Electric field-induced superconducting transition of insulating FeSe thin film at 35 K

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Edited by Laura H. Greene, University of Illinois at Urbana–Champaign, Urbana, IL, and approved March 7, 2016 (received for review October 21, 2015)

It is thought that strong electron correlation in an insulating parent phase would enhance a critical temperature ($T_c$) of superconductivity in a doped phase via enhancement of the binding energy of a Cooper pair as known in high-$T_c$ cuprates. To induce a superconductor transition in an insulating phase, injection of a high density of carriers is needed (e.g., by impurity doping). An electric double-layer transistor (EDLT) with an ionic liquid gate enables such a field-induced transition to be investigated and is expected to result in a high $T_c$ because it is free from deterioration in structure and carrier transport that are in general caused by conventional carrier doping (e.g., chemical substitution). Here, for insulating epitaxial thin films (~10 nm thick) of FeSe, we report a high $T_c$ of 35 K, which is 4× higher than that of bulk FeSe, using an EDLT under application of a gate bias of ±5.5 V. Hall effect measurements under the gate bias suggest that highly accumulated electron carrier in the channel, whose area density is estimated to be $1.4 \times 10^{15}$ cm$^{-2}$ (the average volume density of 1.7 × 10$^{13}$ cm$^{-3}$), is the origin of the high-$T_c$ superconductivity. This result demonstrates that EDLTs are useful tools to explore the ultimate $T_c$ for insulating parent materials.

**Prediction**

Electric double-layer transistor | iron-based superconductors | high-density carrier accumulation

**Significance**

One of the key strategies for obtaining higher superconducting critical temperature ($T_c$) is to dope carriers into an insulating parent material with strong electron correlation. Here, we examined electrostatic carrier doping to insulator-like thin (~10-nm-thick) FeSe epitaxial films using an electric double-layer transistor (EDLT) structure. The maximum $T_c$ obtained is 35 K, which is 4× higher than that of bulk FeSe. This result demonstrates that EDLTs are useful tools to explore the ultimate $T_c$ for insulating parent materials, and opens a way to explore high-$T_c$ superconductivity, where carrier doping is difficult by conventional chemical substitution.

Author contributions: H. Hiramatsu and H. Hosono designed research; K.H., H.S., H. Hiramatsu, T.K., and H. Hosono performed research; and K.H., H.S., H. Hiramatsu, T.K., and H. Hosono wrote the paper.
The authors declare no conflict of interest.
This article is a PNAS Direct Submission.

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This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1520810113/-/DCSupplemental.
approximately 10-nm-thick FeSe films grown on STO (001) single-
substrate, clear Kikuchi patterns in the reflective high-energy
electron diffraction (RHEED) pattern, a step-and-terrace
structure with a terrace width of 120 nm, and no step-bunching
are observed in Fig. 1 C and E (see the cross-section of the STO
substrate surface in Fig. S2B). Heteroepitaxial growth of the
FeSe film on STO is confirmed by the RHEED pattern in Fig. 1D
(2θ-fixed φ scan of FeSe 200 in-plane diffraction is also
shown in Fig. S1B), and the film has an atomically flat surface
with root-mean-square roughness of 0.6 nm (Fig. 1F). It was
confirmed that the chemical composition is 1:1:1 in the FeSe
atomic ratio (measured with an electron probe microanalyzer).
Fig. 1G shows ρ-T curves of the 11-nm-thick FeSe film com-
pared with a 110-nm-thick film. The thick film (110 nm) did not
show zero resistance when T was decreased to 4 K, whereas
superconductivity with an onset Tc ~ 9 K was confirmed by its
external magnetic field dependence (Fig. 1H), i.e., a negative
shift of Tc with increasing external magnetic field. However, in
the case of the thin films (11 nm thick, see Fig. S3 for de-
termination of the thickness by X-ray reflectivity measure-
ment), the ρ-T curve shows insulator-like behavior, i.e., ρ
increased with decreasing T. The lattice parameters of the
11-nm-thick films are a_{film} = 0.3838 nm for the a axis (see Fig.
S4 for in-plane XRD patterns) and c_{film} = 0.5448 nm for the c
axis (calculated from the peak position of out-of-plane FeSe
004 diffraction, Fig. S1A). Because the values of a bulk sample
are reported to be a_{bulk} = 0.37704 nm and c_{bulk} = 0.55161 nm
(19), there is in-plane tensile strain ([a_{film} − a_{bulk}] / a_{bulk} = +1.8%) but out-of-plane compressive strain ([c_{film} − c_{bulk}] = −1.2%). These results indicate that the insulator-like behavior of the epitaxial
film originates from the in-plane tensile strain, as reported in ref. 15.
Because the insulating state is the main focus of this study, we se-
lected the thin (~10 nm) FeSe epitaxial layer as an active channel
layer for the EDLT.

