Scanning tunneling microscopic observation of enhanced superconductivity in epitaxial Sn islands grown on SrTiO₃ substrate

Zhibin Shao², Zongyuan Zhang², Hui Yuan², Haigen Sun², Yan Cao², Xin Zhang², Shaojian Li², Habakubaho Gedeon², Tao Xiang³, Qi-Kun Xue¹,², Minghu Pan¹,²

¹School of Physics, Huazhong University of Science and Technology, Wuhan 430074, China
²State Key Laboratory of Low-Dimensional Quantum Physics, Tsinghua University, Beijing 100084, China
³Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

Abstract

Recent experimental and theoretical studies of single-layer FeSe film grown on SrTiO₃ have revealed interface enhanced superconductivity, which opens up a pathway to promote the superconducting transition temperature. Here, to investigate the role of SrTiO₃ substrate in epitaxial superconducting film, we grew a conventional superconductor β-Sn (bulk $T_c \sim 3.72$ K) onto SrTiO₃ substrate by molecular beam epitaxy. By employing scanning tunneling microscope and spectroscopic measurements, an enhanced $T_c$ of 8.2 K is found for epitaxial β-Sn islands, deduced by fitting the temperature dependence of the gap values using the BCS formula. The observed interfacial charge injection and enhanced electron–phonon coupling are responsible for this $T_c$ enhancement. Moreover, the critical field of 8.3 T exhibits a tremendous increase due to the suppression of the vortex formation. Therefore, the coexistence of enhanced superconductivity and high critical field of Sn islands demonstrates a feasible and effective route to improve the superconductivity by growing the islands of conventional superconductors on perovskite-type titanium oxide substrates.

Keywords:
Sn islands/SrTiO₃ Interface-enhanced superconductivity Molecular beam epitaxy Scanning tunneling microscope Scanning tunneling spectroscopy

1. Introduction

Raising superconducting transition temperature even up to room temperature is one of the most fascinating and challenging issues in condensed matter physics. In general, one can improve superconducting transition temperatures effectively by applying the high pressure to chemically-doped cuprates and iron-based superconductors [1,2]. A number of efforts have been devoted to study two-dimensional superconductors [3]. Recent report on large enhancement of superconductivity in single-layer FeSe film on SrTiO₃ (0 0 1) substrate, whose superconducting gap ($\Delta \sim 15–20$ meV) and superconducting transition temperature (above 65 K) are about one order of magnitude higher than the bulk values ($\Delta \sim 2.2$ meV, $T_c \sim 8$ K), has received extensive attention in the superconductivity area [4]. The overall U-shaped superconducting gap implies a conventional s-wave pairing, which has stimulated great interest in searching the underlying mechanism of enhanced superconductivity. It was believed that the interface charge transfer [5–13] and the interface-enhanced electron–phonon coupling [10–13] are responsible for enhanced superconductivity. Subsequently, single-layer K₂Fe₄Se₅ [12], FeTe₁₋ₓSe [14] films on SrTiO₃ (0 0 1) and single-layer FeSe on BaTiO₃ [8], SrTiO₃ (1 1 0) [15] or TiO₂ (0 0 1) [16] also showed to exhibit the enhanced superconductivity. Therefore, a new feasible pathway to improve the superconducting transition temperature by fabricating the heterostructure of superconductor/perovskite-type titanium oxide is pointed out. It is natural to ask whether similar enhanced mechanism remains valid for conventional superconductor grown on titanium-oxide-type substrate. To answer this question, Sn islands were prepared on the SrTiO₃ (0 0 1) substrate and topographic images and electronic properties were investigated by means of low temperature scanning tunneling microscope/spectroscopy (STM/S). By comparing the observed characteristic of the quantum well states with the previous study [17], we confirm that the formed Sn islands are superconducting β phase (bulk $T_c \sim 3.72$ K). The increase of the effective width of the quantum well, implies the interfacial charge injection transferred from the substrate. Subsequent narrow-energy-range

