Synthesis, characterization, Hall effect and THz conductivity of epitaxial thin films of Fe chalcogenide superconductors

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Abstract

Method of synthesis of high-quality thin films of Fe chalcogenides, Fe(Te,Se) and FeSe are **studied**. By investigating the correlation between T_c and structural parameters, it is concluded that a compressive strain is introduced on the films on CaF₂ substrate, which leads to an increase of T_c than on oxide substrates. Properties both in the normal state and in the superconducting state are measured. Results are discussed in terms of the possibility of further increasing T_c of this material.

Keywords

THz conductivity, Hall effect, superconductivity, epitaxial film, Fe(Se,Te), PLD technique

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I. Introduction

The discovery of iron-based superconductors has attracted much attention for both fundamental studies and practical applications[1]. Among many different Fe based superconductors, iron-chalcogenide superconductors[2] (11 Fe Ch), Fe(Se, Te) is most interesting, in the sense that these materials have the highest potential for higher T_c superconductors. Although they have the simplest crystal structure, and have the T_c values which are rather low compared with those of other family members of Fe based superconductors, the T_c values increase strongly by the applied pressure[3,4,5]. In addition, substitution, intercalation of alkaline atoms *etc.* increases T_c up to 30 -45 K in a different, but closely related crystal structure.[6,7,8] Moreover, recently, high T_c superconductivity was reported in single unit cell-thick FeSe films on SrTiO₃ substrates[9]. Although it is unclear whether this phenomenon is characteristic of the interface, this report provides another example showing that 11 FeCh has potential as a very high T_c superconductor. Therefore, anisotropic pressure effects of 11 FeCh on T_c are of great interest. Some previous studies on the film growth of the optimally doped Fe(Se, Te) have suggested that the in-plane (ab-plane) compressive strain can increase the T_c value above that of bulk crystals and improve superconducting properties[10-13]. Thus, we expect the similar effect also for Te free FeSe. (Indeed, T_c values of FeSe films reported so far[14-20] are rather low, whose lattice constants were similar to those of bulk crystals.)

More importantly, a key factor determining the superconducting characteristics is the in-plane orientation. In particular, films on some substrates, such as YSZ, do not have good in-plane orientation[21,22]. Our TEM observation clearly shows that this is closely related with the diffusion of oxygen into the FeCh from the substrate[23].

Therefore, we used CaF₂ as a substrate, and leading to a higher T_c value than that of bulk crystal[12]. In this paper, we report the PLD fabrication of high-quality epitaxial thin films of 11 FeCh on CaF₂ substrates. We demonstrate that, also for FeSe, the films are compressed along the a-axis. What is remarkable is that T_c^{zero} of FeSe reach 11.4 K, which is approximately 1.5 times higher than that of bulk crystals. We also report physical properties both in the normal state and in the superconducting state (ac and dc conductivity, Hall effect), and discuss the significance of the results in terms of the possibility to further increase T_c .

2. Film synthesis and experimental techniques

All of the films in this study were grown by the PLD method with a KrF laser[21,22]. Polycrystalline pellets were used as targets. The substrate temperature, the laser repetition rate, and the back pressure were 280 °C, 10 Hz, and 10⁻⁶ Torr, respectively. Commercially available CaF₂ (100) substrates were used for the present experiments. Low substrate temperature is the key for the fabrication of well c-axis oriented 11 FeCh thin films with high T_c values[16,18]. The thicknesses of the grown films were measured using a Dektak 6M stylus profiler and were estimated to be 60–235 nm. The crystal structures and the orientations of the films were characterized by four-circle X-ray diffraction (XRD) with Cu K α radiation at room temperature. In particular, a-axis lattice constants of the films were calculated from the positions of the 001–004 reflections and the 200 reflection, respectively. The electrical resistivity and Hall effect were measured for six-terminal patterned samples using a physical property measurement system (PPMS) from 2 to 300K under magnetic fields of up to 9 T applied perpendicularly to the film surface. Superconductivity was also confirmed by the magnetization measurement; T_c^{onset} measured by magnetization correspond to T_c^{zero} measured by electrical resistivity.

