Chemical pressure effect of the electron-doped FeSe films with an electric double-layer-transistor structure

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Abstract. We investigated chemical pressure effect of the electron-doped FeSe₁₋ₓSₓ and FeSe₁₋₀.₅Te₀.₅ on LaAlO₃ (x ≤ 0.25, y ≤ 0.5) with the electric double layer transistor structure. Tc of all the FeSe₁₋ₓSₓ and FeSe₁₋₀.₅Te₀.₅ films except y = 0.5 is increased by doping electron with gate voltage V_G = +5 V. Tc of the electron-doped FeSe₁₋ₓSₓ and FeSe₁₋₀.₅Te₀.₅ is decreased monotonically by substituting Se for both S and Te. The behavior is similar to those of the intercalated FeSe₁₋ₓSₓ and FeSe₁₋₀.₅Te₀.₅ and the electron-doped FeSe₁₋₀.₅Te₀.₅ with the solid-ion-conductor field-effect transistor structure, but quite different from that of the pristine FeSe₁₋ₓSₓ and FeSe₁₋₀.₅Te₀.₅. This difference is considered to originate from the difference of the Fermi surface topology, which suggests that the superconducting mechanism of the electron-doped FeSe is different from that of the pristine FeSe.

1. Introduction
Iron-based superconductors (IBSCs), which have Fe atoms at the conducting planes, have attracted much attention [1]. FeSe is the most suitable material to understand the superconductivity of IBSCs because it has the simplest crystal structure among the IBSCs. Although the superconducting transition temperature, Tc, of bulk FeSe crystal is 9 K at ambient pressure [2], which is lower than those of other iron-based superconductors, it increases by the various methods. Tc of FeSe is increased to about 40 K when the hole Fermi surface at Γ point disappears by the alkali-metal and the organic-ion intercalation [3–9] or electron doping with the electric double layer transistor (EDLT) structure [10–13]. Tc ~ 65 K, estimated from the superconducting gap closing temperature, is also reported in single layer FeSe, in which the interfacial effect between FeSe film and SrTiO₃ substrate is considered to be essential for high Tc [14–16]. Although there is a report of an observation of Tc over 100 K by an in-situ resistivity measurement for a monolayer film [17], there has been no succeeding reproducible observation of Tc > 65 K by resistivity measurement [18]. Rather, some papers reported much lower Tc than 65 K [14,19], and a possibility has been pointed out that the gap at Tc ~ 65 K observed by ARPES is just a fluctuation phenomena.

For bulk FeSe, the chemical pressure effect by substituting Se for S or Te is intensively studied. The structural phase transition from the tetragonal to orthorhombic phase, T_s, at 90 K in FeSe [2] is suppressed by substituting Se for both S and Te, in spite of the fact that the direction of the chemical pressure is opposite. The structural phase transition is believed to
have the electronic origin and is called the nematic transition [20, 21]. \( T_c \) of FeSe\(_{1-y}Te_y \) films abruptly increases to 23 K just at the tetra./ortho. boundary, while \( T_c \) of FeSe\(_{1-x}S_x \) films monotonically decreases [22–24]. To search for higher \( T_c \), it is interesting to study the chemical pressure effect for the electron-doped FeSe. FeSe\(_{1-x}S_x \) and FeSe\(_{1-y}Te_y \) films are suitable to investigate the chemical pressure effect for the electron-doped FeSe because the systematic change of composition is possible even inside the miscibility gap for bulk samples [22, 23].

In this paper, we report the chemical pressure effect for the electron-doped FeSe films with \( x \leq 0.25 \) and \( y \leq 0.5 \). \( T_c^{\text{onset}} \) of the electron-doped FeSe is decreased from 40-45 K by substituting Se for S or Te. The obtained phase diagram of electron-doped FeSe\(_{1-x}S_x \) and FeSe\(_{1-y}Te_y \) films is rather different from that of pristine FeSe\(_{1-x}S_x \) and FeSe\(_{1-y}Te_y \) films, which is considered to originate from the difference of the Fermi surface topology. The difference of the phase diagram suggests that the superconducting mechanism of the electron-doped FeSe is different from that of the pristine FeSe.