https://doi.org/10.1016/j.scib.2018.09.006
2018 Science China Press. Published by Elsevier B.V. and Science China Press. All rights reserved.
spectrum measured at 4.25 K reveals a symmetric superconducting gap, accompanied by some obvious dip-hump features. The second derivative of tunneling conductance \((d^2I/dV^2)\) spectrum shows two characteristic phonon modes with energies \(\sim9.75\) and \(\sim12.75\) meV, well matching with the phonon modes of bulk Sn and SrTiO\(_3\). It suggests that an additional electron–phonon interaction channels may open and be further enhanced by interfacial effects. This conclusion is evidenced subsequently by a large BCS ratio \(2\Delta(0)/k_B T_c\). From the temperature dependence of superconducting gap, the estimated zero temperature gap \((\Delta(0))\) and superconducting transition temperature \(T_c\) are found to be 2.05 meV and 8.2 K, both obviously higher than the bulk one (0.575 meV and 3.72 K). The obtained \(2\Delta(0)/k_B T_c\) (5.8) is also larger than the bulk value, suggesting that the SrTiO\(_3\) substrate plays an important role in the enhanced electron–phonon interaction. Therefore, this enhanced \(T_c\) may result from the combined interfacial charge injection and the enhanced electron–phonon interaction. Moreover, a tremendous increase of critical field is observed, caused by the size effect that leads to the suppression of the vortex formation. Our experimental observation reveals that enhanced \(T_c\) and high critical field coexist in Sn islands grown SrTiO\(_3\) substrate. More importantly, our work suggests that growing conventional superconductor islands on perovskite-type titanium oxide substrates, is a feasible and effective route to improve the superconducting transition temperature.

2. Methods

The preparation of the substrate and the growth of Sn islands were carried out in a standard MBE system with a base pressure of \(2 \times 10^{-10}\) Torr. The Nb-doped (0 0 1)-orientated single crystal SrTiO\(_3\) substrate was heated to 1,330 K for 1 h in UHV MBE chamber to obtain a clean and uniform surface. Sn from a high-purity source (99.999%) was deposited onto the SrTiO\(_3\) substrate at 300 K for 4 h from Knudsen cells. After deposition, the sample was annealed at 300 K for 6 h. For the STM/S measurements, a low-temperature STM system (Unisoku USM-1300), which is capable of cooling the sample down to 400 mK and applying a magnetic field up to 13 T perpendicular to the sample surface, was used for the topographic observation and spectroscopy (STS) measurement. The low bias (energy) \(dI/dV\) tunneling spectra were measured using a lock-in technique with a bias modulation of 0.5 mV at 879.321 Hz. The large-energy scale \(dI/dV\) tunneling spectra were measured using a bias modulation of 5 mV. A tungsten tip, whose oxide layer covering the apex was removed in situ by electron-beam heating, was used in all topographic observations and STS measurements.