Ac conductivity in THz region was measured by a home made transmission type time-domain spectrometer[24]. A merit of this technique is both of the real and the imaginary parts of complex conductivity are obtained directly from the complex transmission data, which means that the Krammers-Kronig transformation is not necessary. Thus, this technique is valuable particularly for materials whose conductivity spectrum is far from an ordinary Drude type even in the THz frequency region.

3. Experimental results

3.1 Film characterization

Our films are well c-axis oriented, which is confirmed by $\omega - 2\theta$ X-ray diffraction studies. Furthermore, the ϕ scans of the 101 reflection of the film shows a clear four-fold symmetry with the full widths at half maximum (FWHM) of four peaks of $\Delta\phi \approx 1.0^\circ$ [12]. We have also confirmed the in-plane orientation to be FeCh[100]//CaF₂[110], representing that our films are epitaxially grown[25].

Figure 1 shows the calculated a- and c-axis lengths of the grown films of FeSe as a function of the film thickness. It is clear that the both axis lengths are dependent on the film thickness. In particular, the a-axis decreases as the film thickness increases up to

150 nm, and then the a-axis slightly increases for films with larger thickness. This behavior is similar to that observed in Fe(Se, Te) films on LaAlO₃[10]. The authors in Ref. 10 explained that this thickness dependence is due to Volmer-Weber type growth of the Fe(Se, Te) film, which we believe is also the case with FeSe films on CaF₂. Compared with the lattice parameters for bulk single crystals ($a=3.7756\pm0.02\text{\AA}$, $c=5.526\pm0.03\text{\AA}$)[6-8], the films grown on CaF₂ are compressed along the a-axis and are simultaneously elongated along the c-axis. Such short a-axis lengths of the FeSe films cannot be explained simply by the difference between the lattice constants of the substrate and the overlayer because the lattice constants of CaF₂ ($a/\sqrt{2} = 3.863\text{\AA}$) are longer than the a-axis of FeSe. Our TEM study on Fe(Se,Te) suggests that the penetration of F⁻ ions from the CaF₂ substrates into the films is a possible mechanism for the contraction of the a-axis lengths of our films[23]. We believe that the same explanation is applicable also for FeSe.

Fig. 2 shows the temperature dependence of the resistivities of the grown films of FeSe_{0.5}Te_{0.5} and FeSe, whose T_c^{zero} are 19 K and 12 K, respectively. These T_c^{zero} s are higher than that of bulk crystals, and the magnitudes of the resistivity at room temperature are almost the same or smaller than those of bulk single crystalline samples[25-28]. It is noted that our films on CaF₂ show higher T_c^{zero} even for films with much smaller thickness than those reported in Ref. 20. For instance, for FeSe films with thicknesses less than 100 nm, $T_c^{\text{zero}}=9.33\text{K}$ is also far better than the previously reported results for films on oxide substrates with (101) orientation ($T_c^{\text{zero}}\approx 6.5\text{K}$ for 140 nm, $T_c^{\text{zero}}\approx 8\text{K}$ for 1.5 μm)[13,15]. The thickness dependence of T_c^{zero} is similar to that of the a-axis length of the films; T_c^{zero} increases with increasing film thickness up to 150 nm and further increase of thickness results in the decrease in T_c^{zero} . For 11 FeCh, the T_c^{zero} values have a strong correlation with c/a [21,25], which is shown in Fig. 3 for FeSe. This suggests that the increase of T_c^{zero} in our films is caused by the compressive strain.

Anyway, we can safely mention that it becomes possible to investigate physical properties of 11 FeCh films, since samples with sufficient quality have been prepared. Below, we discuss some of these both above and below T_c , **which is the temperature at which the resistivity drops to a half of its value in the normal state.**

3.2 Properties above T_c (in the normal state)

Figure 4 shows the complex conductivity of FeSe films at 120 K and 90 K, both of which are above T_c . Frequency dependence of conductivity are well expressed by an ordinary

Drude formula,

$$\sigma(\omega) = \sigma_0 \frac{1}{1 - i\omega\tau},$$

where ω and τ is angular frequency and relaxation time of the quasi-particle, respectively, and σ_0 is dc conductivity.

