Surface Atomic Layer Superconductors: Beyond Conventional Two-Dimensional Systems

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ABSTRACT

Two-dimensional (2D) superconductors with truly atomic-scale thickness, high crystallinity, and sharp interfaces are recently under extensive investigations. This has become possible with the substantial developments in nanotechnology and ultrahigh vacuum–low temperature combined technology. In this article, progress in such 2D superconductors is reviewed, with a main focus on surface atomic layers on semiconductor surfaces. The new findings and on-going progress includes unexpected robustness of 2D superconductivity, direct imaging of Josephson vortices and the proximity effect, manifestation of the Rashba effect, and fabrication of 2D heterostructures with organic molecules. The outlook for the realization of novel superconductivity will be presented as a final remark.

INTRODUCTION

Recent remarkable progress in nanotechnology has now allowed researchers to fabricate two-dimensional (2D) materials and probe them using advanced experimental techniques, resulting in an explosive growth of investigations in this field [1]. Unlike conventional quasi-2D inorganic and organic conductors or amorphous-like ultrathin metal films, these 2D materials feature truly atomic-scale thickness, high crystallinity, and a sharp interface at the substrate. This has led to findings of unexpected physical properties of the materials and novel phenomena, such as Dirac electrons and the half-integer quantum Hall effect in graphene [2]. One of the fundamental questions regarding 2D materials is whether they can become superconducting at all. It is not trivial to answer to this question, because superconductivity is on the verge of transition to normal or insulating states in 2D systems; in contrast to the 3D counterpart, even a small degree of defects and disorder could destroy superconductivity due to the electron localization and/or loss of macroscopic superconducting coherence [3]. Note that, in 2D materials, the surface and interface occupy almost all portions, where structural and chemical disorders are readily introduced. Nevertheless, recent studies have unambiguously shown that the answer is actually positive, not only theoretically, but also experimentally; superconductivity with sufficient robustness has been found and studied in various types of 2D materials [4].

In this article, we will focus on the recent progress in superconductivity in metal atomic layers on semiconductor surfaces [5-7]. They often reconstruct themselves, due to strong chemical bonding to the substrate, to exhibit unique structural and electronic properties [8]. This system might seem a simple extension of conventional metal thin films, but there is an essential difference in terms of their atomic-scale thickness and high crystallinity. In this sense, they should be regarded as a member of the new 2D superconductors.

One important feature regarding the atomic layers on semiconductor substrates is the fact that a rather reactive metal layer is exposed to the surface. This requires the application of advanced ultrahigh-vacuum (UHV) techniques for their investigation in order to avoid contamination and degradation due to air exposure. It means that all experiments must be performed at very low-temperatures (LT) and in an ultrahigh vacuum (UHV) simultaneously, and sometimes also under strong magnetic fields. This is the reason that the possibility of superconductivity in surface atomic layers was not explored until very recently. Despite this technical challenge, the existence of a superconducting layer on the top surface allows us to use surface-sensitive experimental tools such as scanning tunneling microscopy (STM) and angle-resolved photoemission spectroscopy (ARPES). This enables one to access important microscopic information on the structural and electronic properties of 2D superconductors. For this purpose, the usage of a UHV environment is ideal because it can eliminate all possible influences of atomic-scale contaminations, which is otherwise difficult to realize.

It is fair to mention here that the studies on 2D superconductors have a long history. They have mostly been focused on materials with poor crystallinity such as granular and amorphous films. This is mainly because of the difficulty in preparing a highly crystalline film using a conventional experimental technique. Nevertheless, the studies on such 2D superconductors have been very successful, leading to the finding of fundamental quantum phenomena such as a superconductor-insulator (S-I) and Kosterlitz-Thouless-Berezinskii (KTB) transitions [3,9]. Particularly, the topological character of the latter phenomenon was central to the Nobel Prize in Physics in 2016. The insight and knowledge accumulated in these previous studies give a basic background for understanding the physics of new 2D superconductors.

