Effects of adsorbed molecular ordering to the superconductivity of a two-dimensional atomic layer crystal

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The effect of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) adsorption on the physical properties of the two-dimensional (2D) atomic layer superconductor (ALSC) 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 superconducting transition temperature T_c of this ALSC, and the molecular spin tends to decrease it. Owing to its large electron affinity and its nonexistent spin state, the adsorption of PTCDA was expected to increase T_c. However, the PTCDA adsorption dopes only a small number of holes in the In layers and causes a suppression of T_c with a sharp increase in the normal-state sheet resistance followed by an insulating transition. Taking the disordering of the arrangement of PTCDA into account, we conclude that the increase in resistance is due to the localization effect originating from the random potential that is induced by the disordered PTCDA molecules. The present result also indicates the importance of the crystallinity of a 2D molecular film adsorbed on ALSCs.

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I. INTRODUCTION

In the past few decades, atomic layer superconductors (ALSCs) epitaxially grown on semiconductor surfaces have been intensively studied as a very fascinating platform for understanding the physical properties of two-dimensional (2D) superconductors (SCs) [1–6]. Intriguing physical phenomena, which require understanding beyond a three-dimensional conventional SC [7], have been reported for such 2D systems, e.g., enhanced in-plane critical magnetic field above the Pauli paramagnetic limit [8–11]. Furthermore, the combination of spin physics, which arises from the presence of both the spin-orbit coupling and broken inversion symmetry, with superconductivity has the possibility of the creation of novel superconducting states [12,13]. 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 ALSCs to surface adsorbates, a new method for tuning the superconducting transition temperature T_c by constructing 2D heterostructures consisting of an ALSC and well-ordered organic molecules was reported [14]. In this previous study, two different metal phthalocyanines, CuPc and MnPc, were adsorbed on the ALSC In/Si(111)-($\sqrt{7} \times \sqrt{3}$) [referred to as ($\sqrt{7} \times \sqrt{3}$)-In hereafter]. ($\sqrt{7} \times \sqrt{3}$)-In consists of a double In atomic layer on Si(111) and forms a ($\sqrt{7} \times \sqrt{3}$) supercell with a quasisquare lattice [15–17]. It has spin-polarized metallic surface bands in the normal state [18,19] and becomes superconducting at approximately 3 K [1–3,20,21]. Even though the two phthalocyanine molecules form similar ordered structures on ($\sqrt{7} \times \sqrt{3}$)-In, T_c was found to be enhanced by 5% with the use of CuPc, while T_c was rapidly suppressed in the case of MnPc adsorption. This T_c modification was explained as the consequence of a competition between a positive effect of hole doping [22] 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 T_c [14,23–25]. In order to

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fully understand the effect of molecular adsorption on the physical properties of ALSCs, further investigations using different types of organic molecules are needed. 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) is known to form highly ordered layers on several metal surfaces [26,27] 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 [28,29] 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 of T_c were observed. Moreover, a sharp increase in the normal-state resistance that eventually undergoes an insulating transition without 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 of superconductivity and the insulating transition are due to the random potentials induced by the disordered arrangement of PTCDA molecules, which would 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 for improving the superconductivity in 2D systems consisting of an ALSC and organic molecules.

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 beamline 13 of Saga Light Source, Japan, equipped with an A-1 analyzer (MB Scientific AB). The transport experiment was performed using the four-point probe method in a home-built ultrahigh vacuum (UHV) apparatus [2,20], and the STM observation was done using a low-temperature STM (UNISOKU Co. Ltd.). An *n*-type Si(111) substrate (1–5 Ω cm) was used for photoelectron spectroscopy (PES) and low-temperature STM, and a nondoped one (>1000 Ω cm) was used for transport measurements. $(\sqrt{7} \times \sqrt{3})$-In was prepared by depositing approximately three monolayers (MLs) of In on a clean Si(111) surface at 300 K, followed by 600 K annealing for a couple of minutes. The sample quality was confirmed first by the observation of sharp spots in low-energy electron diffraction and then by the sharp electronic states in PES and by the atomic arrangement of an atomically uniform surface with flat terraces in STM. [The obtained STM images were in good agreement with those of $(\sqrt{7} \times \sqrt{3})$-In formed by two In layers reported in Refs. [14,23].] PTCDA (purity > 98%) was well degassed in UHV before deposition and deposited on the substrate kept at room temperature with deposition rates slower than 0.3 ML/min. 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 UHV conditions.

