PTCDA into account, we conclude that the increase in conductivity results from the localization effect resulting from the random potential that is induced by the disordered PTCDA molecules. The present result also indicates the importance of the crystallinity of 2D molecular film adsorbed on ALSs.

I. INTRODUCTION

In the past decades, atomic-layer superconductors (ALSCs) epitaxially grown on semiconductor surfaces have been intensively studied as a very fascinating platform for studying the physical properties of two-dimensional (2D) superconductors (SCs) [1–5]. Intriguing physical phenomena, which require understanding beyond a 3D conventional SC [6], have been reported such for 2D systems, e.g., enhanced in-plane critical magnetic field above the Pauli paramagnetic limit [7–10]. Furthermore, the combination of spin physics, which arises from the presence of both the spin-orbit coupling (SOC) and broken inversion symmetry, with superconductivity has possibility of creating novel superconducting states [11, 12]. In terms of applications as well as fundamental science, further development of this field demands improvement and control of superconducting properties. By utilizing the high sensitivity of ALSs to surface adsorbates, a new method for tuning the superconducting transition temperature (T_c) by constructing 2D heterostructures consisting of well-ordered organic molecule, has been reported [13]. In this study, two different metal phthalocyanines, CuPc and MnPc, were adsorbed on an ALS In/Si(111)-($\sqrt{7}\times\sqrt{3}$) (referred to as ($\sqrt{7}\times\sqrt{3}$)-In, hereafter). The ($\sqrt{7}\times\sqrt{3}$)-In consists of double In atomic layer on Si(111), and form a ($\sqrt{7}\times\sqrt{3}$) supercell with a quasi-square lattice [14–16]. It has spin-polarized metallic surface bands in normal state [17, 18], and become superconducting at approximately 3 K [1–3, 19, 20]. Even though the two molecules have similar ordered structures on ($\sqrt{7}\times\sqrt{3}$)-In, T_c was found to be enhanced by 5% when using CuPc, while the T_c was rapidly suppressed for MnPc adsorption. This T_c modification was explained as the consequences of a competition between a positive effect of hole doping [21] from the molecules into ($\sqrt{7}\times\sqrt{3}$)-In and a negative effect of the exchange interaction between the conduction-electron spin and the local spin in the molecules. However, no organic molecules except CuPc and ZnPc have ever been reported to increase the T_c [13, 22–24]. In order to better conceptualize the effect of molecular adsorption on the physical properties of ALSCs, further investigations using different type of organic molecules are needed. 3,4,9,10-perylene-tetracarboxylic-dianhydride (PTCDA) is known to form highly ordered layers on selected metals [25, 26], and thus has been used as a prototypical molecule to study properties at the organic molecule-metal interface. Furthermore, PTCDA is also used as an electron acceptor due to its large electron affinity, whose value is much larger than that of CuPc in the isolated state [27, 28], and has no spin states. This means that PTCDA would be a potential candidate to achieve a higher T_c of ($\sqrt{7}\times\sqrt{3}$)-In.

In this paper, we report the electronic structure, conductivity, and atomic structure of PTCDA adsorbed ($\sqrt{7}\times\sqrt{3}$)-In, which were established by high-resolution angle-resolved photoelectron spectroscopy (ARPES), transport measurements, and scanning tunneling microscopy (STM), respectively. Although a large amount of hole doping and an increase in T_c were expected from the electronic properties of PTCDA, only a small amount of hole doping and a suppression in T_c were observed. Moreover, a sharp increase in the normal-state resistance that eventually undergoes an insulating transition without the destruction of the metallic character of $(\sqrt{7}\times\sqrt{3})$-In was observed. Taking the disordering of adsorbed PTCDA into account, we conclude that the suppression in superconductivity and the insulating transition are due to the random potentials induced by disordered-arranged PTCDA molecules, which possibly scatter the conduction electrons and cause carrier localization in the 2D In layer. Our findings suggest that molecular films with high crystalline quality are indispensable to improve the superconductivity in 2D systems consisting of an ALSC and organic molecules.

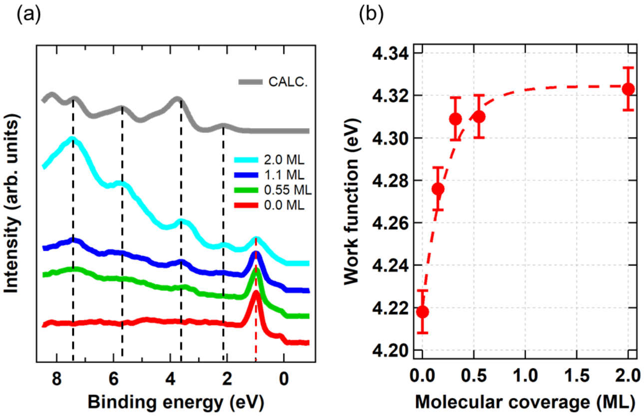

FIG. 1. Coverage-dependent (a) valence band spectra and (b) work function of PTCDA adsorbed $(\sqrt{7}\times\sqrt{3})$-In. The spectrum indicated by a gray solid line in (a) shows the calculated DOS of and isolated PTCDA molecule.