Although only briefly mentioned in this article, recent progress in other atomic layer superconductors is also remarkable. For example, the application of field-effect transistor (FET) devices with an electric double layer (EDL) as a gate electrode has now enabled one to turn many insulating materials into superconductors [10,11]. Double-layer graphene intercalated with Ca was found to become superconducting [12]. Furthermore, monolayers of FeSe were epitaxially grown on a $SrTiO_3$ substrate, which was found to exhibit a surprisingly high transition temperature (T_c) of 40 - 100 K [13,14]. The mechanism regarding the occurrence of high T_c is now under debate, but it should be ascribed to the substrate and/or interface effects. They manifest themselves due to the atomic-scale thickness of the system. Readers are referred to related review articles [4,15,16], including the ones in the present feature issue.

FINDING SURFACE ATOMIC LAYER SUPERCONDUCTORS

Superconducting atomic layers in the 2D limit, in the sense that there is only a single quantized mode in the out-of-plane direction, was first found for atomically flat

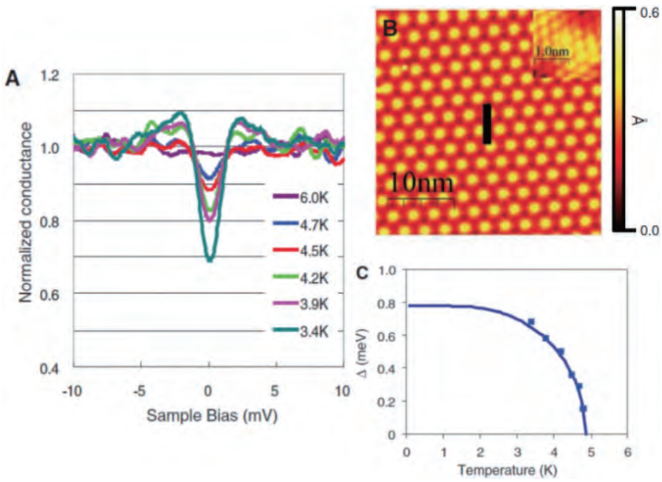

Fig. 1: Superconductivity of 2ML-thick Pb atomic layers on a Si(111) substrate revealed by STM measurements. (a) *dI/dV* spectra taken with an STM, showing the superconducting energy gaps below T_c = 4.9 K. (b) Atomic-scale STM image of a 2ML-thick Pb layer. (c) Temperature dependence of the energy gap plotted with a BCS-predicted curve. S. Y. Qin *et al.*, Science **324**, 1314 (2009). Reprinted with permission from AAAS.

Pb films grown on the Si(111) surface [5]. The active superconducting layer of Pb was only 2 monolayer (ML) thick, excluding a Pb buffer layer at the interface (i.e., 3ML in total). Scanning tunneling spectroscopy (STS) using an LT-STM revealed the opening of a superconducting energy gap at T_c = 3.65 or 4.9 K, depending on the type of the buffer layer (Fig. 1). The study showed that the temperature dependence of the detected energy gap closely followed the BCS-predicted curve. When a Pb layer is thinned to 1ML thickness, it reconstructs itself by forming chemical bonds with the silicon atoms of the substrate; the representative two phases are referred to as Si(111)-SIC-Pb and Si(111)-($\sqrt{7}\times\sqrt{3}$)-Pb surface reconstructions (where SIC stands for "striped incommensurate" and $\sqrt{7}\times\sqrt{3}$ for the periodicity against the ideal Si(111) surface). Similarly, a 2ML-thick In layer forms a reconstructed surface called Si(111)-($\sqrt{7}\times\sqrt{3}$)-In. These three kinds of surface atomic layers were also found to become superconducting at T_c = 1.83, 1.52, 3.18 K through STS measurements [6]. For Si(111)-SIC-Pb, vortices were observed under the application of a magnetic field through spectroscopic mapping. This gives an estimation of the Ginzburg-Landau (GL) coherence length of this system, ξ_{GL} = 49 m. ARPES measurements by the same group also revealed highly dispersed electronic bands of Si(111)-SIC-Pb that cross at the Fermi level. In addition, the temperature dependence of the width of the relevant electronic bands indicated an enhanced electron-phonon coupling compared to that for a bulk