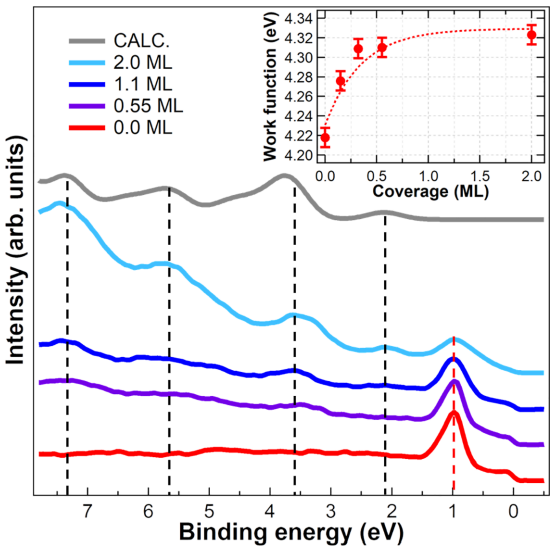

FIG. 1. Coverage-dependent valence band spectra of PTCDA adsorbed $(\sqrt{7} \times \sqrt{3})$-In (the four spectra from the bottom) and the calculated DOS of an isolated PTCDA molecule (the uppermost spectrum). The inset shows the change in the work function with respect to the PTCDA coverage.

III. RESULTS AND DISCUSSION

The PTCDA coverage-dependent valence band spectra obtained with a photon energy $h\nu$ of 40 eV are shown in Fig. 1. The intensity of the prominent peak observed at a binding energy E_B of approximately 1 eV (indicated by a red dashed line) on the pristine $(\sqrt{7} \times \sqrt{3})$-In decreases, and the intensities of the four peaks at $E_B \sim 2.1$, 3.6, 5.7, and 7.3 eV (indicated by black dashed lines) develop as the molecular coverage increases. Taking into account the molecular orbital (MO) spectra reported in previous studies [30–32], we attribute the $E_B \sim 2.1$ eV peak 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 MOs for an isolated PTCDA molecule (the uppermost spectrum), we conclude that the origin of all four peaks is the MOs of PTCDA. [The calculation was performed using the GAMESS program [33,34] with the Becke three-parameter Lee-Yang-Parr (B3LYP) method and a triple split valence basis set 6-311G**, and the MO energies were shifted so that the HOMO peak coincides with 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 in the case of strongly interacting systems [35], suggest a rather weak interaction between PTCDA and $(\sqrt{7} \times \sqrt{3})$-In. This weak interaction is supported by the agreement in work function of the 2 ML PTCDA adsorbed $(\sqrt{7} \times \sqrt{3})$-In shown in the inset of Fig. 1 and that of a thick PTCDA film [36]. That is, the very small change in work function at coverages higher than 1 ML indicates that the surface dipole of PTCDA adsorbed

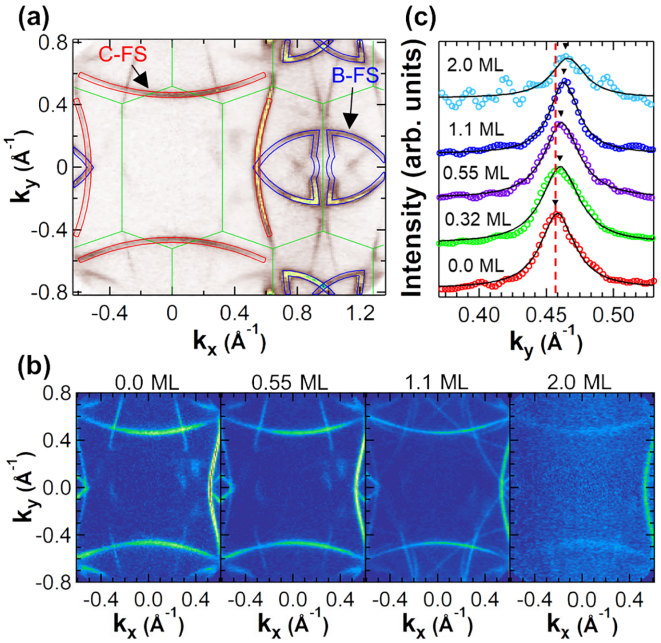

FIG. 2. (a) FS of pristine $(\sqrt{7}\times\sqrt{3})$-In. The green solid lines show the $\sqrt{7}\times\sqrt{3}$ Brillouin zone, and the red and blue solid lines enclose part of the circular and butterfly-shaped FSs, respectively. The k_x and k_y axes correspond to the $[1\bar{1}0]$ and $[11\bar{2}]$ directions. (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.

on $(\sqrt{7}\times\sqrt{3})$-In and that of a thick PTCDA film are quite similar, and therefore, the charge transfer between PTCDA and $(\sqrt{7}\times\sqrt{3})$-In is negligible. Moreover, the negligible shift in E_B indicates that PTCDA is hardly distorted on $(\sqrt{7}\times\sqrt{3})$-In.