We fabricated EDLTs using a thin insulating FeSe layer, as
shown in Fig. 2A. The ionic liquid N,N-diethyl-N-methyl-N-
(2-methoxyethyl)-ammonium bis-(trifluoromethylsulfonyl)imide
(DEME-TFSI) was used as the gate insulator. Fig. 2B shows the
cyclic transfer characteristics [drain current (I_D) versus gate bias
(V_G)] of the FeSe EDLT under a drain voltage V_D = +0.5 V
measured at T = 220 K. A positive V_G up to +4 V was applied to
the gate electrode, which accumulates carrier electrons in the
FeSe surface. When V_G = +3.1 V was applied, I_D began in-
creasing. The maximum I_D in the transfer curve reached 45 μA at
V_G = +4 V, along with an on−off ratio of ~2. The gate leakage
current (I_G, shown in Fig. 2B, Bottom) also increased with in-
creasing V_G up to +4 V, but it was 3 orders of magnitude lower
than I_D in the whole V_G region. After applying V_G = +4 V, I_D
returned to the initial value when V_G was decreased to 0 V. A large
hysteresis loop is observed because of the slow response of
ion displacement in the ionic liquid. Notwithstanding there is a
slight parallel shift in the slope of I_D−V_G curves, and I_D and
I_G are almost double, 84 μA at V_G = +4 V; its origin is considered to be the slow response of ion displacement, which is the same as the
hysteresis loop. This is because the shape and hysteresis width in
the second loop are very similar to those in the first loop. In
addition, we confirmed that there was no change in the I−V
characteristics in the channel layer at V_G = 0 before and after the
cyclic measurements (see Fig. S5 for the I−V characteristics).
Here, we point out that it has been reported that EDLT using an
STO channel exhibits similar characteristics, i.e., it also turns on at
about V_G = +3 V (8). In addition, it has recently been reported that
oxygen vacancies are induced in an oxide-based EDLT and the
metal state is stabilized even after removing the gate bias and
ionic liquid (10). However, the above results in Fig. 2 and Fig. S5
guarantee that the observed results are reversible and reproducible.
These results demonstrate that the origin of superconductivity by
applying gate bias, which will be shown in Fig. 3 later, is not due to
the modification of the surface chemical/mechanical structures but
the electrostatically accumulated carriers.

Fig. 3 summarizes carrier transport properties of the FeSe
EDLT, where V_G was applied at 220 K and kept constant during
the measurements with decreasing T. As shown in Fig. 3A, the
sheet resistance (R_s)−T curves at V_G = 0−3.5 V almost overlap in
the whole T range. In contrast, when V_G is increased to +3.75 V, 
R_s in the normal-state region slightly decreases, indicating that the
induced carrier density is increased by applying V_G = +3.75 V.
When V_G = +4 V is applied, a broad R_s drop is observed at 8.6 K
transport properties very complicated. In addition, the electronic structure of this insulator-like FeSe epitaxial film is still unclear. However, to roughly estimate the electron density accumulated in the channel surface by positive $V_G$, we subtracted the 1/e$R_H$ value (corresponds to the carrier density for a single band model) at $V_G = 0$ V from all of the 1/e$R_H$ values on an assumption that the linear decrease in $R_H$ with increasing $V_G$ in the $R_H$ range from 3.75 to 5.5 V corresponds to the increase in the sheet density of the accumulated electrons $\Delta N_{\text{c}} = (1/e)(R_H(V_G = x) - 1/e)(R_H(V_G = 0)) \times r$, where $r$ is thickness of the FeSe channel (8.3 nm). Then we built a phase diagram (Fig. 4). $T_c$ vs. ($V_G$ or $R_H$ at 40 K) are also shown in Fig. S7 for comparison. At 8.1 $\times$ 10$^{-13}$ cm$^{-2}$ ($V_G = +4$ V), onset $T_c$ of 8.6 K, which is close to that of bulk (16), was observed as seen in Fig. 3B. If we suppose that the whole channel layer is accumulated by electrons, the average electron density is estimated to be 9.8 $\times$ 10$^{20}$ cm$^{-3}$. This value is consistent with the native carrier concentration in bulk FeSe, the order of 10$^{20}$ cm$^{-3}$ (22). With linear increase in $\Delta N_{\text{c}}$ up to 1.4 $\times$ 10$^{20}$ cm$^{-3}$ (the average carrier density of 1.7 $\times$ 10$^{20}$ cm$^{-3}$), the maximum onset $T_c$ of 35 K was observed. This result suggests that FeSe has a potential exhibiting such a high $T_c$ if such high-density carrier doping is possible. Actually, it is reported that external high pressures lead to this high-$T_c$ superconductivity (27–37 K) (24, 25) without impurity doping, demonstrating its high-$T_c$ potential.