II. EXPERIMENTAL DETAILS

High-resolution ARPES measurements were conducted at the Bloch beamline of MAX IV, Sweden, which is equipped with a DA30-L analyzer (Scienta Omicron), and the beamline 13 of Saga Light Source, Japan, equipped with a A-1 analyzer (MB Scientific AB). The transport experiment was performed using the four-point probe method in a home-built UHV apparatus [2, 19] and the STM observation was done using a low-temperature STM (UNISOKU Co. Ltd.). An n-type Si(111) substrate (1-5 Ωcm) was used for PES and LT-STM, and a non-doped one (>1000 Ωcm) for transport measurements. $(\sqrt{7}\times\sqrt{3})$-In was prepared by depositing approximately three monolayers of In on a clean Si(111) surface at 300 K, followed by a 600 K annealing for a couple of minutes. The sample quality was confirmed by the observation of sharp spots in low energy electron diffraction (LEED). PTCDA (purity > 98%) was well degassed in UHV before deposition. The PTCDA thickness was monitored with a quartz balance and calibrated by PES and STM. The sample was maintained below 20 K during all PES measurements and at 4.7 or 80 K in STM. All sample preparation and experiments were performed under ultrahigh vacuum (UHV) conditions.

III. RESULTS AND DISCUSSION

The PTCDA coverage-dependent valence band spectra and change in work function obtained with a photon energy ($h\nu$) of 40 eV are shown in Figs. 1(a) and (b), respectively. In the valence band spectra, the intensity of the prominent peak observed at a binding energy (E_B) of approximately 1 eV on the pristine $(\sqrt{7}\times\sqrt{3})$-In (indicated by a red dashed line in Fig. 1(a)) decreases, and the intensities of the four peaks (indicated by black dashed lines) develop as the molecular coverage increases. Taking into account the MO spectra reported in previous studies [29–31], we attribute the peak located at approximately $E_B = 2.1$ eV to the highest-occupied molecular orbital (HOMO) of PTCDA. Furthermore, by considering the good agreement between the relative E_B of the observed four peaks and those of the theoretically obtained molecular orbitals (MOs) for an isolated PDCDA (the gray spectrum), we conclude the origin of all the four peaks to be the MOs of PTCDA. (The calculation was performed using the GAMESS program [32, 33] with the B3LYP method and 6-311G** basis set, and the MO energies were shifted so that the HOMO peak coincides the experimental spectra.) The negligible shift in E_B of the MOs and the invisible molecule-derived features within the energy gap region of PTCDA, unlike the case of strongly interacting systems [34], suggest the rather weak interaction between PTCDA and $(\sqrt{7}\times\sqrt{3})$-In. This weak interaction is supported by the saturation in work function at ca. 1 ML where the value is in accordance with that of the work function of a thick PTCDA film [35]. The negligible change in work function at coverages higher than 1 ML indicates that the surface dipole of PTCDA adsorbed on $(\sqrt{7}\times\sqrt{3})$-In and that of a thick PTCDA film are equivalent, and therefore that the charge transfer between PTCDA and $(\sqrt{7}\times\sqrt{3})$-In is negligible and also that PTCDA is hardly distorted on $(\sqrt{7}\times\sqrt{3})$-In.

We have measured the Fermi surfaces (FSs) at different PTCDA coverages with $h\nu = 40$ eV. Figure 2(a) shows the FS of the pristine $(\sqrt{7}\times\sqrt{3})$-In obtained from a summation of the photoelectron intensity within a 20 meV energy window from the Fermi level. This FS, which consists of two types of FSs (a circular Fermi surface that is mainly formed by electrons located at the outermost In layer and a butterfly-shaped Fermi surface mainly formed by electrons located at the In layer connected to Si), is in good agreement with the experimental and calculated ones reported previously [10, 13, 17, 18, 21]. The circu-