2. Method

All the FeSe\(_{1-x}S_x \) and FeSe\(_{1-y}Te_y \) films were grown on LaAlO\(_3 \) substrates by the pulsed laser deposition (PLD) method with a KrF laser [13, 22–24]. An EDLT structure was fabricated on the grown FeSe\(_{1-x}S_x \) and FeSe\(_{1-y}Te_y \) films. The ionic liquid DEME-TFSI was used as the dielectric [13]. Details of the film growth and the fabrication of the EDLT structure were described elsewhere [13, 22–24]. Before applying a gate voltage \( V_G \), the temperature dependence of the electrical resistivity was measured.

Figure 1 shows the temperature dependence of the normalized resistivity of the pristine FeSe\(_{1-x}S_x \) and FeSe\(_{1-y}Te_y \) films. All the films showed the superconducting transition at low temperatures. Then, the temperature was increased to 240-250 K with \( V_G = +5 \) V to electrochemically etch the surface dead layer of the thin films and to dope electron while monitoring the electrical resistance \( R \) and the gate current \( I_G \). The induced carrier density, \( n_{\text{ext}} \), for \( V_G = +5 \) V estimated from the capacitance of the ionic liquid DEME-TFSI [25] is about \( 6 \times 10^{14} \) cm\(^{-2} \).

Figure 2 shows the temporal variation of \( R \) and \( I_G \) in a series of the typical etching process. \( R \) increased slightly while maintaining \( T = 245 \) K and \( V_G = +5 \) V because the electrochemical reaction was induced, leading to the decrease of the thickness. Then, \( T \) was decreased down to 150 K with \( V_G = +5 \) V to stop the electrochemical reaction, and the temperature dependence of the electrical resistivity was measured again.

![Figure 1](image1.png)

**Figure 1.** Temperature dependence of the normalized resistance, \( R/R(150 \text{K}) \), of (a) FeSe\(_{1-x}S_x \) thin films and (b) FeSe\(_{1-y}Te_y \) thin films.
3. Result and Discussion

Figure 3 shows the shift of the temperature dependence of the resistivity of the FeSe$_{1-x}$S$_x$ and FeSe$_{1-y}$Te$_y$ films as the etching process was repeated. $T_c$ of all the films changes and saturates by repeating the etching procedure. This behavior is the same as the previous result [13]. All the films except $y = 0.5$ showed higher $T_c$ after the etching. For example, $T_c^{\text{onset}}$ of the FeSe$_{0.94}$S$_{0.06}$ film is increased from about 6 K to 37 K after the etching.

Figure 4 shows the temperature dependence of the temperature derivative of the resistivity of the etched FeSe$_{0.94}$S$_{0.06}$ films. The pristine sample showed the structural phase transition at about 60 $\sim$ 65 K, estimated from the kink anomaly. It seems that a kink anomaly still remains at 60 $\sim$ 65 K even after the etching. This may suggest that the electron-doped FeSe still has the structural phase transition. However it is also possible that the observed kink anomaly was due to the contribution of the non-doped layers. Actually, for FeSe flakes with an EDLT structure, $T_s$ is suppressed by applying $V_G = +4$ V [12] and $T_c$ abruptly jumped to 45 K just after the suppression of $T_s$, while $T_s$ and $T_c$ of FeSe under $V_G \leq +3$ V were almost the same as those of the non-doped FeSe. In addition, according to an angular resolved photoelectron spectroscopy (ARPES) study [26], the similar behavior was observed in the three-monolayer-thick FeSe with K adsorption. Thus, here we believe that $T_s$ is suppressed by the electron-doping even for the doped part of our films.

Figure 5(a) shows the obtained phase diagram of the pristine and the electron-doped FeSe$_{1-x}$S$_x$ and FeSe$_{1-y}$Te$_y$ films. $T_c$ of the electron-doped films decreases monotonically with substituting Se for both S and Te. In particular, in electron-doped FeSe$_{0.5}$Te$_{0.5}$, it is just 7 K, which is much lower than that of electron-doped FeSe, 42 K.

