Fabrication of FeSe$_{1-x}$ superconducting films with bulk properties

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Abstract. We have fabricated high-quality FeSe$_{1-x}$ superconducting films with a bulk $T_c$ of 11–12 K on different substrates, Al$_2$O$_3$(0001), SrTiO$_3$(100), MgO(100), and LaAlO$_3$(100), by using a pulsed laser deposition technique. All the films were grown at a high substrate temperature of 610 °C, and were preferentially oriented along the (101) direction, the latter being to be a key to fabricating of FeSe$_{1-x}$ superconducting thin films with high $T_c$. According to the energy dispersive spectroscopy data, the Fe:Se composition ratio was 1:0.90±0.02. The FeSe$_{1-x}$ film grown on a SrTiO$_3$ substrate showed the best quality with a high upper critical magnetic field [$H_{c2}(0)$] of 56 T.

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1. Introduction

A new iron age has occurred in the field of superconductivity and started when the discovery of the LaFeAsO$_{1-x}$F$_x$ superconductor in 2008 gave rise to a huge interest in depressed superconductivity division [1]. Over the past two years, an enormous number of papers have been published and more than 70 new iron-based superconductors have been discovered [2]. Generally, iron-based superconductors are classified as REFeAsO (1111 family, RE: rare earths), AFe$_2$As$_2$ (122 family, AE: alkaline earths), AFeAs (111 family, A: Li, Na), and FeCh (11 family, Ch: chalcogens). Among these families, a tetragonal phase FeSe is an attractive material for finding the origin of iron-based superconductors due to its simple crystal structure [3]. It has just superconducting layers without block layers, and its superconducting critical temperature ($T_c$) is very sensitive to change in the strain. Although the $T_c$ of bulk FeSe is as low as 8.5 K, its $T_c$ can be raised to 37 K under pressure [4, 5]. In addition, the $T_c$ of FeSe$_{0.5}$Te$_{0.5}$ thin films can be enhanced to 21 K by controlling the biaxial strain [6].

However, compared with Te- or S-doped superconductors [7, 8], research on pure FeSe superconductors is rarely carried out. Synthesis of single-phase FeSe superconductors with a tetragonal structure is not easy because it has several types of phases, such as tetragonal (PbO-type), hexagonal (NiAs-type), and Fe$_7$Se$_8$ phases [3, 9]. Moreover, most of them, except for the tetragonal phase, are known to be ferromagnetic phases [10]. According to recent reports [11], the possibility of ferromagnetism was presented in FeSe thin films with a tetragonal structure at temperature near room temperature, but this issue is still under debate.

Nevertheless, the observation of superconductivity in the tetragonal phase of FeSe by Hsu et al. [3] has offered a new member (11 family) to the class of iron-based superconductors. Also, an expectation of a higher $T_c$ in FeTe than in FeSe, which is caused by strong paring [12], has brought about active research on the Fe-Te-Se system [6, 7, 13]. If the intrinsic properties are to be investigated precisely, undoped FeSe or FeTe single crystals with large sizes or thin films are required because isovalent substitution induces lattice strain due to the different ionic sizes.

Very recently, Han et al. [14] and Si et al. [15] reported the appearance of superconductivity in FeTe films due tensile stress effects and oxygen incorporation, respectively, while no superconductivity was observed in bulk samples [8]. In the case of FeSe films, only a few papers have been published [16, 17, 18], and the experimental results are still unsatisfactory compared to those for bulk samples. Furthermore, there has been little progress in the growth of pure FeSe films whereas some research groups have fabricated high-quality Te-doped FeSe thin films [6, 19].

In this work, we report the fabrication of FeSe$_{1-x}$ films with a bulk $T_c$ of 11 – 12 K on several types of substrates, Al$_2$O$_3$(0001) [AO], SrTiO$_3$(100) [STO], MgO(100), and LaAlO$_3$(100) [LAO], by using a pulsed laser deposition (PLD) technique. All samples were grown at a high substrate temperature of 610 °C and showed high upper critical fields with a (101) preferred orientation.
Fabrication of FeSe\(_{1-x}\) superconducting films with bulk properties

2. Experiments

Homemade FeSe targets having a stoichiometric ratio of Fe:Se = 1:1 were used in this study, and the laser beam was generated by using a Lambda Physik KrF excimer laser (\(\lambda = 248\) nm). Our PLD system is described in detail elsewhere [20, 21]. A laser energy density of 1.15 J/cm\(^2\), a high repetition rate of 48 Hz, and high substrate temperature (\(T_s\)) of 610 °C were used for the deposition of FeSe\(_{1-x}\) films in a high vacuum state of \(\sim 10^{-5}\) Torr. The high frequency of the laser is favorable for the fabrication of films containing highly-volatile materials [20, 21]. High growth rates of 5 – 6 nm/s were obtained under these growth conditions. The compositional ratio of the deposited films was Fe:Se = 1:0.90 ± 0.02.