Figure 5 shows the temperature dependence of σ_0 and τ as a function of temperature. A change takes place both in σ_0 and τ around at 100 K, which is close to the structural transition temperature, T_s (= 90 K)[29]. In particular, the

change in τ is very big, whereas that in σ_0 is rather small. Since $\sigma_0 / e^2 \tau = n / m^*$ in the Drude model (e is electronic charge, n is quasi-particle number density, and m^* is effective mass), the data in Fig. 5 represents that n/m^* decreases sharply around T_s with decreasing temperature.

Figure 6 shows the temperature dependence of Hall coefficient, R_H , of an FeSe film with T_c of 11.4 K. Here again, a big change takes place around T_s , and R_H becomes largely positive at low temperatures. It is interesting to see the result of an ARPES study [30] where they reported a big change in the electronic structure around T_s only in the electron Fermi surfaces at M point. Taking this information into account, our Hall effect data suggest the decrease of electron contribution below T_s . Thus, in the low temperature limit, we can regard that the dominant contribution to the transport properties is by holes around Γ point. It is well established that in Fe based superconductors many properties can be understood by an effective two carrier model reduced from the exact 5 band model. Thus, starting from a two carrier model composed by one electron band and one hole band, the above result suggests that in the low temperature limit, R_H can be expressed by a single hole, $R_H = 1 / n_h e$, where n_h is the hole density. By combining the conductivity data shown in Fig. 5 with the R_H data in Fig. 6, we obtained parameters as $n_h = 1.0 \times 10^{21} \text{ cm}^{-3}$, $m_h/m_0 = 1.3$ (m_0 is the free electron mass), and $\tau_h = 0.026 \text{ ps}$ at 20 K, for instance. These numbers, particularly that of m_h , may suggest that FeSe is not strongly correlated, which is in contrast to Fe(Te,Se). However, other data than the effective mass should piled up to make this suggestion more convincing.

3.3 Properties below T_c (in the superconducting state)

Figure 7 shows the temperature dependence of the resistivity of an FeSe film under magnetic fields up to $\mu_0 H = 9 \text{ T}$ applied along the c-axis. From this data, the upper

critical field is estimated as a function of T_c by using the conventional

Werthamer-Helfand-Hohenberg (WHH) theory. $B_{c2}^{H//c}$ increases almost linearly as the temperature decreases. The slight positive curvature of $B_{c2}(T)$ observed at very low fields may derive from the multiband nature of this material[31]. Our values ($B_{c2,0}^{H//c}$

=33 T; theoretically predicted number is $B_{c2,0}^{H//c} = 22.8$ T) is higher than any reported value for FeSe thin films that was estimated in the same way[17,19]. This also leads to a Ginzburg-Landau coherence length of $\xi_{ab}(0) \approx 38.0$ Å, which is longer than that of FeSe_{0.5}Te_{0.5} thin films on CaF₂ substrates[12]. These aspects of FeSe thin films on CaF₂ should be beneficial for applications of these materials.

Next, we discuss the conductivity spectrum in the THz region. For this issue, we focus on Fe(Se,Te), since the T_c value of FeSe is at maximum 12 K currently. This is slightly insufficient for extracting parameters in the superconducting state in the low temperature limit, using our THz measurement system. Figure 8 shows the conductivity spectrum (frequency dependence of conductivity) of an Fe(Te,Se) film with $T_c=18$ K at several fixed temperatures. At low temperatures, the real part shows a dip and the imaginary part is inversely proportional to the frequency. Both of these are clear signs of superconductivity. From the position of the dip in the real part, superconducting gap is estimated, leading to $2\Delta = 4.2$ meV ($2\Delta/k_B T_c = 2.7 \pm 0.5$). These are in good agreement with previously published numbers obtained by different techniques for bulk crystals[32,33,34].

Figure 9 shows the temperature dependence of conductivity at fixed frequencies, where dc conductivity data are also shown in the panel for the real part. Above T_c , conductivity values agree with dc values, considering possible experimental errors for different techniques. The imaginary part is finite even above T_c . However, this does not mean that the superfluid remains finite far above T_c . Indeed, in the real part around T_c , there is no pronounced peak, which is definitely different from the case of cuprate superconductors[24,35,36]. This means that the superconductivity fluctuation of Fe(Se,Te) is not so prominent as was in cuprates. Therefore, a finite imaginary part above T_c should be regarded as the contribution from quasiparticles. To proceed further, we analyze the data using a two fluid formula; a Drude quasiparticle plus a superfluid,