3. Results and discussion

For the conventional superconductor \(\beta\)-Sn, one of allotropes of Sn element, the growth modes have been intensely investigated on the Si(1 1 1) substrate [17–20]. Here, we deposited Sn on a SrTiO\(_3\) substrate at room temperature. There are two Sn phases existing in phase diagram and only \(\beta\)-Sn is stable at room temperature and superconducting at low temperature. Similar to Si(1 1 1) substrate, the Sn atoms initially form a wetting layer covering the surface of SrTiO\(_3\) substrate in order to release the strain induced by the lattice mismatch. Subsequently, self-assembled Sn small particles form regularly above the wetting layer (Fig. 1) and further merge into larger islands when the coverage increases (Fig. 1b). Previous study of Sn islands on Si(1 1 1) [17] shows that a phase transition from \(\alpha\)-Sn to \(\beta\)-Sn occurs at the thickness of 4 monolayer (ML) (thinner than 1.46 nm), above which the Sn thin films exhibit \(\beta\)-Sn phase uniformly. Here, the thickness of Sn islands prepared in our experiment is about 8.8 nm. Therefore, we believe these Sn islands on STO are \(\beta\)-phase Sn. We perform wide-energy-range spectroscopic measurements at the center of the island with a height of 8.8 nm (about 30 layers in thickness). The prominent quantum well states (QWS) can be clearly observed at both sides of Fermi level, as shown in Fig. 1c. The similar quantum well states features were observed at the \(\beta\)-Sn islands on Si(1 1 1) with same thickness [17], suggesting that the islands prepared in our experiment are superconducting \(\beta\)-Sn phase. It is worth noticing that the energy separation of QWS peaks located near Fermi level here (0.57 eV) is obviously smaller than that of the one grown on Si(1 1 1) (about 0.75 eV). As we know, the electronic state of a metallic thin films grown on semiconductor substrate can be simply considered as a particle (electron) bound within one-dimensional finite potential well [21]. The energy separation of adjacent quantum well states is inversely proportional to the thickness of thin films. Compared to the islands with same thickness on Si(1 1 1) substrate, an obvious decrease of energy separation suggests that the increase of the effective width of the quantum well. The charge transfer can change the scattering potential of electrons near the interface, enabling the effective width of quantum well to be increased. Considering that high temperature annealing can introduce 2D electron gas on the surface of SrTiO\(_3\) substrate due to oxygen vacancies [5,22,23], thus such charge transfer originated from substrate can be responsible for the increase in the width of the quantum well.

To further explore the density of states near Fermi level, the narrow-energy-range tunneling spectrum was performed, as shown in the top panel of Fig. 2a. A symmetric tunneling gap with a pair of weak peaks located at \(\pm 4.8\) mV opening around Fermi
level, is observed. A well-defined tunneling gap opens symmetrically around Fermi level in the spectra, usually seen as a typical characteristic of superconductivity. As we know, superconducting transition temperature of bulk β-Sn is 3.72 K, which has been reported seven decades ago [24]. However, no related experimental evidence of enhanced superconductivity in β-Sn has been reported so far, except for an enhancement of superconducting gap in Sn nanoparticles arisen from quantum fluctuation [25]. The superconducting gap was acquired on the β-Sn islands at 4.25 K, which has been intensively discussed in the conventional and high-Tc system [3.72 K].

In addition to the superconducting gap, the pseudogap, which has been extensively discussed in the conventional and high-Tc superconductor [26–30], also exhibits a gap-like feature with a noticeable depression in density of states around Fermi level even at the temperature above Tc. Its notable feature is insensitive to the variation of temperature, in contrast to the superconducting gap. To rule out the possibility of pseudogap, we investigate the evolution of the tunneling gap with temperature. Fig. 2c shows a series of spectra taken with different temperatures. An obvious feature is that the tunnelling gap gradually degrades as the temperature increases and totally vanishes at 8.5 K, suggesting this gap is sensitive to the variation of the temperature. We fit the spectra using by the Dynes function with single isotropic s-wave gap [31],

$$\frac{dI}{dV} \propto \int_{-\infty}^{\infty} \text{Re} \left[ \frac{|E - i\Gamma|^2}{(E - i\Gamma)^2 - \Delta^2} \right] \times \left( \frac{\text{Exp}[\epsilon V]}{\epsilon V + \text{Exp}[\epsilon V]} \right) d\epsilon,$$

where $\Delta$ is superconducting gap, $\Gamma$ is an effective broadening factor and $T$ is the measured temperature. The fitting curves match well with the experimental data. The corresponding gap values as a function of temperature are represented in Fig. 2d. By fitting the gap values using the BCS gap formula [32], we find that the data matches well with the BCS theory. The zero temperature energy gap $\Delta(0)$ and critical temperature $T_c$ are found to be 2.05 meV and 8.2 K respectively, both significantly higher than the bulk one (0.575 meV and 3.72 K) [24,33]. Thus, the resulting BCS ratio, $2\Delta(0)/kT_c$, is equal to be 5.8, also larger than that in the bulk (2.4/5kTc = 3.51).