The crystal phases and orientations of the fabricated FeSe\(_{1-x}\) films were investigated by using x-ray diffraction (XRD). The surface morphology and thickness were checked by using scanning electron microscopy (SEM). The elemental composition ratio was analyzed by using energy dispersive spectroscopy (EDS) based on the results for a standard stoichiometric sample. A vibrating sample measurement system (SQUID-VSM, Quantum Design) and a physical property measurement system (PPMS, Quantum Design) were used for the study of their superconducting properties.

3. Results and discussion

The temperature dependences of the resistivity (\(\rho\)) of the FeSe\(_{1-x}\) films are shown in figure 1. A Se deficiency of \(x = 0.10 \pm 0.02\), which was comparable with previously reported samples [3, 18], was examined by using EDS. All of the deposited films showed a \(T_c,90\%\) of 11 – 12 K and a \(T_c,10\%\) of \(\sim 8\) K, and their transition widths (\(\Delta T_c\)) decreased with increasing residual resistivity ratio (RRR); these data are summarized in table 1. All these data are very close to the previous results for bulk samples [3, 4, 22] and show a higher \(T_c,10\%\) and a narrower \(\Delta T_c\) than previously reported [16, 17, 18]. In figure 1(a), the \(\rho(T)\) of the film grown on a STO substrate is multiplied by 5 because it has small values compared with those of the other film. The change of slope around 120 K seems to originate from the influence of a spin-density wave (SDW) [12, 22, 23].

Figure 1(b) is a magnified view near the superconducting transition temperature; the resistivity values are normalized to those at 15 K. The inset shows the temperature dependence of the magnetization (\(M\)) of the FeSe\(_{1-x}\) film fabricated on a STO substrate. The clear diamagnetic signal indicates that it has good bulk superconductivity. Although the irreversible temperature of \(\sim 6\) K in the \(M - T\) curve is lower than the \(T_c\) obtained from \(\rho(T)\), obtaining the superconducting signal from magnetization measurements in FeSe superconductors is not easy due to its intrinsic magnetism [24] or its magnetic impurities, such as hexagonal FeSe phases and Fe impurities [3, 25].

Figure 2 shows the \(\theta - 2\theta\) scan XRD patterns of FeSe\(_{1-x}\) films prepared on the Al\(_2\)O\(_3\)(0001) and SrTiO\(_3\)(100) substrates. Our samples are mainly oriented along the (101) direction of the tetragonal (T) structure, but other phases exist in tiny amounts,
Fabrication of FeSe$_{1-x}$ superconducting films with bulk properties

Figure 1. (a) Resistivity as functions of temperatures for FeSe$_{1-x}$ films grown on several types of substrates, and (b) an enlarged view near the superconducting transition temperature, with the resistivity values normalized to those at 15 K. The inset of (b) shows the field-cooled (FC) and the zero-field-cooled (ZFC) measurements for an FeSe$_{1-x}$ film grown on a SrTiO$_3$ substrate at $H = 20$ Oe.

such as hexagonal (H) FeSe and Fe$_7$Se$_8$. The lattice constants for the $a$- and $c$-axis are 3.769 Å and 5.490 Å, respectively, which are close to the values observed in the bulk samples [3]. No peak shift is detected regardless of the substrate. We believe that this is

Table 1. Summary of the $\rho(T)$ data of figure 1: superconducting transition temperatures $T_{c,90\%}$ (90% of $\rho_n$) and $T_{c,10\%}$ (10% of $\rho_n$), where $\rho_n$ is the normal state resistivity near $T_c$, $\Delta T_c = T_{c,90\%} - T_{c,10\%}$, and RRR ($= \rho_{300K}/\rho_n$). Fe:Se data are the composition ratios, obtained from EDS, of the FeSe$_{1-x}$ films fabricated on the different substrates.

