Superconducting transition of FeSe/SrTiO₃ induced by adsorption of semiconducting organic molecules

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We prepared superconducting and nonsuperconducting FeSe films on $SrTiO_3(001)$ substrates (FeSe/STO) and investigated the superconducting transition induced by charge transfer between organic molecules and FeSe layers by low temperature scanning tunneling microscopy and spectroscopy. At low coverage, donor- and acceptor-type molecules adsorbed preferentially on the nonsuperconducting and superconducting FeSe layers, respectively. Superconductivity was induced by donor molecules on nonsuperconducting FeSe layer, while the superconductivity was suppressed near acceptor molecules. The corresponding evolutions of electronic states and work function were also resolved by scanning tunneling microscopy. These results illustrate the important role played by local electron concentration in the superconducting transition of FeSe/STO.

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I. INTRODUCTION

The enhanced superconductivity of single-layer FeSe grown on SrTiO₃(001) substrates (FeSe/STO) has attracted intense research interests both in experiment and theory [1–12]. The electron concentration in FeSe layers is believed to play a vital role in the superconducting (SC) transition of FeSe/STO [5–8], and tremendous efforts have been devoted to tune the electron concentration by post-annealing [5,7,13,14], alkali metal atom deposition [15–18], and gate voltage [8,14,19]. Organic molecule adsorption has been widely used to tune the charge carrier densities in transition metal chalcogenides [20], graphene [21,22], topological insulators [23], and cuprate superconductor films [24]. The electron concentration in substrates was either increased or decreased by depositing donor- or acceptor-type molecules [22,25].

Organic molecules may also provide a convenient way to tune the electron concentration in FeSe/STO. Compared to alkali metal atoms, organic molecules are stable in ambient conditions and can be easily evaporated from Knudsen cells. Furthermore, the structural effect of FeSe/STO can be minimized by choosing closed-shell molecules physisorbed on the substrate, i.e., via van der Waals interaction, enabling us to study the SC transition primarily driven by local electron concentration. On the other hand, the post-annealed FeSe/STO substrate, which has co-existing electron-doped first layer and nearly neutral second layer [5–7,26], may introduce interesting adsorption phenomena to donor or acceptor molecules.

Here we report the selective adsorption behaviors of typical donor- and acceptor-type molecules on ultrathin FeSe/STO with co-existing SC and non-SC areas. Local work function (LWF) measurements and density functional theory (DFT) calculations reveal the interfacial charge transfer induced by the donor- and acceptor-type molecules. The

corresponding superconductivity inducement/suppression due to the increase/decrease of local electron density is observed. Additionally, DFT calculations reveal the interfacial charge transfer without significant lattice modification, suggesting that those organic molecules are good candidates for electronic tuning of superconductivity on FeSe/STO.

II. EXPERIMENTAL AND THEORETICAL METHODS

The experiments were performed in a UNISOKU ultrahigh vacuum (UHV) low temperature scanning tunneling microscope system combined with a molecular beam epitaxy (MBE). The FeSe films were grown on Nb-doped (0.5% wt) $SrTiO_3(001)$ (STO) substrates by the reported method [1]. The as-grown samples were post-annealed at 470 °C for 6 hours in UHV condition to make the first layer FeSe SC [1,5,26]. We used typical donor and acceptor molecules dibenzotetrathiafulvalene (DBTTF) and 7,7,8,8-tetracyanoquinodimethane (TCNQ) [22], whose chemical structures are depicted in Fig. 1(a). The DBTTF and TCNO molecules were evaporated onto the as-grown or annealed FeSe/STO sample from evaporators at 410 K and 390 K, respectively. After deposition, the sample was transferred into the cryostat of scanning tunneling microscope with a base pressure better than $1.0 \times$ 10^{-10} Torr. Polycrystalline Pt-Ir tips, cleaned by electron beam bombardment and verified on Ag/Si(111), were used in the scanning tunneling microscopy and spectroscopy (STM/STS) measurements. The STM topographic images were acquired in constant-current mode with the bias voltage applied to the sample with respect to the tip. Unless otherwise specified, the experiments were performed at 4.9 K, and the STS were measured with a bias modulation of 1 mV at 987.5 Hz.