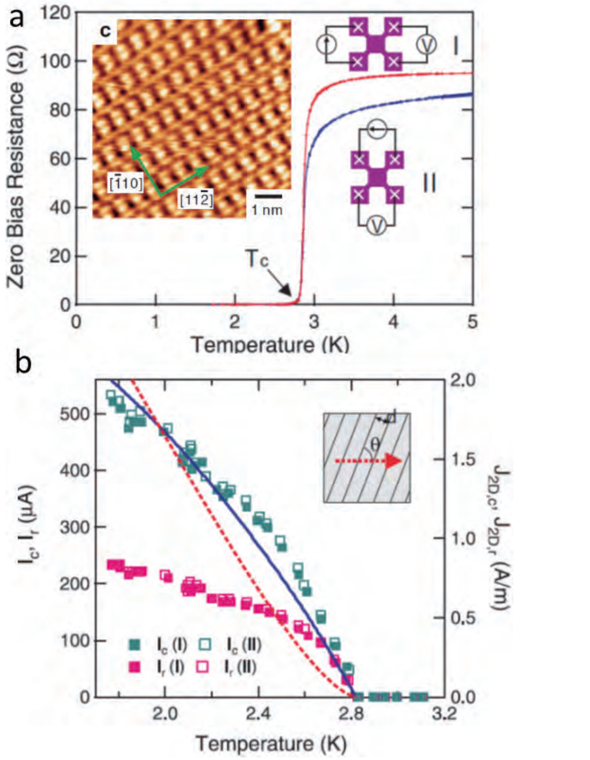

Fig. 2: (a) Superconducting transition of Si(111)-($\sqrt{7}\times\sqrt{3}$)-In revealed by electron transport measurements. The inset shows an STM image of the sample surface. (b) Temperature dependence of 2D critical current density of Si(111)-($\sqrt{7}\times\sqrt{3}$)-In. (green squares). The solid curve is a fit to the Ambegaokar-Baratoff equation. The red squares indicate the retrapping current in the *I-V* characteristics. Reprinted from T. Uchihashi *et al.*, Phys. Rev. Lett. **107**, 207001 (2011).

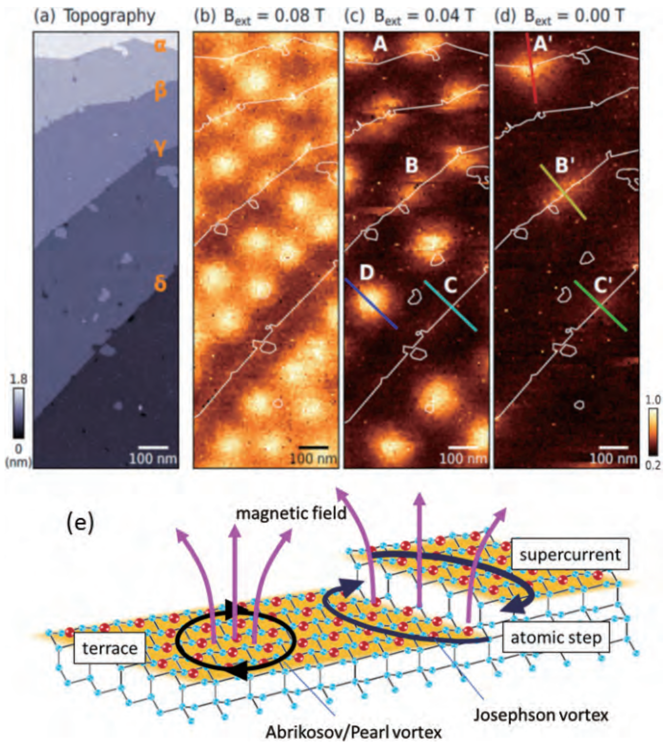

Fig. 3: STM images of superconducting vortices. (a) topographic image of Si(111)-($\sqrt{7}\times\sqrt{3}$)-In. (b)-(d) *dI/dV* Images taken at $V = 0$. The bright regions correspond to the cores of vortices. In (d), Josephson vortices are trapped along the atomic steps. (e) Schematic diagram showing a usual (Abrikosov/Pearl) vortex and a Josephson vortex. The latter is located at the atomic step. (a)-(d): Reprinted from S. Yoshizawa *et al.*, Phys. Rev. Lett. **113**, 247004 (2014).

Pb crystal. This suggests a BCS-type superconductivity and the important role of the interface and/or substrate for realizing it.