$$\sigma_1(\omega) = \sigma_0 \frac{1}{1 + (\omega\tau)^2} (1 - f_s),$$

$$\sigma_2(\omega) = \sigma_0 \frac{(\omega\tau)^2}{1 + (\omega\tau)^2} (1 - f_s) + \sigma_0 \frac{1}{\omega\tau} f_s,$$

$$f_s \equiv \frac{n_s(T)}{n_N(T > T_c)},$$

where f_s is a superfluid fraction, n_s and n_N are superfluid density and normal fluid density at corresponding temperature T , respectively. Figure 10(a) shows the temperature dependence of τ at fixed frequencies. At the lowest frequencies, τ increases with decreasing temperature, and continues to increase even below T_c . This is a well known behavior for superconductors where dominant scattering mechanism is an inelastic scattering. Cooper-pair formation causes big change in the density of states of the quasiparticle, and largely affects the inelastic scattering. One should note that this does not necessarily mean that the mechanism of the cooper pair formation has an electronic origin. For higher frequencies, the increase of τ is not observed. This is just because the frequency is larger than the superconducting gap, leading to an excitation of quasiparticles by the electromagnetic wave.

Figure 10(b) shows τ as a function of frequency at fixed temperatures. Here the data taken at microwave frequencies[37] are also shown. At low temperatures, τ depends on frequency as $1/\omega^\alpha$ only below 1 THz, and there is no special feature above the superconducting gap. This is consistent with the fact that no definite feature on the second gap was observed in the conductivity spectrum in Fig. 8. These behaviors are slightly different from the early data taken at optical frequencies[32]. At present we do not know the reason of discrepancy. However, as was already described, the data at THz frequencies do not need Krammers-Kronig transformation, giving a more direct data on conductivity. This might be related with the discrepancy.

From the imaginary part of conductivity, the low temperature penetration depth of 460 nm is obtained, which is in good agreement with numbers obtained in previous studies[37,38,39,40]. Figure 11 shows the temperature dependence of superfluid fraction f_s as a function of normalized temperature T/T_c . Here again, the data taken in microwave region are also shown. Similar to the microwave data, development of f_s with decreasing temperature is rather gradual, and remains about 30 % even at 0.6 T/T_c . This is in sharp contrast with the data in other Fe based superconductors; for example 70 % in LiFeAs at 0.6 T/T_c [31]. We have interpreted this behavior to be due to dirty to clean crossover with decreasing temperature, related to the increase of τ with decreasing temperature[37]. Thus, even in high quality epitaxial films of 11 FeCh, a “dirty” feature still remains at high temperatures around T_c . It is well established that

11FeCh has considerable amount of excess Fe in many cases[26]. Indeed, the excess Fe suppresses T_c . Not only affecting T_c value, it might also affect the degree of superconducting condensation. The “dirty” feature observed in the temperature dependence of f_s of a very high quality epitaxial film of 11 FeCh may be related to the excess Fe.

4. Discussion

Based on the above experimental results, we discuss the possibility of further increasing T_c of 11 FeCh as a potentially feasible material as high T_c superconductor.

The result shown in Fig. 3 clearly shows that a strong compressive strain is introduced in our films on CaF_2 , leading to higher T_c . However, c/a dependence of T_c of FeSe is weak compared with that of Fe(Se, Te), and the T_c values of FeSe films under anisotropic compression are unlikely to reach 37 K, which is accomplished by hydrostatic pressure[3,4]. Therefore, the simultaneous compression of the c - and a -axis lengths may be a key to realize a very high T_c material based on 11 FeCh. We should note, however, that the relation between T_c and c/a is simplistic and is only a guiding principle in the search for high T_c materials. To understand the relation between T_c and crystal structure, we should evaluate specific structural parameters, such as the Ch-Fe-Ch angle[41] and/or the Ch height from the Fe layer.[42]

Next, the normal state study showed that the structural phase transition largely affects the electron Fermi surface. Previously, we investigated Hall effect in Fe(Se,Te) having various different resistivity vs temperature curves, and it is concluded that keeping itinerancy for both of holes and electrons down to low temperatures is a key for the emergence of superconductivity[43]. Thus, if we can suppress the decrease of electron contribution possibly caused by the structural phase transition, higher T_c might be expected in FeSe, and also for other 11 FeCh.