First-principle calculations were performed using the Vienna Ab initio Simulation Package (VASP) code [27–29]. The interactions between valence electrons and ionic cores were described with the projector augmented wave (PAW) method [30]. We adopted the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) formula for the exchange-correlation functional [31]. The electron wave

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FIG. 1. (a) Chemical structures of DBTTF and TCNQ molecules. (b) The STM image (2.0 V/50 pA) of a post-annealed FeSe/STO sample. (c) The STM image (2.5 V/30 pA) of DBTTF molecules on post-annealed FeSe/STO. Inset: The STM image (2.0 V/50 pA) of DBTTF molecules on as-grown FeSe/STO. (d) The STM image (5.0 V/50 pA) of TCNQ molecules on post-annealed FeSe/STO. The scale bars are 20 nm. (e) Adsorption schematics of the DBTTF/TCNQ molecules on the non-SC (second layer)/SC (first layer) post-annealed FeSe/STO.

functions were expanded in plane wave basis with an energy cutoff of 400 eV. The molecule/FeSe system was modeled using a slab model containing an isolated molecule adsorbed on a single-layer FeSe. The supercell of FeSe layer is $6 \times 4 \times 1$ and $4 \times 4 \times 1$ for DBTTF and TCNQ, respectively. A vacuum layer of thickness more than 15 Å was used. All molecule/FeSe structures were fully optimized by allowing all degrees of freedom of the systems to relax until the force acting on each atom was smaller than 0.05 eV/Å. The tetrahedron method with Blöchl corrections [32] was used in the total energy calculations to achieve a high accuracy. The Γ point sampling in the Brillouin zone (BZ) is used to obtain the optimized adsorption configurations because of the large computational expense, while a fine Monkhorst-Pack k-mesh of $5 \times 5 \times 1$ is adopted to calculate the charge transfer between FeSe film and organic molecules.

III. RESULTS AND DISCUSSION

A. Selective adsorption

We prepare four types of FeSe/STO samples for comparison: annealed single-layer FeSe/STO that is SC uniformly, as-grown single-layer FeSe/STO that is non-SC uniformly, annealed FeSe/STO with second layer FeSe islands on the first layer that contains SC (first layer) and non-SC areas (second layer), and as-grown FeSe/STO with second layer FeSe islands on the first layer that is non-SC uniformly but with distinct topography on the surface (see Fig. S1 of Supplemental Material [33]). As an example, Fig. 1(b) shows the STM image of a post-annealed FeSe/STO sample with coexisting first and second FeSe layers. After post-annealing, the first layer shows the characteristic trenchlike defect lines, distinguishing from the second layer, which is distributed along the step edge and nearly intact except for few isolated Se vacancies [1,2,13]. As shown in Fig. S2 of Supplemental Material [33], the STS measured on the first layer shows a SC gap of ~ 20 meV, while the second layer exhibits a non-SC semiconductor or bad metal-like electronic structure near the Fermi level, in agreement with previous reports [1].

When the donor- or acceptor-type molecules are deposited on the FeSe/STO samples, selective adsorption behaviors are clearly observed-donor-type DBTTF molecules adsorb on non-SC area preferentially while acceptor-type TCNQ molecules adsorb on SC area preferentially. More specifically, on the post-annealed sample, DBTTF molecules adsorb dominantly on the non-SC second layer and form islands at a low molecular coverage [Fig. 1(c)], while the TCNQ molecules adsorb preferentially on the SC first FeSe layer of the post-annealed sample [Fig. 1(d)]. But on the non-SC as-grown sample, DBTTF molecules adsorb both on the first and second layers, as shown in the inset of Fig. 1(c). These organic molecules are closely packed, forming self-assembled DBTTF islands or random TCNQ clusters on FeSe/STO, indicating a weaker molecule-substrate interaction than the intermolecule interaction. Detailed descriptions are presented in the Supplemental Material [33].

The selective adsorption behaviors of DBTTF and TCNQ molecules are essentially related to the local electron density of the substrate, i.e., whether the area is SC or not, rather than the morphology or thickness of the FeSe films. This can be interpreted by the charge-transfer property of the molecules and the electron concentration in respective FeSe regions. The donor-type DBTTF molecules tend to donate electrons to the substrate and, consequently, are preferentially adsorbed on the non-SC area where the local electron concentration is lower than the SC area [5–7,26]. In contrast, the acceptor-type TCNO molecules tend to extract electrons from the substrate and are preferentially adsorbed on the SC area where the electron concentration is higher. Similar selective adsorption behaviors induced by charge density inhomogeneity have been reported—an acceptor molecule, F16CuPc, preferred to adsorb on more negatively charged monolayer graphene than bilayer graphene on SiC substrate [34,35].