More direct evidence of superconductivity in surface atomic layers on silicon was obtained through electron transport measurements by the author's group [7]. The temperature dependence of the four-terminal resistance of Si(111)-($\sqrt{7}\times\sqrt{3}$)-In exhibited a sharp drop to zero around 3 K, demonstrating a superconducting transition (Fig. 2a). Above 3 K, the decrease in resistance was found to be gradually accelerated toward the transition point. This precursory behavior can be well explained by the superconducting fluctuation effects, which are caused by temporal formation of Cooper pairs above T_c [17]. Excellent fits to theoretical predictions show the 2D character of this system [18]. The KTB transition, another indication of 2D superconductivity, seems also to be observable. Current-voltage (*I-V*) characteristics of this system showed a minute but finite resistance around the zero bias, which rapidly decreased with decreasing temperature [18]. A more recent study showed that the *I-V* characteristics followed a non-linear form of $V \propto I^a$, where the exponent factor a crossed the value of 3 at $T = T_{KTB}$ ($< T_c$), which was an indication of the KTB transition [19]. Nevertheless, it lacked a jump from the value $a = 1$ at $T = T_{KTB}$ that was expected for the KTB transition, leaving room for further investigations on this issue.

One unexpected aspect of the superconductivity of this system is its robustness. The critical supercurrent density J_c determined from *I-V* characteristics is as large as 6×10^5 A/cm^2 at 1.8 K [7]. This value is comparable to those found for practical superconducting materials used in magnets and electric power cables, and is surprisingly large considering the expected fragility of 2D superconductivity. Note that the transport measurements were conducted with macroscopically separated probes, meaning that coherent supercurrents could run over a long distance through atomically thin layers. Furthermore, the temperature dependence of J_c followed the Ambegaokar-Baratoff equation [17] (Fig. 2b), indicating that observed supercurrents were regulated at Josephson junctions. Their most likely locations are atomic steps, since they terminate and separate the superconducting atomic layers on flat terraces. Strong influences of atomic steps on superconducting vortices were clarified by spatial mapping of differential conductance (dI/dV) spectra acquired with an LT-STM (Fig. 3a-d) [20]. While the usual vortices are normal-like at their cores and appear circular in shape, they recovered superconductivity when trapped at an atomic step and became elongated in the parallel direction. Such vortices were attributed to Josephson vortices, indicating that an atomic step can work as a Josephson junction (Fig. 3e).

Another surface atomic layer on silicon, Si(111)-SIC-Pb, was also confirmed to undergo superconducting transition at 1.1 K through electron transport measurements by another group [21]. Furthermore, 2ML-thick Ga grown on GaN(0001) was also found to become superconducting [22]. In this case, T_c = 3.8 K is significantly higher than that for T_c = 1.08 K of bulk Ga. This indicates the strong effect of the GaN substrate for the enhancement of superconductivity, reminiscent of high T_c superconductivity of monolayer FeSe on $SrTiO_3$ [13,14]. The signature of the KTB transition was also detected in this system from the temperature dependence of nonlinear I-V characteristics.

Since the T_c of Si(111)-SIC-Pb is less than 2 K, the surface is still in the normal state at the ^{4}He temperature (= 4.2 K). Nevertheless, this atomic layer can be turned into a superconductor through the proximity effect of nearby thicker Pb islands, which has a solid superconductivity at this temperature. This phenomenon was observed through detection of an energy gap using an LT-STM [23,24]. Notably, the proximity-induced superconductivity was found to be enhanced when the relevant area was confined by superconducting islands or by atomic steps. This phenomenon was attributed to multiple Andreev-reflections [25]. Such proximity-induced superconducting layers were also found to host a vortex when magnetic field was applied [26]. The vortex was interpreted as a Josephson vortex, which penetrates through a normal part of a Josephson junction.

Although the mechanism of superconductivity in surface atomic layers has not been clarified yet, it is likely to be of the conventional electron-phonon interaction type. While they are unlikely to be high-T_c superconductors due to the lack of strong electron correlation effects in elemental metals, this simplicity is advantageous when one constructs a complex hybrid system based on them. This idea may be realized by introducing the Rashba effect and organic molecule-based heterostructures, as will be discussed in the following sections.