The third point we should focus is the issue of the excess Fe. The above results suggest that the excess Fe plays important roles on superconductivity; T_c values and degree of condensation, f_s . Recently, we have clarified that an appropriate “vacuum” annealing improved the superconducting characteristics, as a result of the oxidization of excess Fe[44]. Such additional treatment should improve the condensation, and probably leads to higher T_c .

Finally, it should also be noted that our films on CaF_2 do not require any buffer layers. Our results for these binary or ternary system will pave the way for the application of iron-based superconductors.

5. Conclusion

In conclusion, we have **studied** a technique to fabricate high-quality epitaxial films of 11 FeCh using CaF_2 substrate, where a compressive strain was turned out to be introduced successfully, leading to higher T_c . By investigating physical properties such as complex conductivity and Hall effect both above and below T_c , several specific features have been figured out. Based on these, we briefly discussed the possibility to further increase T_c and to improve superconducting characteristics.

Our results in these binary and ternary systems are very promising, and **these materials** can be a good candidate for the application of iron-based superconductors, **such as the base materials for superlattice fabrication and Josephson junction fabrication.**

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Figure Captions

Figure 1. a - and c -parameters of a FeSe film grown on CaF_2 as a function of the film thickness. A Dashed line is those of bulk crystals.

Figure 2. Temperature dependences of the resistivities of $\text{FeSe}_{0.5}\text{Te}_{0.5}$ and FeSe. with several different thicknesses grown on CaF_2 . Arrows indicate the typical value of T_c of bulk crystals, and the insets show the magnification around T_c .

Figure 3. T_c^{zero} values for five FeSe films on CaF_2 as a function of c/a . The values for bulk single crystals[26–28] and a film on oxide substrate[18] are also plotted for comparison. A dashed line is a guide for the eye.

Figure 4. Complex conductivity spectra, $\sigma(\omega)$, of an FeSe flim of 60nm thickness grown on CaF_2 at (a) 120 K and (b) 90 K. Gray lines are the Drude fit.

Figure 5. Temperature dependences of (a) τ and (b) σ_0 obtained by the Drude fit for the FeSe film of 60nm thickness shown in Fig. 4. A solid line in fig. (a) is a guide for the eye. The temperature of the structural transition in bulk crystals, $T_s^{\text{bulk}}=90$ K is also shown in both figures.

Figure 6. Hall coefficient, R_H , of an FeSe film of 150 nm thickness as a function of temperature. The temperature of the structural transition in bulk crystals, $T_s^{\text{bulk}}=90$ K is also shown in both figures.

Figure 7.(a) dc resistivity of a FeSe film of 150 nm thickness as a function of temperature and magnetic field, which is parallel to the c axix. (b) T_{mid} vs corresponding magnetic field, B . The inset shows a linear fit of the same data.

Figure 8. Conductivity spectra, $\sigma(\omega)$, of $\text{FeSe}_{0.5}\text{Te}_{0.5}$ (60 nm) at different temperatures mainly below $T_c=18\text{K}$; (a) real part, σ_1 (b) imaginary part, σ_2 . Solid curves are the Drude fit for the data above T_c .

Figure 9 Complex conductivity of of $\text{FeSe}_{0.5}\text{Te}_{0.5}$ (60 nm) as a function of temperature at different fixed frequencies. (a) real part, σ_1 (b) imaginary part, σ_2 . Solid lines are the guide for the eye, and a gray curve in (b) is the temperature dependence of dc

resistivity, to show the position of T_c .

Figure 10 (a) Quasiparticle scattering time, τ , of FeSe_{0.5}Te_{0.5} (60 nm) as a function of the reduced temperature, T/T_c . Solid lines are the guide for the eye. (b) Quasiparticle scattering rate, $1/\tau$, of the same sample as a function of frequency. Data taken at a microwave frequency were also shown. Dashed lines are guide for the eye.

Figure 11. superfluid fraction, f_s , of FeSe_{0.5}Te_{0.5} film (60 nm) as a function of the reduced temperature, T/T_c . For comparison, the data of FeSe_{0.4}Te_{0.6} taken at microwave frequencies [37] and the microwave data in LiFeAs [31] are also shown.

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