B. Charge transfer between molecules and FeSe/STO

To reveal the electronic modification induced by molecules adsorption, we first measure STS curves in a large bias range, as shown in Fig. 2(a). The non-SC pristine second layer FeSe shows a prominent electronic state at -0.15 V. When the tip is laterally moved towards the DBTTF island, this feature



FIG. 2. (a) Averaged dI/dV spectra in a large bias range measured on the second layer FeSe near a DBTTF island. A spectrum measured on the first layer FeSe is shown for comparison. The curves are vertically shifted. The *a* is the FeSe lattice parameter. (b) Typical *G*-*z* curves measured on the superconducting first layer, bare nonsuperconducting second layer, and the region near DBTTF, with a zoom-in part in the inset. All these curves were measured with a fixed bias voltage of 0.5 V.

gradually fades out. Finally, the STS curve becomes similar to that measured on the SC first layer.

The electron doping from DBTTF molecules to FeSe is evidenced by the LWF measurements. Based on a onedimensional tunneling model that neglects the band structure of the STM tip and sample, the averaged work function is extracted by fitting the tunneling conductance G(G = I/V)by $G \propto \exp(-2\sqrt{2m\Phi}z/\hbar)$, where *m* is the bare electron mass and $\Phi = (\Phi_{tip} + \Phi_{sample})/2$ is the averaged work function of tip and sample. Since the work functions are measured with the same tip, the obtained averaged work function is used to evaluate the LWF of respective sites. Figure 3(b) shows the typical G-z curves measured at 0.5 V on the SC first layer, bare non-SC second layer, and the region near the DBTTF island. By repeated measurements on different sites, the averaged work functions of those areas are determined to be $4.91 \pm 0.05 \,\text{eV}$, $5.11 \pm 0.08 \,\text{eV}$, and $4.98 \pm 0.10 \,\text{eV}$, respectively. The lowered LWF near the DBTTF molecule is attributed to the lift of Fermi level by electron doping from DBTTF molecules. Similarly, it can be deduced that the lower work function on the first layer than the second layer is due to the electron doping from the STO substrate, which is in agreement with previous angle-resolved photoemission spectroscopy (ARPES) results [6,7].

The DFT calculations are performed to further investigate the charge transfer between DBTTF/TCNQ molecules and the single-layer FeSe. Based on total energy calculation, the optimized adsorption configurations for DBTTF/FeSe and TCNQ/FeSe are shown in Figs. 3(a) and 3(b), respectively. The two molecules are both physically adsorbed on FeSe via weak van der Waals interaction, and the maximum distance between the molecular plane and top Se atoms in FeSe is 3.72 Å for DBTTF/FeSe and 3.41 Å for TCNQ/FeSe. The physisorption of both molecules are in agreement with experimental observations (see the Supplemental Material [33]).

To study the charge redistribution upon the molecular adsorption on FeSe substrate, differential charge density (DCD) of the most stable adsorption configuration for each



FIG. 3. The top views (upper) and side views (bottom) of the charge rearrangement of (a) DBTTF and (b) TCNQ on single-layer FeSe. Cyan (yellow) color indicates charge depletion (accumulation) region. (c) and (d) The planar averaged charge density $\Delta \rho$ induced by DBTTF and TCNQ adsorption on single-layer FeSe, respectively. The arrows on the bottom axis indicate the positions of bottom Se atoms (Se-b), Fe atoms, top Se atoms (Se-t), and DBTTF/TCNQ molecules in the *z* direction, respectively.

molecule/FeSe system is calculated by [22]

$$\Delta \rho_{\rm mol/FeSe} = \rho_{\rm mol/FeSe} - \rho_{\rm mol} - \rho_{\rm FeSe}, \qquad (1)$$

where $\rho_{\rm mol/FeSe}$, $\rho_{\rm mol}$, and $\rho_{\rm FeSe}$ are the charge density of the adsorbed system, the charge density of the molecule, and the charge density of the single-layer FeSe, respectively. The results are also shown in Figs. 3(a) and 3(b). The charge accumulation region mainly locates around DBTTF for DBTTF/FeSe, while the charge depletion region locates around the TCNQ molecule for TCNQ/FeSe, clearly indicating the opposite charge transfer directions of the two molecule/FeSe systems. We define the planar averaged DCD as $\Delta \rho_{\text{mol/FeSe}}(z) = \int \Delta \rho_{\text{mol/FeSe}}(x, y, z) dx dy$ [see the calculation results in Figs. 3(c) and 3(d)]. Integrating DCD via $Q = \int_{z}^{0} \Delta \rho_{\text{mol/FeSe}}(z) dz$, we obtain the amount of the interfacial charge transfer quantitatively, i.e., the amount of the interfacial charge transfer from one molecule to the substrate for DBTTF/FeSe and TCNQ/FeSe are 0.095 e and -0.39 e, respectively.