ATOMIC LAYER SUPERCONDUCTORS WITH THE RASHBA EFFECT

Since atomic layers on semiconductor substrates are exposed to the surface, they lack space inversion symmetry regardless of its crystal structure. This means that an internal electric field is present in the out-of-plane direction in general. In this situation, if the atomic layer consists of a heavy-element metal with a large spin-orbit interaction (SOI), it naturally leads to occurrence of the Rashba effect [27]. The Hamiltonian of this effect is expressed as follows:

$$\mathcal{H}_R(\vec{k}) = \alpha_R(\vec{\epsilon}\times\vec{k}) \cdot \vec{\sigma}. \tag{1}$$

where $\vec{k}=(k_x, k_y, 0)$ is the kinetic momentum, α_R is the strength of the Rashba SOI, $\vec{\epsilon}$ is the unit vector perpendicular to the 2D xy plane, and $\vec{\sigma}$ is the Pauli matrices. In case of a simple free-electron-like band, the Rashba effect lifts its spin degeneracy and splits the band into two, which are chirally spin-polarized in opposite directions in the momentum space (Fig. 4a). This phenomenon has attracted intense interest from the viewpoint of spintronics in recent years, and was also observed directly for atomic layers on semiconductor surfaces through ARPES measurements [28,29].

Since superconductivity is driven by the instability of electrons near the Fermi level, the Rashba effect can have

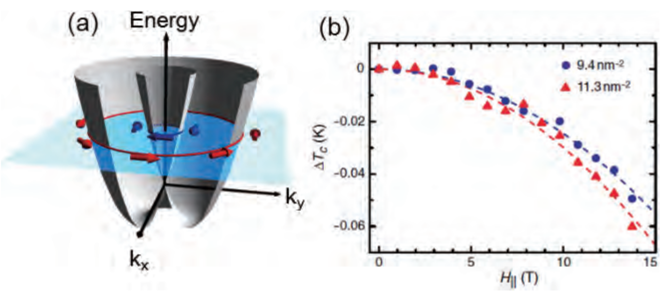

Fig. 4: (a) Schematic view of chirally spin polarized electronic band induced by the Rashba effect. The arrows indicate the spin polarization directions.
(b) $H_{//}$ dependence of the decrease in T_c ($\equiv \Delta T_c$) for Pb films on a GaAs substrate with n = 9.4 and 11.3 nm^{-2}.(n: areal density of Pb atoms). The dashed lines are the best parabolic fits. (b): Reprinted from T. Sekihara *et al*., Phys. Rev. Lett. **111**, 057005 (2013) Copyright 2013 by the American Physical Society.