Figure 5(b) compares our data with those in literatures [5, 6, 8, 15, 27, 28]. Our results are consistent with those in the intercalated FeSe qualitatively. $T_c$ of the intercalated FeSe decreases monotonically with substituting Se for both S and Te. Although the superconductivity was not completely suppressed for the intercalated FeSe$_{0.3}$Te$_{0.7}$, an experiment with single crystals via solid-ion conductor field-effect transistor (SIC-FET) revealed that $T_c$ is suppressed from 14 K.
FeSe$_{1-x}$S$_x$  FeSe  FeSe$_{1-y}$Te$_y$

$x = 0.25$  $x = 0.06$  $y = 0.3$  $y = 0.5$

Figure 3. Shift of the temperature dependence of the resistance, $R$ of the etched FeSe$_{1-x}$S$_x$ and FeSe$_{1-y}$Te$_y$ thin films as the etching process was repeated. Arrows indicate the direction of the etching. The etching times dependence of $T_{c\text{onset}}$ is also shown.

Figure 4. The temperature derivative of the resistivity of the etched FeSe$_{0.94}$S$_{0.06}$ thin films. The black arrow indicates $T_s$ and the orange arrow indicates the direction of the etching.
down to zero by the electron doping [27]. The slight difference in $T_c$ between the intercalated FeSe$_{1-x}$S$_x$ and FeSe$_{1-y}$Te$_y$ and the electron-doped FeSe$_{1-x}$S$_x$ and FeSe$_{1-y}$Te$_y$ with EDLT could derive from the difference of the crystal structures. These results suggest that a quantum critical point of the superconductivity of electron-doped FeSe is around $y = 0.5$. The difference in $T_c$ behaviors under chemical pressure may suggest the different superconducting mechanism between pristine and electron-doped FeSe. These two systems have different Fermi surface topologies. Pristine FeSe has both hole and electron Fermi surfaces, and the scattering between hole and electron pockets is considered to be important for the superconductivity [29,30]. On the other hand, electron-doped FeSe has electron Fermi surfaces alone, where the pairing interaction can be different. It is important to investigate the $V_G$ dependence of $T_c$ to clarify the relation between the superconductivity of pristine and electron-doped FeSe.

Finally we compare our results with those of monolayer FeSe$_{1-y}$Te$_y$/SrTiO$_3$. Although the sharp resistive transition has not been reported yet except in [17], the superconducting gap of the monolayer FeSe$_{1-y}$Te$_y$/SrTiO$_3$ estimated from ARPES is almost unchanged by substituting Se for Te [16], which suggest that $T_c$ is almost unchanged by negative chemical pressure for monolayer FeSe. The result is distinctly different from our results. This difference of $T_c$ dependence on Te content may suggest that the superconducting mechanism of the monolayer films is different from that of the electron-doped films. However, it is also possible that the superconducting transition temperatures of the monolayer films are lower than the superconducting gap closing temperatures due to strong fluctuations in such a two-dimensional system. Thus, further resistivity studies for the monolayer films is still needed urgently to finally settle the issue.

![Figure 5](image-url)  
Figure 5. (a) The phase diagram of the pristine and the electron-doped FeSe$_{1-x}$S$_x$ and FeSe$_{1-y}$Te$_y$ films. (b) The comparison of $T_c$ with the other literatures. Data from the intercalated FeSe$_{1-x}$S$_x$ [5] and FeSe$_{1-y}$Te$_y$ [6,8], the electron-doped FeSe and FeSe$_{0.5}$Te$_{0.5}$ with SIC-FET [27,28] and the monolayer FeSe$_{1-y}$Te$_y$/SrTiO$_3$ [16] are also plotted.

4. Conclusion
We investigated the chemical pressure effect of the FeSe$_{1-x}$S$_x$ and FeSe$_{1-y}$Te$_y$ films by fabricating an EDLT structure, and obtained the phase diagram of electron-doped FeSe$_{1-x}$S$_x$ and FeSe$_{1-y}$Te$_y$ films ($V_G = +5$ V). $T_c$ of almost all the FeSe$_{1-x}$S$_x$ and FeSe$_{1-y}$Te$_y$ films was increased while that of the FeSe$_{0.5}$Te$_{0.5}$ film was decreased. $T_c$ of the electron-doped films...
decreases monotonically with substituting Se for S and Te, while the contrastive behavior was observed for the pristine films. The difference of the phase diagrams is considered to originate from the difference of the Fermi surface topology, which suggests that the superconducting mechanism of the electron-doped FeSe is that of the pristine FeSe. Our result demonstrates that the chemical pressure is not favorable for increase of $T_c$ of electron-doped FeSe at least at $V_G = +5$ V.

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