Interface-Induced High-Temperature Superconductivity in Single Unit-Cell FeSe Films on SrTiO$_3$ *

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We report high transition temperature superconductivity in one unit-cell (UC) thick FeSe films grown on a Se-etched SrTiO$_3$(001) substrate by molecular beam epitaxy (MBE). A superconducting gap as large as 20 meV and the magnetic field induced vortex state revealed by in situ scanning tunneling microscopy (STM) suggest that the superconductivity of the 1 UC FeSe films could occur around 77 K. The control transport measurement shows that the onset superconductivity temperature is well above 50 K. Our work not only demonstrates a powerful way for finding new superconductors and for raising T_C, but also provides a well-defined platform for systematic studies of the mechanism of unconventional superconductivity by using different superconducting materials and substrates.

Searching for superconducting materials with a high transition temperature (T_C) is one of the most exciting and challenging fields in physics and materials science. Although superconductivity has been discovered for more than 100 years, the copper oxides are so far the only materials with T_C above 77 K, the liquid nitrogen boiling point.[1,2] The interface enhancement of electron-phonon coupling[3] and epitaxial strain[4] have previously been employed to increase the T_C of superconductors. In this Letter, we report an interface engineering method for dramatically raising the T_C of superconducting films. By growing atomically flat ultrathin films of superconducting β phase FeSe[5] on STO (001) substrates, we show the signatures of superconducting transition around 77 K.

The superconducting β-phase FeSe[5] and STO (001) substrates have a lattice mismatch of 2.5% (the lattice constant of bulk FeSe is smaller than that of STO) The dielectric constant ε of STO is 300. Under usual preparation conditions, the STO surfaces always contain some Sr or Ti clusters and other defects. We develop a new technique, named Se molecular beam etching, to obtain an atomically smooth STO surface (the STO substrates were heated to 950℃ under the Se flux for 30 min in the UHV chamber). The resulted surface morphology is shown in Fig. 1(a), which is basically free of defects. An atomically sharp interface between FeSe and STO is thus expected. We choose the binary alloy FeSe,[5] the simplest material among the recently discovered iron-based superconductors,[6] as the first system to test our idea simply because the MBE growth conditions for stoichiometric and single crystalline FeSe films have been well established.[7,8]

The Nb-doped (001)-orientated single crystal STO (Shinkosha) was chosen as a substrate for MBE-STM (Unisoku) experiment. After the Se flux treatment as mentioned above, the 1 UC FeSe films were grown by co-evaporating Fe (99.995%) and Se (99.9999%) from Knudsen cells with a flux ratio of ∼1:10 as the substrate was heated to 450℃. The growth rate is approximately 0.06 monolayer/min. Then the FeSe film was gradually annealed up to 550℃ for several hours. The scanning tunneling spectra (STS) were acquired using the lock-in technique with a bias modulation of 1 mV at 931 Hz. For the transport experiment, the insulating single crystal STO (001) was chosen as the substrate without Se etching treatment. The post-growth annealing process is similar to that mentioned above. Before being transferred out of the growth chamber, a 20-nm-thick amorphous Si film was deposited on the FeSe films at 150 K as a protection layer. The transport measurements were performed by using the standard four-probe ac lock-in method.

FeSe grows on the Se-etched STO(001) via a typical layer-by-layer mode. Figure 1(b) gives an STM topographic image of the atomically flat surface after

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deposition of the ∼1-UC-thick FeSe film. One UC FeSe along the c-axis is made of a Se-Fe-Se triple layer and has a thickness of 0.55 nm on STO, as schematically shown in Fig. 1(c). The zoom-in image in Fig. 1(d) reveals a perfectly ordered Se-terminated (001) lattice, the same as that of FeSe grown on graphene/SiC(0001).[7] The in-plane lattice constant is 3.8 Å, suggesting a 1% tensile strain in the FeSe films. High energy resolution STS measurement reveals a clear signature of superconductivity.
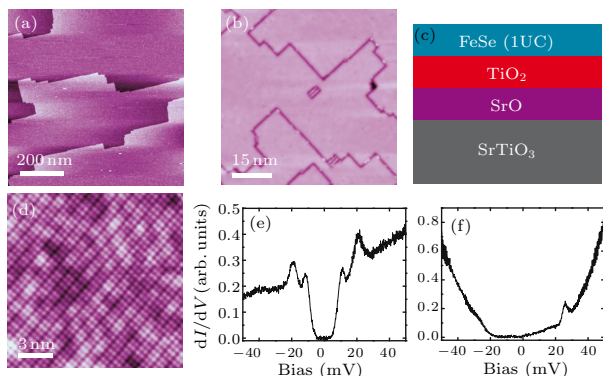