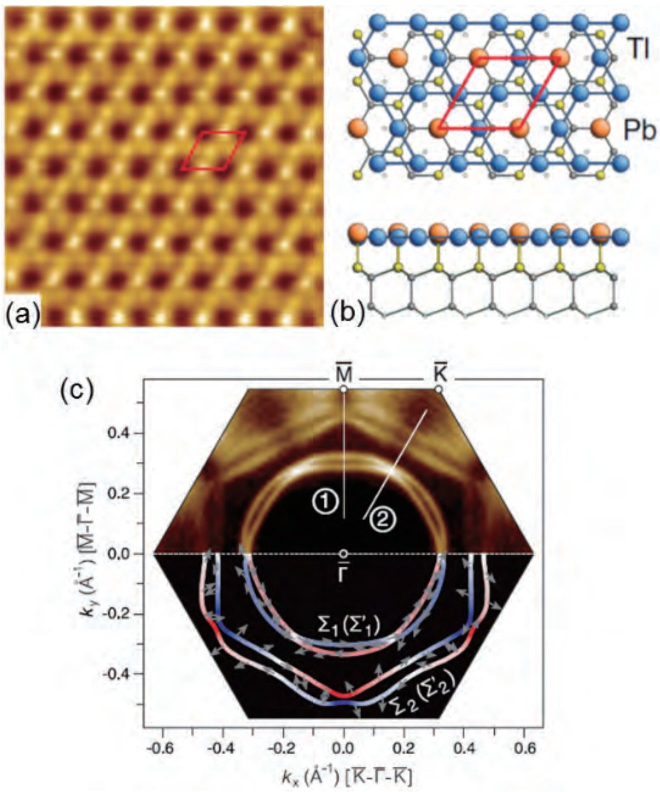

Fig. 5: (a)(b) STM image (a) and atomic structural model (b) of a Si(111)-($\sqrt{3}\times\sqrt{3}$)-TlPb surface. (c) Experimental (upper panel) and calculated (lower panel) Fermi contours of the Si(111)-($\sqrt{3}\times\sqrt{3}$)-TlPb. Reprinted from A. V. Matetskiy *et al.*, Phys. Rev. Lett. **115**, 147003 (2015). Copyright 2015 by the American Physical Society.

strong influences on superconductivity through a spin-split Fermi surface [30,31]. The Cooper pair of conventional BCS-type superconductors consists of two electrons with anti-parallel spins, resulting in a spin-singlet state. This is no longer true when the Fermi surface is chirally spin-split; in general, the Cooper pair is made of a mixture of spin-singlet and spin-triplet states. Furthermore, the superconductivity can become very robust against the magnetic field. Usually, a strong magnetic field aligns the electron spins and consequently destroys Cooper pairs. In the presence of the Rashba effect, however, the critical magnetic field can exceed the limit due to this paramagnetic pair-breaking effect (the Pauli limit). Note that, in a bulk 3D material, superconductivity is suppressed by the orbital pair-breaking effect, which arises from the disruption of orbital motions of electrons by a magnetic field. In contrast, in 2D superconductors, this orbital effect should be absent when the field is applied in the in-plane direction. Therefore, superconductivity is suppressed only through the paramagnetic pair-breaking effect and the influence of the Rashba effect may manifest itself.

The possibility of such “Rashba superconductors” has been explored using rare-earth metal compounds that lack crystalline space-inversion symmetry [31]. However, since they are typical heavy fermion systems with strong electron correlations, their analysis may not be straightforward. In this regard, the atomic layer superconductors with the Rashba effect will be advantageous.

So far, the influence of magnetic fields on Rashba-type atomic layer superconductors was investigated through electron transport measurement using quench-condensed Pb monolayers [32]. The samples were prepared on a cleaved GaAs substrate and measured in situ in a ^{3}He-cooled cryostat so that they could not be degraded by exposure to air. It was found that the T_c of the Pb monolayer decreased only 2% under an in-plane magnetic field of 14 T, showing remarkable robustness of superconductivity (Fig. 4b). The result was ascribed to the strong Rashba effect and elastic electron scattering. The analysis suggested a manifestation of the helical state, a novel superconducting state where the order parameter is spatially modulated in one direction. The in-plane critical field for this system was estimated to be as large as ~100 T. Nevertheless, there was no direct evidence of the Rashba spin splitting of the Fermi surface, because of inaccessibility of surface sensitive probes in this experiment.

The first atomic layer superconductor for which the Rashba effect was confirmed is Si(111)-($\sqrt{3}\times\sqrt{3}$)-TlPb [33]. The samples were fabricated by first preparing Si(111)-(1×1)-Tl surface and then additionally depositing 1/3ML of Pb (Fig. 5a,b). A superconducting transition at T_c = 2.25 K was detected through electron transport measurements, while the Rashba spin-split Fermi surface was confirmed through ARPES measurements and *ab initio* calculations (Fig. 5c). The maximum energy splitting of the surface bands at the Fermi level amounts to 250 meV. The possibility of a novel superconducting state in this system was investigated using an LT-STM [34]. The spectral shape of the superconducting energy gap was not of the simple *s*-wave function, but rather suggests that it could be fitted using combined *s*- and *p*-wave functions. In an analogous experiment using Si(111)-($\sqrt{7}\times\sqrt{3}$)-Pb, an unexpectedly large pair-breaking parameter was obtained based on the analysis of the superconducting energy gap structure [35]. This was attributed to scattering of the spin triplet part of the Cooper pair wavefunctions. Although these results suggest the presence of an anisotropic energy gap and anomalous superconductivity, the determination of the wave symmetry is not straightforward. Thus, the identification of the Rashba-effect driven novel superconducting state is still an open issue.