The Fermi surfaces (FSs) obtained from a summation of the photoelectron intensity from the Fermi level to $E_B = 20$ meV with $h\nu = 40$ eV at different PTCDA coverages are shown in Fig. 2. The FS of the pristine $(\sqrt{7}\times\sqrt{3})$-In [Fig. 2(a)], which consists of two types of FSs (a circular FS that is formed mainly by electrons located at the outermost In layer and a butterfly-shaped FS formed mainly by electrons located at the In layer connected to Si), is in good agreement with the experimental and calculated ones reported previously [11,14,18,19,22]. The circular and butterfly-shaped FSs are indicated as C-FS and B-FS, respectively, in Fig. 2. The FSs obtained after PTCDA deposition [Fig. 2(b)] show that the increase in PTCDA coverage leads to an intensity drop of the FS but not to a significant modulation in its shape. (The presence of more FSs at 1.1 ML is due to the existence of two other domains that are rotated 120° each; that is, the sample is a triple-domain $(\sqrt{7}\times\sqrt{3})$-In, but this does not affect the discussion.) 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.

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

PTCDA coverage (ML)	Radius (Å^{-1})	Δ holes
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

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 the 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 coverages 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 FS and the Brillouin zone formed by the In atoms as in Ref. [22].) 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 above 1.0 ML, as will be discussed below. Despite its larger electron affinity, 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 only the energy level alignment is not sufficient.

In order to obtain further information about the interaction between PTCDA and $(\sqrt{7}\times\sqrt{3})$-In, we 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 an increase in intensity and no remarkable change in the spectral shape as the PTCDA coverage increases. E_B of the two O 1s components and their relative intensity agree well with those of thick PTCDA films [37–39]. On the other hand, although the relative intensity of the two C 1s components shows agreement with those of thick films [37–39], there is a difference in the E_B separation. That is, the separation of the two C 1s 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 carboxylic group, like the case of PTCDA adsorbed on a Sn-covered Si(111) surface [39].

Since the small hole doping and the observation of circular FS even after PTCDA adsorption indicate the possibility of a change in T_c of $(\sqrt{7}\times\sqrt{3})$-In, we performed

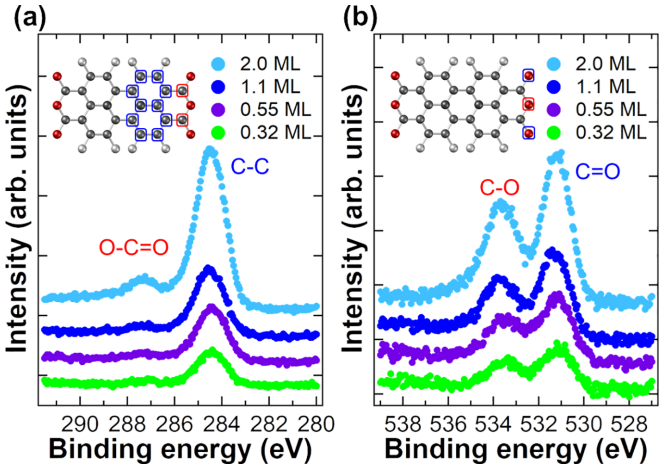

FIG. 3. (a) C 1*s* and (b) O 1*s* core-level spectra from PTCDA on $(\sqrt{7} \times \sqrt{3})$-In at different coverages. The top left inset in each panel displays the molecular structure of PTCDA with chemically inequivalent C and O atoms.

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 previous reports [1–3,20,21]. As shown in Fig. 4(a), 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 [14]. Furthermore, the normal-state sheet resistance at ∼3.5 K shows a sizable increase after

