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2009 J. Phys.: Condens. Matter 21 235702
(http://iopscience.iop.org/0953-8984/21/23/235702)

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Preparation and superconductivity of iron selenide thin films

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Received 12 January 2009, in final form 24 April 2009
Published 15 May 2009
Online at stacks.iop.org/JPhysCM/21/235702

Abstract

FeSe$_x$ ($x = 0.80, 0.84, 0.88, 0.92$) thin films were prepared on SrTiO$_3$(001) (STO), (La, Sr)(Al, Ta)O$_3$(001) (LSAT), and LaAlO$_3$(001) (LAO) substrates by a pulsed laser deposition method. All of the thin films show single-phase and $c$-axis oriented epitaxial growth, and are superconducting. Among them, the FeSe$_{0.88}$ thin films show a $T_{c,\text{onset}}$ of 11.8 K and a $T_c$ of 3.4 K. The upper critical magnetic field is estimated to be 14.0 T.

(Some figures in this article are in colour only in the electronic version)

Since the discovery of LaFeAsO$_{1−x}$F$_x$ superconductor [1], progress has been made very rapidly and four kinds of iron-based superconductors in total have been found [1–10]: (1) F-doped ROFeAs quaternary compounds (1111 phase, R = La, Ce, Pr, Nd, Sm, Gd, etc) [1–5], (2) double-FeAs-layered A Fe$_2$As$_2$ ternary compounds (122 phase, A = Ca, Sr, Ba, with or without alkali metal doping) [6, 7], (3) single-FeAs-layered LiFeAs ternary compounds (111 phase) [8, 9], and (4) $\alpha$-FeSe binary compounds (11 phase) [10]. Among them, $\alpha$-FeSe is very interesting since it possesses the simplest crystal structure; in particular, it is the arsenic-free compound and therefore less toxic in nature in comparison with the other three kinds of pnictide compounds. For such superconductors, the superconducting transition temperature can be enhanced up to 27 K/13.5 K ($T_{c,\text{onset}}/T_c$) under high pressure [11], and 15.3 K/11.8 K ($T_{c,\text{onset}}/T_c$) via Te substitution [12, 13]. For experimental research into intrinsic physical properties [14–16] and device applications [17], development of high quality epitaxial thin films is necessary. Therefore attempts have been made to obtain epitaxial and superconducting arsenide thin films [18–20]. For example, F-doped LaOFeAs thin films have been made and show an onset of superconductivity of 11 K [18], while for LaOFeAs thin film without F doping no superconducting transition was observed [19]. Hiramatsu et al [20] had fabricated Co-doped SrFe$_2$As$_2$ thin films which showed a $T_{c,\text{onset}}$ of 20 K and a complete superconducting transition at $\sim$15 K. It should be indicated that thin films in all these studies regarding the 1111 phase and 122 phase have nearly phase pure epitaxy with minor impurity phases inside [18–20]. In this paper, we report the synthesis of iron selenide superconductor FeSe$_x$ ($x = 0.80, 0.84, 0.88, 0.92$) thin films. By pulsed laser deposition, we obtained single-phased, $c$-axis oriented epitaxial films. The films show a $T_{c,\text{onset}}$ of 11.8 K and a $T_c$ of 3.4 K with $x = 0.88$. The upper critical field is estimated to be 14.0 T.

The thin films were pulsed laser deposited in a vacuum chamber with base pressure better than $4 \times 10^{-5}$ Pa. An XeCl excimer laser (308 nm wavelength) with a repetition rate of 2 Hz and power density of 100 mJ mm$^{-2}$ was used to irradiate a polycrystalline FeSe$_x$ ($x = 0.80, 0.84, 0.88, 0.92$) target, which was sintered twice at 600°C for 24 h in vacuum sealed quartz tubes after the mixtures of Fe and Se powders were thoroughly ground. The x-ray diffraction (XRD) pattern of one such prepared target ($x = 0.88$) and also its $R-T$ and $M-T$ measurement results ($x = 0.88$) are reproduced in figure 1(a) and figure 2(a), respectively. It can be seen that the main synthesis product is tetragonal $\alpha$-FeSe with the minor impurity hexagonal $\beta$-FeSe, indicated by a star symbol for its strongest diffraction line; cf figure 1(a). From its $R-T$ measurement, the zero-resistance temperature is 5.2 K and the onset temperature is 14.4 K; from its $M-T$ measurement, the transition temperature is 7.9 K, as shown in figure 2(a).

It is worthy of note that plotting the XRD intensity on a logarithmic scale is common for identifying and for recognizing the weaker diffraction peaks, rather than plotting on a linear scale. The humps of about 200 cps in intensity for...
small diffraction angles ($10^\circ$–$30^\circ$) are artifacts arising from the diffractometer.