Fig. 1. (a) STM topography (800 nm×800 nm, sample bias V_S=0.3 V, tunneling current I_t=24 pA) of STO(001) surface annealed at 950°C under Se molecular flux in UHV MBE chamber. (b) STM topography (67 nm×67 nm) of the 1-UC-thick FeSe film on STO(001). Grain boundaries appear as trenches along the ⟨100⟩ or ⟨010⟩ direction. V_S=3.1 V, I_t=29 pA. (c) Schematic structure (side-view) of the FeSe films on the STO substrate along the c-axis. Some of the O atoms in the TiO$_2$ plane might be substituted by Se atoms. (d) Atomically resolved STM topography (12.8 nm×12.8 nm) showing the Se terminated FeSe (001) lattice. V_S=0.6 V, I_t=51 pA. (e) Tunneling spectrum taken on the 1-UC-thick FeSe film on STO(001) at 4.2 K revealing the appearance of superconducting gap. Four pronounced superconducting coherence peaks appear at ±20.1 mV and ±9 mV, respectively. (f) Tunneling spectrum taken on the 2-UC-thick FeSe films, which reveals a semiconductor-like (non-superconductive) behavior. High resolution STM image (not shown here) indicates that the in-plane lattice constants of the 1 UC and 2 UC films are the same.

Figure 1(e) shows the tunneling spectrum taken on the 1 UC FeSe at 4.2 K. The film exhibits an overall U-shaped conductance spectrum: a zero conductance region near the Fermi level (E_F) and an unusually large superconductive gap Δ=20.1 meV defined by half the distance between the two sharp peaks in Fig. 1(e). This value is almost one order of magnitude larger than Δ∼2.2 meV for bulk FeSe (T_C=9.4 K[9]) measured using the same instrument.[7,8] The ratio of $2\Delta/k_B T_C$ is ∼5.5 (k_B is the Boltzmann constant) for bulk FeSe. If we assume that the same superconducting mechanism holds for both the freestanding and strained FeSe films, the gap of 1 UC FeSe will lead to a superconducting transition at ∼80 K. Although such estimation is very rough, we expect that the transition temperature could very likely exceed 77 K. The

FeSe/STO heterostructure is the first system we have tested. Optimization of T_C with improved FeSe/STO interface quality and with other heterostructure systems can be envisioned.

Figure 2 shows the dI/dV spectra of the 1 UC FeSe superconducting gap at different temperatures. From 4.2 K to 23.6 K, there is no obvious change in the gap size although the coherence peaks gradually fade out, which clearly reveals the robust superconductivity of the films. In spite of the thermal drift, the superconducting gap is still clearly visible at 42.9 K. Measurement at higher temperatures (such as 77 K) is attempted. However, due to very large thermal drifting in our STM system, no reliable spectra could be obtained. While this experiment shows additional evidence for superconductivity, the occurrence of superconductivity in the 1 UC films on STO is confirmed by the presence of superconducting vortices under magnetic field. Figure 3(a) shows the zero bias conductance spectra mapping of a surface region shown in Fig. 3(b), where a vortex is clearly observed. Figure 3(c) displays a series of tunneling spectra taken at the points indicated by the dots in Fig. 3(a). Towards the vortex center, the coherence peaks are gradually suppressed while the gap size remains unchanged.
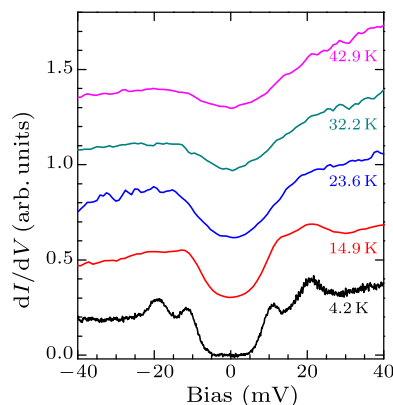

Fig. 2. The dI/dV tunneling spectra of 1 UC FeSe on the Se-etched STO(001) surface at different temperatures.