| substrate | $T_{c,90\%}$(K) | $T_{c,10\%}$(K) | $\Delta T_c$(K) | RRR    | Fe:Se  |
|-----------|----------------|----------------|----------------|--------|--------|
| Al$_2$O$_3$ | 10.5           | 8.2            | 2.3            | 4.5    | 1:0.91 |
| SrTiO$_3$  | 11.4           | 8.3            | 3.1            | 4.2    | 1:0.92 |
| MgO        | 11.7           | 8.1            | 3.6            | 3.4    | 1:0.88 |
| LaAlO$_3$  | 11.2           | 7.7            | 3.5            | 3.3    | 1:0.91 |
Fabrication of FeSe$_{1-x}$ superconducting films with bulk properties

Figure 2. $\theta - 2\theta$ scan XRD patterns of the FeSe$_{1-x}$ films grown on Al$_2$O$_3$(0001) and SrTiO$_3$(100) substrates. The preferred orientation is seen to be along the (101) direction (T: tetragonal, H: hexagonal).

Figure 3. SEM images of the FeSe$_{1-x}$ films grown on several different substrates: (a) Al$_2$O$_3$, (b) SrTiO$_3$, (c) MgO, and (d) LaAlO$_3$. All surface morphologies show well-linked states without cracks.

due to the growth direction of the film being along the (101) direction rather than along the c-axis or the ab-axis. Wang et al. [16] reported that the orientation of the T(101) direction is the key to fabricating FeSe$_{1-x}$ films with strong superconductivity.

The surface morphologies of the FeSe$_{1-x}$ films on the AO, STO, MgO, and LAO substrates were checked by using scanning electron microscopy (SEM), as shown in figure 3. The SEM images, (a), (b), (c), and (d), show that compared with previous reports [13, 26], all films have well-connected morphologies without cracks, which is one factor in obtaining higher-quality samples with a sharper superconducting transition. The white tiny grains in figure 3(b) were shown to be Fe particles by using EDS. Films grown on LAO had larger Fe lumps than ones grown on STO. These Fe lumps, which
Fabrication of FeSe\textsubscript{1-x} superconducting films with bulk properties

Figure 4. $\rho(T)$ curves for FeSe\textsubscript{1-x} films on SrTiO\textsubscript{3} substrates under magnetic fields up to 7 T for a field parallel to the substrate plane. The inset presents the linear fittings for $H_{c2}(T)$ at $\rho_{90\%}$, $\rho_{50\%}$, and $\rho_{10\%}$.

were ferromagnetic, are a possible source of the proximity effect that accompanies a suppression of $T_c$.\textsuperscript{[27]} These locally weakened superconducting regions generate a broad superconducting transition. The thicknesses determined from the SEM cross-sectional images in (a), (b), (c), and (d) are 1.5, 1.6, 1.6, and 1.8 $\mu$m, respectively.

Finally, we investigated the temperature dependence of the upper critical magnetic field ($H_{c2}(T)$) for the FeSe\textsubscript{1-x} films. Figure 4 displays the $\rho - T$ curves of the film prepared on a STO substrate for various magnetic fields from 0 to 7 T, and the inset shows the fitting of $H_{c2}(T)$. The data points were obtained from the $\rho - T$ curves for three defined criteria; $\rho_{90\%}$ (90\% of $\rho_n$), $\rho_{50\%}$ (50\% of $\rho_n$), and $\rho_{10\%}$ (10\% of $\rho_n$) are equivalent to critical temperatures of $T_{c,90\%}$, $T_{c,50\%}$, and $T_{c,10\%}$, respectively. The values of $H_{c2}(0)$ at $\rho_{90\%}$ are 58, 56, 50, and 57 T for films grown on AO, STO, MgO, and LAO substrates, respectively, which were estimated by using a linear extrapolation\textsuperscript{[14]}. These high values of $H_{c2}(0)$ open up the possibility for practical applications, provided we can grow better films with higher values of $T_c$.

4. Conclusions

In summary, we have deposited FeSe\textsubscript{1-x} films with bulk superconducting properties on various types of substrates, Al\textsubscript{2}O\textsubscript{3}(0001), SrTiO\textsubscript{3}(100), MgO(100), and LaAlO\textsubscript{3}(100), by using a pulsed laser deposition system. All films were preferentially oriented along the (101) direction, and showed upper critical fields as high as 50 T. Our results showed that (101)-oriented FeSe\textsubscript{1-x} films with bulk superconductivity could be fabricated at high growth temperature regardless of type of substrate.
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