The above planar averaged DCD method neglects the differential charge density between molecule and FeSe. We further carry out the Bader charge analysis to estimate the interfacial charge transfer [36]. The results show that for the DBTTF/FeSe system, the FeSe substrate obtains 0.05 e and one DBTTF molecule loses 0.24 e comparing to their neutral state, with 0.19 e delocalized around the interface between them. For the TCNQ/FeSe system, the FeSe substrate loses 0.54 e, and one TCNQ molecule obtains 0.34 e. Previous ARPES results showed that ~0.1 e per FeSe unit cell has been transferred from STO substrate via sufficiently annealing



FIG. 4. (a) The STM image $(20 \times 20 \text{ nm}^2, 1.5 \text{ V}/50 \text{ pA}$, differentiated) of DBTTF molecules adsorbed on the second layer FeSe. (b) The STS shows the induced superconductivity near DBTTF molecules on the non-SC second layer FeSe. The upper panel plots the raw data, while the lower panel plots the normalized data. The background for normalization is plotted in red dashed line. (c) Normalized dI/dV spectra taken on the second layer FeSe $\sim 1a$ from the DBTTF island at varied temperatures. The dash lines show the synchronous change of the coherence peaks. (d) The dI/dV spectra taken along AB in (a). The curves are vertically shifted for presentation. (e) The STM image ($50 \times 50 \text{ nm}^2$, 2.5 V/50 pA) of DBTTF molecules adsorbed on the as-grown first layer FeSe. (f) The dI/dV spectra taken along arrow CD in (e). The curves are vertically shifted.

[5,7]. Considering the larger size of the DBTTF molecules $(12.6 \text{ nm} \times 0.5 \text{ nm} \text{ per molecule})$ than a FeSe unit cell, the donor-type molecule has a much weaker capability than STO for electron doping to FeSe.

C. The SC transition induced by molecules

Considering the van der Waals interaction and charge transfer between the molecules and FeSe layer, the DBTTF and TCNQ molecules on FeSe/STO provide an arena to study the influence of electron concentration on SC transition without significant effect on the local lattice structure. Figure 4(a)shows a zoom-in image of the DBTTF island on the second layer FeSe of a post-annealed sample. The FeSe lattice can be clearly recognized in the image, as the unit vectors being indicated by the arrows in the lower left corner. A typical differential conductance dI/dV curve near the DBTTF island (within the distance of 2a, a is the FeSe lattice parameter) is plotted in the upper panel of Fig. 4(b), and the normalized curve is plotted in the bottom panel, which was derived following the method described in Ref. [16]. Two pronounced peaks located at ± 8 meV and the zero conductance with zero bias clearly indicate that the superconductivity is induced by electron doping, although the SC gap is reduced relative to that measured on the annealed first layer FeSe. The normalized dI/dV spectra taken on the second layer $\sim 1a$ from DBTTF island at elevated temperatures from 4.9 K to 24.6 K are plotted in Fig. 4(c). With temperature increasing, the two coherence peaks become weak and gradually merge with each other, while the zero-bias conductance increases. Thus the SC transition temperature is determined to be around 25 K, which is remarkably higher than the bulk FeSe [37,38].

In agreement with the differential conductance spectra in large bias range, the LWF measurement, as well as DFT calculations that reveal the electron accumulation around DBTTF molecules, the SC transition induced by electron doping from DBTTF shows a clear site dependence. As shown in Fig. 4(d) (see also the Supplemental Material [33]), when the tip is positioned 15*a* away from the DBTTF island, the STS curve shows a semiconducting feature with two electronic states at 11 mV and 26 mV, and the occupied density of states are less pronounced than the unoccupied states in the range of -50 mV to 50 mV. When the distance between the tip and DBTTF molecules is less than 3*a*, SC gaps are observed in STS, manifested by two peaks distributed symmetrically with respect to the Fermi level and the zero conductance with zero



FIG. 5. (a) The STM image $(80 \times 80 \text{ nm}^2, 5.0 \text{ V}/50 \text{ pA})$ of TCNQ molecules adsorbed on the first layer FeSe. (b) Zoom-in image $(15 \times 15 \text{ nm}^2, 2.0 \text{ V}/50 \text{ pA})$ of the square in (a). (c) The dI/dV spectra taken along EF in (b). The black arrows indicate the positions of coherence peaks at E. The curves are vertically shifted.

bias. These results indicate the coexistence of the non-SC (pristine second layer FeSe) and SC (around the DBTTF molecules) areas on the surface.