We find that the second UC and thicker films do not superconduct at all, and the observed superconductivity behavior is limited to the very first unit cell of the film above the interface. Shown in Fig. 1(f) is a tunneling spectrum taken on the 2-UC-thick films. There is no superconducting gap and its electronic structure near E_F is characterized by a semiconductor-like behavior, which is different from the freestanding FeSe films grown on graphene/SiC(0001) where the T_C increases almost linearly with the increasing film thickness.[8] The difference indicates that the FeSe/STO interface plays a significant role on the observed superconductivity.

It is difficult to directly measure the superconducting properties of the above mentioned 1-UC FeSe films

by transport measurement. The main reason for this difficulty is that the STO surface after Se beam etching at 950℃ becomes very conductive with resistivity in the order of $10^{-4}\,\Omega\cdot$cm. To carry out transport measurement, we must use the insulating STO(001) substrates that were only treated by O_2 in a tube furnace. A film of the 5 UC FeSe was covered with a 20-nm-thick amorphous Si protection layer for the *ex situ* transport measurement.
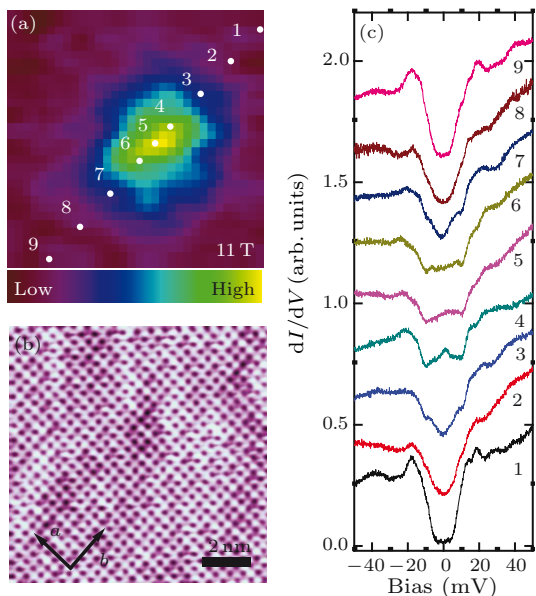

Fig. 3. (a) Zero-bias differential conductance mapping of the vortex state under magnetic field (11 T) at 4.2 K. (b) Simultaneously recorded STM topography (10.6 nm×10.6 nm) of the mapping area shown in (a). V_S=50 mV, I_t=52 pA. (c) The scanning tunneling spectra on and near the vortex core. The locations where the spectra are taken are indicated by the white points marked in (a). Near the vortex core center (points 4, 5 and 6), the superconducting coherence peaks at approximately ±20 meV disappear and bound states at E_F appear. At different locations, there is no change in the superconducting gap size.

As shown in Fig. 4(a), the temperature dependent resistance clearly reveals the occurrence of superconducting transition with an onset temperature of ∼53 K. This value is the highest among more than 30 films grown under the same condition. Typically, a value of ∼40 K is obtained. The superconducting transition is suppressed by magnetic field (see the upper inset in Fig. 4(a)), a typical characteristic of superconductors. To correlate the T_C with gap Δ, we carried out low-temperature STS measurement. Figure 4(b) shows the tunneling spectrum of the 1 UC film grown on the insulating STO under the same condition. A gap of ∼10 meV is clearly observed. Using the same BCS ratio (5.5) mentioned above, we obtain T_C=42 K, which agrees with the transport experiment. Since the 2 UC and thicker films are non-superconducting (see Fig. 4(c)), the transport measurement shown in Fig. 4(a) should only reflect the superconductivity of