Notably, 2D superconductivity induced at the subsurface of MoS_2 and $NbSe_2$ using a device configuration was also found to have very large in-plane critical magnetic fields exceeding the Pauli limit [36-38]. Here, the space inversion symmetry was broken within monolayers of MoS_2 and $NbSe_2$, because of the three-fold symmetry of the lattices. In this case, the spin-orbit interaction of transition metals leads to a huge effective magnetic field and electron spins are locked in the out-of-plane direction, with their polarity depending on the valleys in the momentum space (K and K′ points) [39]. This allows for the realization of a novel superconducting state called Ising superconductivity, for which the in-plain critical magnetic field is strongly enhanced from the Pauli limit. Although this phenomenon is analogous to the one due to the Rashba effect, the direction of the spin polarization is different. In this case, the Rashba effect weakens the robustness of superconductivity against magnetic field.

ATOMIC LAYER-ORGANIC MOLECULE 2D HETEROSTRUCTURE

Thanks to their ultimately small thickness, the macroscopic properties of atomic layer superconductors can be modified by external electric field or surface carrier doping [10,11]. This is because the layer thickness is small to the extent that it is comparable to the electrostatic screening length. For example, carrier doping using an EDL gate and charge transfer from the surface K dopants can significantly enhance superconductivity of atomically thin FeSe layers [40,41]. This "surface sensitivity" should also apply to the effects of surface magnetic adsorbates. In contrast to weak stray magnetic fields, exchange interaction exerted from them can be very strong. Although this interaction is local, it can have a strong influence on the macroscopic properties of an atomically thin 2D material. Supposing that superconductivity still survives, one should be able to create a superconductor that is strongly modified by magnetic interaction [42].

With such a goal in mind, 2D heterostructures consisting of an atomic-layer superconductor and magnetic organic molecules were investigated by the author's group (Fig. 6a,b) [43]. In the experiment, an indium atomic layer on a silicon surface, Si(111)-($\sqrt{7}\times\sqrt{3}$)-In, and phthalocyanine (Pc) molecules were used. The Pc molecule can include a transition metal ion at its coordination center, which has spin magnetic moments at its *d*-orbitals. The T_c of this heterostructure was found to be shifted in a qualitatively different manner depending on the central metal ion of the Pc molecule (Fig. 6c). 1ML-thick Cu-coordinated Pc was found to increase T_c slightly. In clear contrast, Mn-coordinated Pc can strongly suppress T_c. Based on combined experimental analyses and *ab initio* calculations, the result was ascribed to a competition between the charge and spin effects. Namely, hole dop-