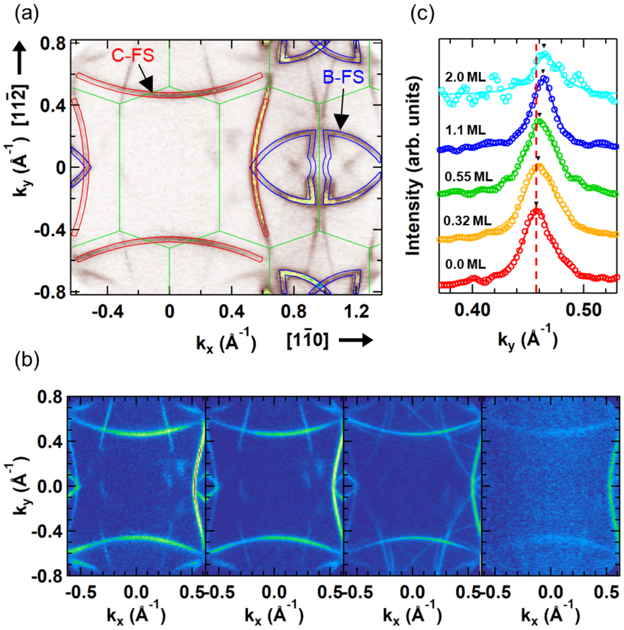

FIG. 2. (a) FS of the pristine $(\sqrt{7}\times\sqrt{3})$-In. The green solid lines show the $\sqrt{7}\times\sqrt{3}$ Brillouin zone, and the red and blue solid lines enclose a part of the circular and butterfly-shaped FSs, respectively. (b) FSs of PTCDA adsorbed $(\sqrt{7}\times\sqrt{3})$-In at different coverages. (c) PTCDA coverage-dependent MDCs obtained from a summation within a k_x range of 0 ± 0.015 Å^{-1}. The open circles are the experimental data and the solid lines overlapping them show the Lorentzian fittings. The peak position in each MDC is indicated by a triangle.

lar and butterfly-shaped FSs are indicated as C-FS and B-FS, respectively, in the figure. The FSs obtained after PTCDA deposition [Fig. 2(b)] show that the increase of PTCDA coverage leads to an intensity drop of the FS but not to a significant modulation in its shape. This result indicates that the interaction between PTCDA and $(\sqrt{7}\times\sqrt{3})$-In does not involve chemical bonding and thus hardly affects the electronic structure of $(\sqrt{7}\times\sqrt{3})$-In. In order to obtain more detailed information about the charge transfer at the interface, we have analyzed the radius of the circular Fermi surface. Figure 2(c) displays the momentum distribution curves (MDCs) at $k_x = 0$ and $k_y > 0$. Hole doping from PTCDA into the In layer would shrink the FSs, and thus increase the separation between the two circular FSs at $k_x = 0$. As shown in Fig. 2(c), the position of the peak in MDC, which is obtained by fitting using a Lorentzian function, shows a small shift toward larger k_y as the PTCDA coverage increases. This means that the adsorbed PTCDA molecules slightly dope holes into the In layer. Table I summarizes the obtained radius of the circular FS at different PTCDA coverage, and the number of holes transferred to an In atom from PTCDA estimated from the experimental result. (The number of transferred holes was obtained by comparing the area of the circular Fermi surface and the Brillouin zone formed by the In atoms as in Ref. [21].) The amount of hole doping continuously increases even above a PTCDA coverage of 1.0 ML. This results from the fact that PTCDA does not grow layer-by-layer on $(\sqrt{7}\times\sqrt{3})$-In and regions uncovered by PTCDA remain at above 1.0 ML as will be discussed below. Despite its large electron affinity, which is larger than that of CuPc, the PTCDA adsorption causes less hole doping into $(\sqrt{7}\times\sqrt{3})$-In than CuPc. This result indicates that discussing the charge transfer at the interface between organic molecules and metal substrates based on the energy level alignment only is not sufficient.

TABLE I. Radius of the circular FS at different PTCDA coverages and the number of holes transferred per In atom estimated from the radius.

PTCDA coverage (ML)	Radius (Å^{-1})	Δ holes (/In atom)
0.0	1.4309 ± 0.0002	-
0.32	1.4288 ± 0.0002	0.0052 ± 0.0005
0.55	1.4279 ± 0.0002	0.0073 ± 0.0005
1.1	1.4262 ± 0.0005	0.0115 ± 0.001
2.0	1.4233 ± 0.002	0.0184 ± 0.005

In order to obtain further information about the interaction between PTCDA and $(\sqrt{7}\times\sqrt{3})$-In, we have measured the coverage-dependent C 1s and O 1s core-levels. In Fig. 3, we show the C 1s and O 1s spectra obtained with $h\nu = 650$ eV at different PTCDA coverages. Both the C 1s and the O 1s spectra show only increase in intensity and no remarkable change in the spectral shape as the PTCDA coverage increases. The E_B of two O 1s components and their relative intensity agree well with those of thick PTCDA films [36–38]. On the other hand, although the relative intensity of the two C 1s components shows agreement with those of thick films [36–38], there is a difference in the separation in their E_B. That is, the separation of the two components in Fig. 3(a) is narrower than those reported in the literature for thick PTCDA films. By considering the origin of the small component at higher E_B, we conclude that the difference in E_B separation results from the small charge transfer from In to the C atoms in the carboxylic group, i.e., C atoms bonded to O atoms, like the case of PTCDA adsorbed on Sn covered Si(111) surface [38].