the first UC FeSe. In order to determine the T_C associated with Δ=20.1 meV directly by transport, preparation of atomically flat insulating STO, which may be carried out with *in situ* MBE or pulse laser deposition without surface treatment, or using other insulating substrates is necessary. We leave this for future experiments.
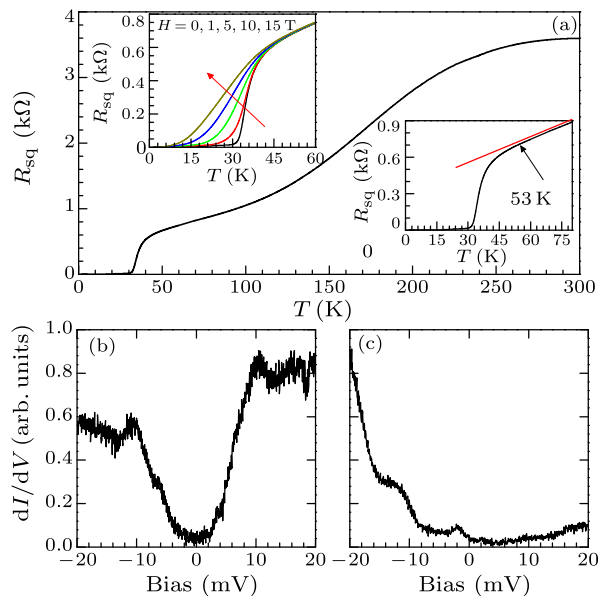

Fig. 4. (a) Temperature dependence of square resistivity (R_{sq}) of a 5-UC-thick FeSe film on insulating STO(001) surface from 0 to 300 K. Upper inset: R_{sq}–T curves at various magnetic fields along the c-axis. Lower inset: the R_{sq}–T curve from 0 to 80 K. (b) Typical dI/dV spectrum of the 1-UC-thick FeSe film on insulating STO(001) surface at 0.4 K (V_S=25 mV, I_t=99 pA). The gap as measured by two coherence peaks is ∼10 meV. (c) The dI/dV spectrum of the 2-UC-thick FeSe film on insulating STO(001) surface at 4.2 K (V_S=25 mV, I_t=47 pA).

While the mechanism for this high T_C superconductivity is not completely clear for the time being, we argue that the interface plays a major role. According to our recent study on ultrathin FeSe films (from 1 UC to 8 UC) grown on graphene/SiC (its dielectric constant $\varepsilon < 1$), the upper limit of T_C for unstrained 1 UC FeSe is 2 K.[8] For bulk FeSe, by applying external pressure T_C can increase by four times (from 9.4 K to 36.7 K) due to lattice compression.[10] Assuming a similar enhancement effect by the epitaxial strain here and taking a simplest estimation, T_C=8–10 K for 1 UC FeSe on STO would be expected. However, this effect is too weak to account for the observed value. One should consider another interface effect, the interface enhanced electron-phonon coupling[3,11] at the FeSe/TiO interface, as demonstrated in monolayer Pb and In films on Si(111) with a very similar structure.[12,13] In the present case, the effect may be further promoted by the polaronic effect associated with the high dielectric constant of STO. Another possibility is formation of two-dimensional electron gas at

the interface,[14] which may cause the high T_C. Further investigation is needed to elucidate the mechanism underlying the observed superconductivity.

Before closing, we would like to point out some implications of our study. (1) In principle, the present method can be applied to any existing superconductor material on any substrate as long as atomically sharp and strongly bonded interface can be formed experimentally. Taking K-doped FeSe[15] as an example, it is recently demonstrated that high-quality films of K-doped FeSe can be prepared on graphene by MBE.[16] If high dielectric constant substrates such as $BaTiO_3$ and $SrTiO_3$ can be used to achieve similar interface effect, one may expect much higher T_C. Therefore, our study points out a straightforward direction to find superconductors with very high T_C. (2) We note that there is a remarkable resemblance in the bonding configuration between FeSe-TiO at FeSe/STO interface and that of cuprate superconductors, for example, CuO-SrO in BSCCO, and that of iron-pnictide superconductors, for example, FeAs-LaO in LaOFeAs. From this point of view, the results presented in this work provide a crucial clue for revealing the secret of unconventional superconductivity: the high T_C of the layered cuprates may very likely result from a single unit cell of the material.[17] By systematically varying the superconducting material and substrate with different dielectric and lattice constants, one can pin down the effect responsible for the gluing mechanism of Cooper pairs. (3) By depositing dielectric gate material on top of the epitaxial superconducting films, which can easily be carried out with the present method, further enhancement in T_C by electrical field effect may be achieved. (4) Because our approach to raising T_C is based on high quality ultrathin films with atomic-layer perfection over macroscopic scale by standard MBE technique, one can easily employ it to develop superconductor electronics and other applications.

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