It is noted that, some satellite dip-hump features can be clearly seen outside of the coherent peaks in the spectrum measured at 4.25 K (Fig. 2a), bearing the striking resemblance to those of phonon modes observed in Pb and FeSe/SrTiO3 system [13,34]. More than that, these dip-hump features fade out simultaneously with the degradation of superconducting gap as the temperature increases and eventually vanishes at 5.56 K (Fig. 2b). This fact suggests that the dip-hump feature intimately is related with the observed superconductivity. In our case, conventional superconducting pairing concluded from our results of BCS fitting, indicates that electrons are bound into Cooper pairs by attractive interactions mediated by phonons. The characteristic energy scales of these phonon modes can be derived from the second derivative of the tunneling conductance. Specifically, for the energy of phonon mode, a pair of a peak at $-\left(A + \Omega\right)$ and a dip at $+\left(A + \Omega\right)$ will develop in the $d^2I/dV^2$ spectrum, where $A$ is the superconducting gap. As shown in the bottom of Fig. 2a, two symmetric dip-hump features can be observed in $d^2I/dV^2$ spectrum at the energies $\pm\left(A + \Omega\right) \sim \pm11.8$ meV and $\pm14.8$ meV. Besides these two prominent dip-hump features, there are two additional pairs of symmetric dip-hump features appearing at 8 and 17 mV respectively. Due to
weak intensity of these additional dip-hump features, we do not take it account as dominant characteristic phonon modes. By subtracting deduced $A(0) \sim 2.05 \text{ meV}$, two characteristic phonon modes ($\Omega$) of $\Omega_1 = 9.75 \text{ meV}$ and $\Omega_2 = 12.75 \text{ meV}$, can be obtained. Previous tunneling measurements [35,36] reveal two characteristic phonon modes of $\sim 11 \text{ meV}$ and $\sim 13.4 \text{ meV}$ in white tin, while SrTiO$_3$ has a TO1 phonon with an energy of $10.8 \text{ meV}$ observed by Hyper-Raman scattering measurement [37,38]. The similar energies of phonon modes suggest that the additional electron–phonon interaction channels may open and be enhanced by interface effect and hence have substantial contribution to the $T_c$ enhancement, although subtle change in energy might be due to the finite size correction. This conclusion is further evidenced by enhanced BCS ratio $2\Delta(0)/k_BT_c$. Bulk $\beta$-Sn is a conventional weak coupling superconductor. When Sn islands was prepared on SrTiO$_3$ substrate, an enhanced BCS ratio ($2\Delta(0)/k_BT_c = 5.8$) can be obtained, larger than the bulk (3.53) and the strong coupled superconductor Pb (4.5). According to the Eliashberg theory [39,40], the increase of $2\Delta(0)/k_BT_c$ reflects an enhancement of electron–phonon interaction.

Compared with the case of Sn film on alumina substrate [41], in which the $T_c$ of the films exhibits an oscillatory behavior with thickness and no obvious enhancement was observed, thus enhanced electron–phonon interaction in the Sn islands should mainly arise from SrTiO$_3$ substrate. In past, the SrTiO$_3$ substrate can significantly promote transition temperature of thin films [4,12,14,15] or even introduce superconductivity into nonsuperconducting parent compound by interfacial effect [42], i.e. charge injection, enhanced electron–phonon coupling and strain. In analogy to the interface-enhanced iron-based superconductor thin films [9,13], the SrTiO$_3$ substrate should play a critical role in the $T_c$ enhancement for Sn islands and be responsible for interfacial charge injection as well as enhanced electron–phonon coupling.