Since the small hole doping and the observation of circular FS even after PTCDA adsorption indicate the possibility of change in T_c of $(\sqrt{7}\times\sqrt{3})$-In, we have performed coverage-dependent transport measurements. The superconducting transition of the pristine $(\sqrt{7}\times\sqrt{3})$-In was confirmed by a steep decrease that reaches 0 Ω/□ in sheet resistance at approximately 3.0 K, which is consistent with the previous reports [1–3, 19, 20]. As shown in Fig. 4(a), the T_c is suppressed when increasing the PTCDA coverage. This is in contrast to the change in T_c expected from hole doping as in the case of CuPc adsorption [13]. Furthermore, the normal-state sheet resistance at 3.5 K shows a sizable increase af-

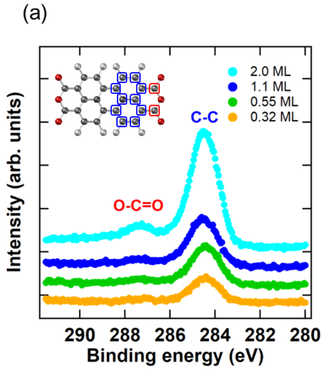

FIG. 3. (a) C 1s and (b) O 1s core-level spectra from PTCDA on ($\sqrt{7}\times\sqrt{3}$)-In at different coverages. The upper left inset in each figure displays the molecular structure of PTCDA with chemically inequivalent C and O atoms.

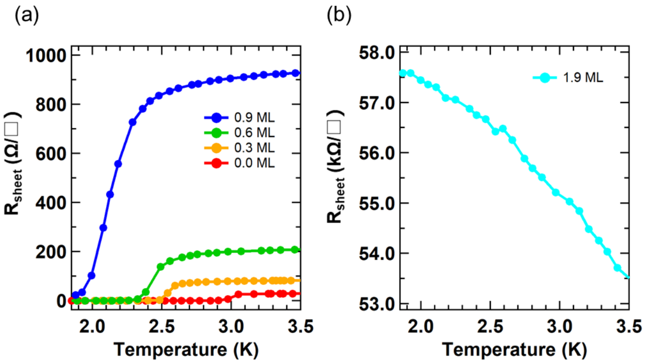

FIG. 4. Temperature-dependent sheet resistance of the PTCDA adsorbed ($\sqrt{7}\times\sqrt{3}$)-In at PTCDA coverages below 1.0 ML (a) and at 1.9 ML (b).

ter PTCDA adsorption, which was not observed in case of several metal-phthalocyanine adsorptions [13, 22, 23]. Moreover, the disappearance of superconductivity and the increase in sheet resistance when decreasing temperature at 1.9 ML reveals the semiconducting or insulating behavior of ($\sqrt{7}\times\sqrt{3}$)-In at this coverage. Since the ARPES measurements confirm that the electronic structure is only modified by a small amount of hole doping and the metallic bands still remain up to 2.0 ML, this transition in conductivity would not be a phase transition accompanied with a gap opening at the Fermi level. It should be noted that the sheet resistance increases up to more than 50 kΩ/□, which drastically exceeds the universal critical sheet resistance $h/4e^2$ (= 6.45 kΩ) of the superconductor-insulator transition in the 2D limit [39–41]. Since PTCDA has no spin states, the magnetic effects cannot be the origin of the suppression in superconductivity. In superconducting thin films, the T_c has been reported to decrease and the sheet resistance to increases by the presense of disorder [39, 41]. This means one possible origin of the results shown in Fig. 4 would be the disordered potential formed on ($\sqrt{7}\times\sqrt{3}$)-In by the adsorbed PTCDA.