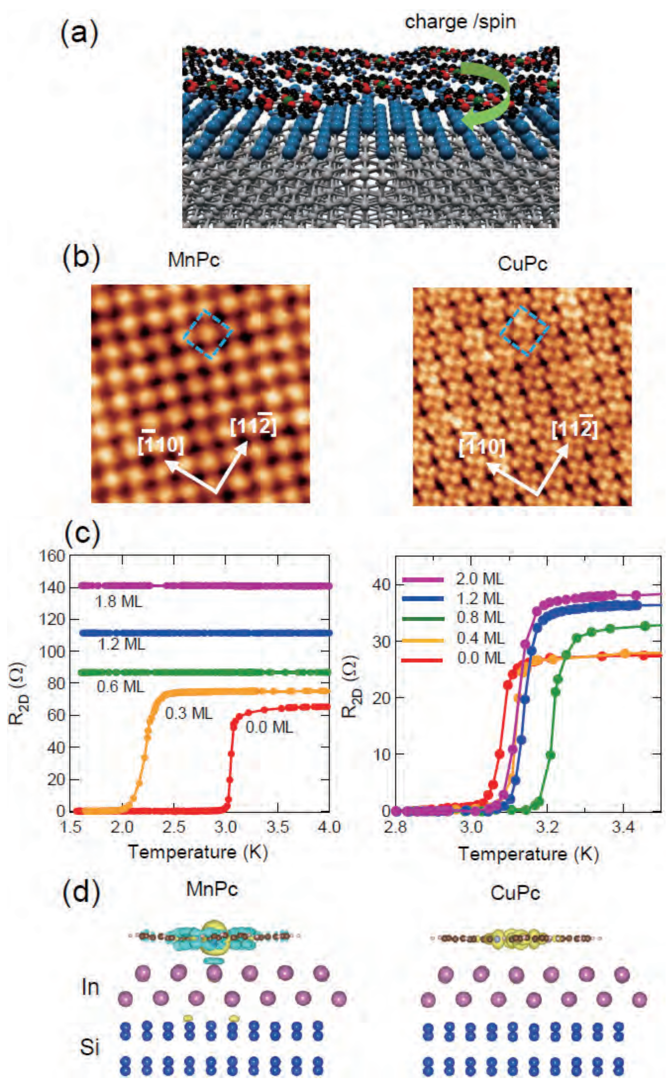

Fig. 6: (a) Schematic illustration of the atomic layer-organic molecule 2D heterostructure. (b) STM images of Si(111)-($\sqrt{7}\times\sqrt{3}$)-In covered with MnPc (left) and CuPc (right). (c) Evolution of the superconducting transition with increasing molecule coverage: MnPc (left) and CuPc (right). (d) Calculated spatial spin distribution. The spin-related d-orbitals of MnPc and CuPc are directed in the out-of-plane and in-plane directions, respectively. Reprinted from S. Yoshizawa *et al.*, Nano Lett. **17**, 2287 (2017).

ing due to the Pc molecules enhances superconductivity while the magnetic moments of Pc molecules suppress it through exchange interaction. Particularly, the directionality of spin-related *d*-orbitals of the coordinated metal ion determines the degrees of the exchange interaction; the in-plane $d_{x2\text{-}y2}$ orbital of Cu^{2+} has a negligibly small effect, while the out-of-plane d_{z2} orbital of Mn^{2+} has a strong interaction and suppresses superconductivity (Fig. 6d).

Since the magnetic molecules are in a paramagnetic state, they can destroy spin-singlet Coopers through spin flipping of conduction electrons [17]. In contrast, if the spins of the molecules are ferromagnetically aligned, this mechanism does not work. Instead, it rather exerts a large effective magnetic field in the order of 10-100 T within the atomic layer through exchange interaction [44]. This will be possible when the temperature is lowered or the inter-molecular interaction is strengthened. Although superconductivity is usually destroyed by a large effective field, it may be retained if a strong Rashba effect is present as discussed above. The demonstration of such a coexistence of superconductivity and ferromagnetism in a 2D heterostructure will be one of the next targets.

This atomic layer-organic molecule system is highly ordered and has an atomically sharp interface, which is difficult if only metals or inorganic materials are used. The degree of coupling at the interface can also be largely tuned by designing appropriate molecules. The system is considered a derivative form of the van der Waals heterostructure [45], and molecular self-assembly techniques will be applicable for it [46].

SUMMARY AND OUTLOOK

In the present article, we have reviewed the recent developments in atomic layer superconductors on semiconductor surfaces, together with brief comparisons to other related systems. The emergence of superconductivity in these ultimately thin 2D layers was firmly established thanks to the combination of state-of-the-art nanotechnology and LT-UHV techniques. Since the superconducting atomic layers are exposed to the surface, surface sensitive probes such as STM and ARPES can be powerful techniques for revealing their microscopic information. This is an advantage in comparison to 2D superconductors buried within a device configuration. The space-inversion symmetry breaking at the surface naturally introduces the Rashba effect. Indications of the Rashba effect in superconductivity is being accumulated. Furthermore, this system can be integrated with organic molecules, which can tune the superconducting properties due to the surface sensitivity.

One of the next challenges will be to make superconductivity and ferromagnetism coexist at an atomic scale, as discussed above. This will help us to explore novel superconducting states [47]. For example, it was predicted that 2D topological superconductors could be created based on the conventional BCS-type superconductor, the Rashba effect, and the exchange interaction exerted from the ferromagnetic layer [48]. Such a heterostructure may also be used to investigate Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) states [49], where a strong magnetic field can be replaced by an effective field of the exchange interaction. Findings of new atomic layer superconductors are also expected because of the existence of a huge variety of surface atomic layers, hopefully with T_c enhanced by the substrate and interface effects. Much unexpected progress is sure to arise in the next decade.

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