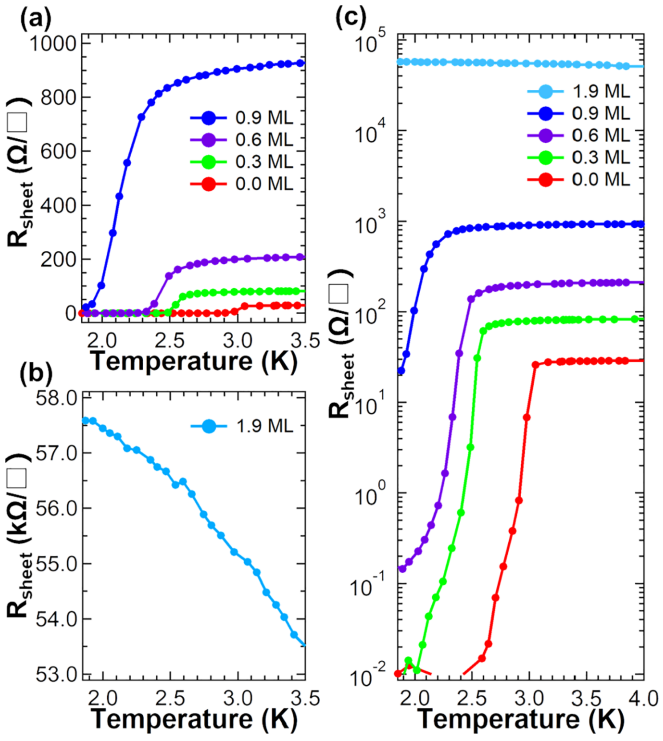

FIG. 4. Temperature-dependent sheet resistance of the PTCDA adsorbed $(\sqrt{7} \times \sqrt{3})$-In at PTCDA coverages (a) below 1.0 ML and(a) at 1.9 ML (b). In (c), the results of (a) and (b) are plotted together with the *y* axis on a logarithmic scale.

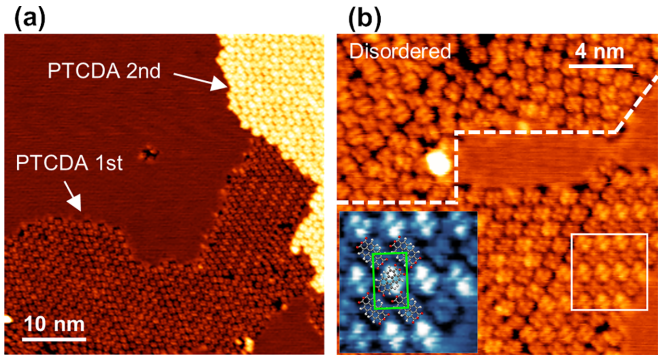

FIG. 5. STM image of the 1.0 ML PTCDA adsorbed $(\sqrt{7} \times \sqrt{3})$-In. The sample bias and tunnel current are −2.0 V and 10 pA. (a) A 50 × 50 nm^2 STM image. The two white arrows indicate the regions covered with one and two PTCDA layers. (b) Closer view of the first PTCDA layer. Regions of ordered and disordered PTCDA molecules are shown below and above the white dashed line. The inset shows an enlarged view of the 5 × 5 nm^2 area outlined by the white solid square, where PTCDA molecules form an ordered herringbone structure. The green rectangle in the inset indicates the unit cell.

PTCDA adsorption, which was not observed in the case of metal-phthalocyanine adsorptions [14,23–25], and the disappearance of superconductivity and an increase in sheet resistance when decreasing temperature at 1.9 ML [Fig. 4(b)] reveal the semiconducting or insulating behavior of $(\sqrt{7} \times \sqrt{3})$-In at this coverage.

The evolution of temperature dependence of sheet resistance is displayed in Fig. 4(c). Since the ARPES measurements confirm that the electronic structure is modified by only 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 [40–42]. Since PTCDA has no spin states, the magnetic effects cannot be the origin of the suppression in superconductivity. In superconducting thin films, T_c has been reported to decrease, and the sheet resistance been reported to increase in the presence of disorder [40,42]. This means that one possible origin of the results shown in Fig. 4 would be a disordered potential formed on $(\sqrt{7} \times \sqrt{3})$-In by the adsorbed PTCDA.

Figure 5(a) shows a 50 × 50 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 the PTCDA deposition follows an island growth mode and not a layer-by-layer one as in the case of CuPc. This suggestion is consistent with the PES results discussed above, in which 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 of PTCDA and does not indicate the molecule is at the same

height as the In layer.] 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 [14,23–25]. In both regions, PTCDA molecules are flat lying like PTCDA adsorbed on various substrates [27].

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 [32,43,44] or metal-terminated semiconductor surfaces [45–47]. 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 with 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 canceled and thus would induce a random electrostatic potential in 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 [48,49]. We therefore conclude that the observed suppression in superconductivity, increase in normal-state sheet resistance, and insulating transition in conductivity result from the random potential induced by disordered PTCDA molecules. This result provides new insight into 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 molecular adsorption on an ALSC. The FSs at different PTCDA coverages indicate that the adsorption causes a slight hole doping into $(\sqrt{7} \times \sqrt{3})$-In without making an appreciable alteration to its electronic structure. Regarding the transport measurements, a suppression of T_c with an increase in the normal-state sheet resistance, followed by an insulating transition, was observed when increasing the PTCDA coverage, although the hole doping and the absence of spin states in the molecule were expected to increase T_c. The unexpected results in conductivity come from the presence of disordered PTCDA molecules on $(\sqrt{7} \times \sqrt{3})$-In, which induces random potentials and thus leads 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 a 2D molecular film in 2D systems consisting of an ALSC and organic molecules.

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