Furthermore, the superconductivity in Sn islands are further evidenced by applying external magnetic field perpendicular to the sample surface. Fig. 3a shows how the spectra vary with the field up to 8 T at 4.25 K. As expected, the zero bias conductance gap and the coherent peaks are gradually suppressed with increasing the applied field. To check whether the vortex forms on Sn islands, the line spectroscopic survey was performed along the blue arrow under 3 T, as shown in the insert figure of Fig. 3b. Although the applied field is as high as 3 T, however, the spectra are found to be highly uniform on the island, suggesting that there is no obvious vortex forming on the islands (Fig. 3b) and the superconducting gap of different locations measured on the island will be quenched simultaneously at the same critical magnetic field. This phenomenon has been also reported in the nanosized Pb islands [43,44]. When the effective radius of the island is smaller than $1.3\xi$ ($\xi$ is the coherence length of the superconductor), the vortex formation is suppressed, leading to a tremendous increment of the critical magnetic field [45,46]. Considering that the bulk Sn possesses a relatively large coherence length of about 200 nm [47], the estimated effective radius of island (230 nm $\times$ 110 nm) is 90 nm, obviously smaller than the coherence length. Thus, the vortex cannot form on the surface of the island. Even though the external magnetic field is applied up to 8 T, the superconducting gap has a tiny residual, suggesting that the critical field is slightly higher than 8 T. To estimate the critical field, the normalized zero bias conductance values were extracted from Fig. 3a. The magnetic field dependence of zero bias conductance shows an

---

![Fig. 3.](image-url)
approximately linear distribution, as shown in Fig. 3c. Substantially, a linear fitting was carried out and the deduced $H_c$ of ~8.3 T is obtained, far larger than the bulk value (0.03 T) [48]. The similar enhancement was also observed in thin films [49], nanowire [47] or nanoparticles [45], suggesting that the size effect can improve the critical field effectively. In addition to the size effect, small electron mean free path can also lead to a much higher critical field, compared to bulk superconductor. As shown in Fig. S6 (online), high-resolution images show a wrinkle-shape surface and reconstructed atomic structure, which can induce electron scattering and reduce the electron mean free path. Small electron mean free path can decrease the superconducting coherence length $\xi$ and increase the effective penetration length $\lambda$, leading to a much higher magnetic field that needed to destroy superconductivity.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.scib.2018.09.006.

4. Conclusions

To conclude, we have successfully prepared superconducting β-Sn islands on the SrTiO$_3$ substrate. Sn islands exhibit an enhanced superconductivity, even persistent above 4.25 K. Our results demonstrate an experimental observation of the interfacial charge injection as well as enhanced electron–phonon coupling stemmed from SrTiO$_3$ substrate, which can attribute to this $T_c$ enhancement. Moreover, the critical field of the Sn islands also exhibits a tremendous increase due to the suppression of the vortex formation. Consequently, the coexistence of the enhancement of $T_c$ and critical field is observed in the Sn islands. In comparison with iron-based thin films grown on SrTiO$_3$, where only single layer exhibits high-$T_c$ superconductivity, conventional superconducting Sn islands here with a height of 8.8 nm (about 30 layers in thickness) still exhibit an enhanced superconductivity. Therefore, our experiment, as an example, demonstrates a feasible and effective route to improve the $T_c$ and $H_c$ of conventional superconductor, which will have widely future application in quantum computation.

Conflict of interest

The authors declare that they have no conflict of interest.

Acknowledgments

This work was conducted at School of Physics, Huazhong University of Science and Technology in China. HY and MHP acknowledge the financial supported by the National Natural Science Foundation of China (11574095 and 11604106).

References

Zhi-Bin Shao received his B.S. degree from Department of Physics, Zhanjiang Normal University. He is now studying for his Ph.D. degree at School of Physics, Huazhong University of Science and Technology. His current research focuses on the epitaxial growth and novel properties of topological and superconducting materials by using molecular beam epitaxy and scanning tunneling microscopy.

Qi-Kun Xue obtained his Ph.D. degree from the Institute of Physics, Chinese Academy of Sciences (IOP, CAS) in 1994. He then worked at Tohoku University, North Carolina State University, and IOP, CAS before joining Tsinghua University in 2005. His current research focuses on low dimensional quantum materials, including superconductors and topological insulators.

Minghu Pan received his Ph.D. degree from Department of Physics, Nanjing University. He is now a Professor working at School of Physics, Huazhong University of Science and Technology. His current research focuses on studying correlated electron materials and low-dimensional materials by scanning tunneling microscopy.