The above observation suggests that applying a gate bias changes the structure and/or the electronic state of the FeSe epitaxial films. Thus, we would like to discuss the origin of this high-$T_c$ superconductivity. First, we discuss the possibility of a chemical reaction between the FeSe channel and the DEME-TFSI ionic liquid. Fig. 5A shows XRD patterns of the FeSe film dipped in DEME-TFSI without an applied gate bias. No impurity phase was detected, which is confirmed by the wide-range pattern from $2\theta = 10$–80° in Fig. S8A, indicating that neither a

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**Fig. 2.** (A) Device structure and photograph of the EDLT using the thin insulating FeSe layer as a channel. (B) Transfer characteristics (drain current $I_D$ versus gate bias $V_G$) of the FeSe EDLT under $V_D = +0.5$ V at $T = 220$ K cyclically measured for two loops. The arrows indicate the $V_G$-sweep directions starting from $V_G = 0$ V. (Bottom) The leakage current ($I_L$) versus $V_G$ is also shown.

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With further increase in $V_G$, this $R_H$ drop shifts to higher $T$. It should be noted that zero resistance is clearly observed at 4 K along with the onset $T = 24$ K when $V_G = +5$ V is applied. From $V_G = +5$ V to $+5.5$ V, there is a clear enhancement of the onset $T_c$ of the $R_H$ drop (from 24 to 35 K) along with reduction of the normal-state resistivity. Fig. 3C shows the magnetic field dependence at $V_G = +5.5$ V, confirming its superconducting transition, i.e., the onset $T_c$ shifts to lower $T$ with increasing external magnetic field. The superconducting state remains even when the external magnetic field is increased to 9 T, indicating that the upper critical magnetic field is considerably higher than 9 T. The upper critical field estimated from Fig. 3C using Werthamer–Helfand–Hohenberg theory (20) is $\sim 70$ T (Fig. S6), which is much higher than that (30 T) of bulk FeSe (21).

To confirm high-density carrier accumulation in the EDLT, we performed Hall effect measurements under applying $V_D$ up to $+5.5$ V. Fig. 3D shows Hall coefficients $R_H$ at 40 K. Positive $R_H$ are obtained at each $V_G$ applied, indicating that the major carrier in the insulator-like FeSe epitaxial films is hole and consistent with the result in a FeSe single crystal (22), although negative $R_H$ in low magnetic fields is also reported in this temperature range (23). At $V_G = 0$ V, the $R_H$ is $+1.1 \times 10^{-2}$ cm$^2$/C, which is slightly higher than $(+2 \times 10^{-3}$ cm$^2$/C) as reported in ref. 22. With increase in $V_G$ to $+3.5$ V, $R_H$ remains almost constant, which is consistent with $R_-T$ curves in Fig. 3D; i.e., they almost overlap in the whole $T$ range. With further increase in $V_G$ up to $+5.5$ V, $R_H$ decreases linearly to $+2.7 \times 10^{-3}$ cm$^2$/C. It is reported that FeSe bulk is a multiband metal, indicating that high-density electrons and holes (both are orders of 10$^{20}$ cm$^{-3}$) (23) intrinsically coexist and make its carrier transport properties very complicated.
Fig. 4. Electronic phase diagram of the FeSe EDLT. Circles and squares show onset $T_c$ ($T_{c,\text{onset}}$) and zero resistivity temperature ($T_{c,\text{zero}}$), respectively. $\Delta N_e$ indicates the accumulated electron sheet carrier density (estimated) under $V_G$. The corresponding $V_G$ are shown in the upper horizontal axis.

chemical reaction between the FeSe film and DEME-TFSI nor a lattice parameter change occurs. We then examined the effect of applying $V_G = +5$ V for 2 h (Fig. 5B). In this case, we also did not observe a change in the XRD patterns (no impurity phase was detected, as confirmed by the wide-range pattern from 20° = 10–80° in Fig. S8B). These results indicate that the FeSe layer is stable against DEME-TFSI solution, and the ions in DEME-TFSI do not intercalate into the FeSe lattice [the interaction of amide ions and/or ammonia molecules with the FeSe lattice induces a distinct expansion of the c-axis length (26)]. Thus, it is plausible that the origin of this high-$T_c$ superconductivity is field-accumulated carrier doping. We speculate that an electronic transition similar to that under high pressures would be related to this high-$T_c$ superconductivity because their maximum $T_c$ values are similar (27–37 K for the high-pressure cases) (24, 25).