On as-grown FeSe/STO, the superconductivity can also be induced by DBTTF molecules. Figure 4(e) shows the STM image of DBTTF molecules adsorbed on the as-grown first layer FeSe. The STS measured on the bare first layer shows a depression of electron states at Fermi level without any sign of coherence peaks [Fig. 4(f)], indicating the non-SC characteristics. With the tip approaching the DBTTF island within 3*a*, two coherence peaks and a U-shaped gap emerge in STS curves. The STS curve measured at 1*a* from DBTTF molecules shows a SC gap of ~10 meV, indicating the SC transition being induced on as-grown FeSe/STO.

In our experiments, the SC transition takes place within 3a (1.2 nm) from the DBTTF island. This length is smaller than the SC coherence length and proximity length of single-layer FeSe/STO. The SC coherence length of single-layer FeSe/STO is measured to be ~2.3 nm in SC vortices under magnetic field [39]. The proximity length of single-layer FeSe/STO is comparable to the SC coherence length, as measured at the in-plane boundary between single- and double-layer FeSe/STO [39].

On the other hand, the superconductivity of FeSe/STO is also influenced by the adsorption of the acceptor-type molecule TCNQ. Figure 5(a) is an STM image of TCNQ molecules on the SC first layer FeSe. At the point about 11*a* away from the TCNQ molecules, the STS shows a U-shaped SC gap at the Fermi level and two coherence peaks at ± 15 meV. As the tip laterally approaches the TCNQ molecules, the superconductivity becomes suppressed—the gap becomes asymmetric with respect to the Fermi level, and the coherence peak above the Fermi level gradually vanishes, until semiconducting characteristics appear. On properly annealed FeSe/STO with enhanced superconductivity, a superconductor-semiconductor transition can be induced by decreasing the local electron concentration.

It is known that the electronic structure of the iron based superconductors is sensitive to the bond lengths and bond angles [40–43]. However, as revealed by our DFT calculations, the charge transfer from the organic molecules to FeSe layer introduces only negligible structural changes: The variation in the Fe-Se bond length is less than 0.007 Å and 0.005 Å, and the variation in Fe-Se-Fe bond angle is less than $0.21^{\circ}(0.4\%)$ and $0.13^{\circ}(0.2\%)$ for TCNQ/FeSe and DBTTF/FeSe, respectively. The experimentally observed change of STS due to molecule adsorption is purely the result of charge transfer.

D. Discussion

Different from K atoms, which tend to adsorb individually at low coverage and spread all over the substrate [16–18], DBTTF (TCNQ) molecules coalesce into islands (clusters) and leave bare FeSe areas, which enable us to study a localized SC transition with spatial resolution. The superconductivity on the first layer FeSe of as-grown sample induced by DBTTF molecules also highlights the difference between DBTTF and K atoms in electron doping of FeSe/STO; the attempts to induce superconductivity on the non-SC first layer FeSe have failed thus far [17]. This failure probably stems from the different influence on the FeSe lattice by K doping and molecule adsorption.

It should be noted that the DBTTF molecule has much lower charge transfer ability than the K atoms. Our DFT calculation reveals that the FeSe layer gets $0.095 \ e$ from one DBTTF molecule based on averaged DCD calculation or that the FeSe layer gets $0.05 \ e$ and the DBTTF molecule loses $0.24 \ e$ by Bader charge analysis. In contrast, it can be estimated that one K atom loses one electron to the substrate [16]. Although the electron doping ability of DBTTF molecules are much lower than that of K atoms, DBTTF molecules are stable in ambient conditions and can be easily removed from FeSe substrate by moderate annealing. Therefore, they are promising candidates as capping layers to protect FeSe/STO not only in $ex \ situ$ transport measurements but also in sample transfer between different vacuum systems instead of Se that suppresses the superconductivity.

IV. CONCLUSIONS

In summary, the superconductivity of FeSe/STO is tuned on/off by adsorption of donor-type DBTTF or acceptortype TCNQ molecules, which modifies the local electron concentration. Besides of selective adsorption behaviors of the molecules, our work emphasizes the role of local electron concentration in the superconductivity enhancement in FeSe/STO. Technically, DBTTF molecules are promising candidates to be used as capping layers to protect FeSe/STO in *ex situ* measurements.

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