Figure 5(a) shows a 200 × 200 nm^2 STM image of ($\sqrt{7}\times\sqrt{3}$)-In covered with 1.0 ML of PTCDA. The coexistence of the first and second PTCDA layers and the presence of uncovered ($\sqrt{7}\times\sqrt{3}$)-In regions indicates that PTCDA deposition follows an island growth mode and not a layer-by-layer one as in case of CuPc. This suggestion is consistent with the PES results discussed above, where the amount of hole doping does not saturate and/or show a maximum at a PTCDA coverage of 1 ML. [The PTCDA molecules of the first layers appear as dark as the ($\sqrt{7}\times\sqrt{3}$)-In region in the STM image, but since no significant changes are observed in the electronic structure of ($\sqrt{7}\times\sqrt{3}$)-In upon PTCDA adsorption this is due to an effect of the electronic states instead of the height of atoms.] The STM image with molecular resolution of the first PTCDA layer reveals a mixture of ordered and disordered regions [Fig. 5(b)]. This means that PTCDA molecules do not form a perfectly ordered molecular layer on ($\sqrt{7}\times\sqrt{3}$)-In like metal-phthalocyanine molecules [13, 22, 23]. In both regions, PTCDA molecules are flat lying like PTCDA adsorbed on various substrates [26]. As shown in the inset of Fig. 5(b), PTCDA molecules form a herringbone structure in the ordered region, which is commonly seen in the first few layers on metal substrates [31, 42, 43] or metal-terminated semiconductor surfaces [44–46]. On the other hand, PTCDA molecules are randomly arranged in the disordered region. The disruption in ordering might be due to the defects of the substrate surface that act as trapping sites and cause different interactions to the surrounding molecules. In the herringbone structure, the electropositive H atoms of PTCDA always face the electronegative O atoms of the neighboring molecule and cancel out the charge distribution within the molecule. In the disordered region, however, the charge distribution cannot be cancelled and thus would induce a random electrostatic potential to the underlying In layer. This would lead the PTCDA molecules to play a role as electron-scatterers that cause carrier localization in the 2D In layer [47, 48]. We therefore conclude that the observed suppression in superconductivity, increase in normal-state sheet resistance, and insulating transition in conductivity would result from the random potential induced by disordered PTCDA molecules. This result provides a new insight toward a rational design for enhancing the superconducting properties of ALSCs.

IV. CONCLUSIONS

In conclusion, we have measured the coverage-dependent electronic structure, resistivity, and molecular arrangement of PTCDA adsorbed ($\sqrt{7}\times\sqrt{3}$)-In, to understand the effect of organic molecule adsorption on an ALSC. The FSs at different PTCDA coverages indicate that the adsorption causes a slight hole doping into

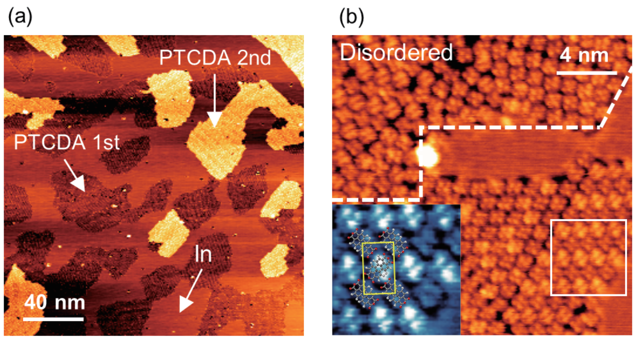

FIG. 5. STM image of the PTCDA adsorbed $(\sqrt{7}\times\sqrt{3})$-In surface at a PTCDA coverage of 1.0 ML. The sample bias and tunnel current are -2.0 V and 10 pA. (a) 200 × 200 nm^2 STM image. The three white arrows indicate the regions of the bare In surface and the first and second layers of PTCDA. (b) Closer view of the first PTCDA layer. Ordered and disordered regions are shown below and above the white dashed line. The inset shows enlarged view of the 5 × 5 nm^2 area outlined by the white solid square, where PTCDA molecules form a herringbone structure. The yellow rectangle in the inset indicates the unit cell.

$(\sqrt{7}\times\sqrt{3})$-In without making appreciable alteration to its electronic structure. Regarding the transport measurements, a suppression in T_c with an increase in the normal-state sheet resistance, followed by an insulating transition has been observed when increasing the PTCDA coverage, though the hole doping and the absence of spin states in molecule were expected to increase the T_c. The unexpected results in conductivity come from the presence of disordering of PTCDA molecule adsorbed on $(\sqrt{7}\times\sqrt{3})$-In, which induces random potentials and thus lead to the localization of conduction electrons in the In layer. This shows that the 2D superconductivity is destroyed due to potential disordering introduced by molecular adsorption, and therefore indicates the importance of the high crystallinity of 2D molecular film in 2D systems consisting of an ALSC and organic molecules.

ACKNOWLEDGMENTS

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