In summary, we grew high-quality ~10-nm-thick FeSe epitaxial films on STO (001) substrates by MBE and confirmed their insulating electrical property. Using the high-quality thin film as a channel layer, we fabricated an EDLT to induce high-$T_c$ superconductivity. Upon applying $V_G = +5.0$ V, an insulator–superconductor transition was induced with an onset $T_c = 24$ K. The highest $T_c$ of 35 K was obtained by applying $V_G = +5.5$ V. This $T_c$ value is significantly enhanced compared with the value of bulk FeSe ($T_c \sim 8$ K). Note that the origin of the superconductivity is not in the STO substrate because the $T_c$ of STO is as low as 0.2–0.4 K even if an EDLT structure is used (8, 27). Hall effect measurements suggest that the high-$T_c$ superconductivity comes from the highly accumulated electron carriers in the FeSe channel surface. The relationship between $T_c$ and accumulated carrier density indicates that $T_c$ in FeSe channel increases monotonically to a breakdown voltage ($V_G > +5.5$ V). The present study provides a way to investigate superconducting transitions even with an insulating parent phase without alteration/deterioration by impurity doping.

Experiments

Heteroepitaxial FeSe thin films were grown on (001)-oriented STO single crystals by the MBE technique. To obtain an atomically flat substrate surface, we performed wet etching of as-received STO using a buffered HF solution, and then thermally annealed at 1,050 °C just before film growth (28). The base pressure of the MBE growth chamber was $<1 \times 10^{-7}$ Pa. We used two types of Knudsen cells (K cells) to extract pure Fe and Se molecular beams: a high-temperature K cell with a carbon heater for Fe (purity: 99.99%) and a normal K cell with a tantalum heater for Se (purity: 99.99%). The temperatures of both K cells were optimized to 1,100 °C for Fe and 140 °C for Se using a beam flux monitor near the substrate. The optimized substrate temperature was 500 °C. The film thicknesses were ~10 and 110 nm, which were determined by least-squares fitting to a fringe pattern obtained by X-ray reflectivity spectroscopy using Cu Kα, monochromated by a Ge (220) crystal. The surfaces of the STO substrates and the FeSe films were observed by in situ RHEED and atomic force microscopy (AFM) in ambient atmosphere.

The structures of the films, such as the crystal orientation, were precisely examined by XRD (source: monochromatic Cu Kα) with an analyzer crystal located in front of the detector. The ω-coupled 2θ-scans in the out-of-plane XRD measurements provided the crystallographic orientation of the film normal to the substrate surface. The tilting angle of the crystallites was obtained by ϕ-fixed ω-scans (out-of-plane XRC). The in-plane crystallographic orientation (i.e., orientation parallel to the substrate surface) was determined by ϕ-coupled 2θ-ω-scans. A 2θ-ω-fixed ϕ-scan also provided the rotational symmetry of the lattice/crystallites in the film plane. All of the axis relations of XRD can be found in ref. 29. The chemical compositions of the films (i.e., atomic ratio of Fe and Se) were determined with an electron probe microanalyzer using wavelength-dispersive spectroscopy mode.

Approximately 10-nm-thick FeSe epitaxial films on STO (001) substrates were used as the transport channel of the EDLT. The FeSe channel layer with a six-terminal Hall bar geometry (channel size: 500 μm long and 200 μm wide) and the Au pad electrodes were deposited using shadow masks. After bonding metal wires to the Au pads with In metal, the channel region was covered with a silica-glass cup (fixed with an epoxy adhesive) to add the ionic liquid. We used the ionic liquid DEME-TFSI as the medium for the gate insulator. The ionic liquid was poured into the silica-glass cup, and then a Pt coil was inserted into the ionic liquid to serve as the gate electrode. All of...
these device setup processes were performed without exposure to air. The device structure is shown in Fig. 2A.

Transfer curves (i.e., the $V_D$ dependence of the drain current $I_D$) were measured with a semiconductor parameter analyzer at 220 K. The temperature dependencies of the resistivity and sheet resistance ($\rho$ and $R_s$), and transverse resistance ($R_{\perp}$, i.e., Hall effect) at 40 K of the films and EDLTs were measured by the four-probe method under external magnetic fields of up to 9 T under an applied gate bias ($V_G$) from 0 to +5.5 V. $V_G$ was applied at 220 K because chemical reaction between FeSe layers and DEME-TFSI occurs at higher temperatures (30) and this temperature is well above the rubber phase-transition temperature of DEME-TFSI 190 K (31).

ACKNOWLEDGMENTS. This work was supported by the Ministry of Education, Culture, Sports, Science and Technology through Element Strategy Initiative to Form Core Research Center. H. Hiramatsu was also supported by the Japan Society for the Promotion of Science (JSPS) Grant-in-Aid for Young Scientists (A) Grant 25709058, JSPS Grant-in-Aid for Scientific Research on Innovative Areas "Nano Informatics” (Grant 25106007), and Support for TokyoTech Advanced Research.