The deposition procedure and parameters were studied and optimized systematically for all four nominal compositions, namely, $x = 0.80, 0.84, 0.88,$ and $0.92,$ for over 150 thin film samples on three kinds of substrates, i.e., SrTiO$_3$(001) (STO), (La, Sr)(Al, Ta)O$_3$(001) (LSAT), and LaAlO$_3$(001) (LAO). The films given in this paper are all about 200 nm thick.

In general, it was found that the pure single-phased, $c$-axis oriented FeSe$_x$ films can be obtained on all three kinds of substrates, as given in figures 1(b) and (c) for those on STO and LSAT, respectively. The deposition parameters of these two films are the same as those for the best films grown on LAO (cf figure 1(f)), the details of which will be given later.

Since the lattice mismatch is the smallest for FeSe$_{0.88}$ films on LAO and also since the physical properties are much better for films on LAO than on STO and LSAT, we concentrate on the LAO cases.

For films with $x = 0.88$ deposited on LAO under different conditions, some of their XRD patterns are given in figures 1(d)–(k) as examples. From the crystal structure point of view, the pure single-phased, $c$-axis oriented FeSe$_x$ films can be obtained for relatively large ranges of deposition pressure and temperature, e.g. from several tenths of a pascal down to vacuum deposition, and from $630$ down to $500^\circ$C; cf figure 2(b), a phase diagram. It is obvious that the films deposited at $620^\circ$C under $3 \times 10^{-4}$ Pa, i.e., vacuum deposition without argon gas intentionally let into the chamber, show the best crystalline quality among all samples studied (cf figure 1(f)). For example, the full widths of half-maximum of the rocking curves of the FeSe$_{0.88}$(001) diffraction peak are $0.18^\circ$ and $0.43^\circ$ (cf figures 1(g) and (h)), respectively, for films deposited under vacuum (cf figure 1(f)) and $10$ Pa (cf figure 1(i)), both at $620^\circ$C. It is interesting to note that usually some kinds of gases are intentionally introduced into the deposition chamber in order to adjust and to control the plume of the pulsed laser deposition, in many studies Ar. In this study, it was found that being with or without Ar does influence the quality of the films, which may call for further studies concerning the detailed information on microstructures and/or homogeneities of the structural and electronic phase(s).

However, the physical properties of the films are not that tolerant of deposition conditions in comparison with their crystal structure. Thin films with good superconducting transitions can only be obtained in a relatively small area of the phase diagram, as shown in figure 2(b). As shown in figures 2(c) and (d), the best performance for superconductivity appears at around $620^\circ$C and $3 \times 10^{-4}$ Pa, with $T_{c,onset}/T_c$ of $11.8$ K/$3.4$ K. This is in accordance with the above crystal structure studies (cf figures 1(f) and (g)).

The surface morphologies of the films shown in figures 1(d)–(f) and 2(c) were observed with a scanning electron microscope (SEM). The results are reproduced in figure 3; it is a bit surprise that the morphologies are quite different although all other parameters are the same, including the composition, deposition pressure, cooling procedure, etc, with only minor changes in deposition temperature. The film deposited at $610^\circ$C under $3 \times 10^{-4}$ Pa is quite smooth, showing a featureless surface, which suggests a Frank–van der Merwe growth mode (cf figure 3(a)); while the film deposited at $630^\circ$C shows a Stranski–Krastanov growth mode (cf figure 3(c)). For film deposited at $620^\circ$C, which shows the best qualities in both structure and superconductivity, the surface features just lie in between the ones at $610$ and $630^\circ$C; either Frank–van der Merwe growth with nanometer-scale dots precipitated on the surface or an early stage of Stranski–Krastanov growth (cf figures 3(b) and (d)). However, it possesses microcracks which are $\sim 1$ $\mu$m away from each other and are aligned along the principal axes of LAO, i.e., [100] or [010]. This may result from the difference in crystalline structure between the LAO and FeSe$_x$, the former of which is pseudo-cubic and the later tetragonal. The minor lattice distortion originating from

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![Image](image.png)

**Figure 1.** X-ray diffraction spectra of FeSe$_{0.88}$: (a) target, (b) film on STO at $620^\circ$C under $3 \times 10^{-4}$ Pa, (c) film on LSAT at $620^\circ$C under $3 \times 10^{-4}$ Pa, (d) film on LAO at $610^\circ$C under $3 \times 10^{-4}$ Pa, (e) film on LAO at $630^\circ$C under $3 \times 10^{-4}$ Pa, (f) film on LAO at $620^\circ$C under $3 \times 10^{-4}$ Pa, (i) film on LAO at $620^\circ$C under $10$ Pa, (j) film on LAO at $620^\circ$C under $20$ Pa, and (k) film on LAO at $620^\circ$C under $30$ Pa. Rocking curves of the (001) peaks of the films given in (f) and (i) are reproduced in (g) and (h), respectively.
Figure 2. (a) Dependence of the resistance and magnetization (lower right inset) on temperature for the FeSe$_{0.88}$ target pellet, with the upper left inset an enlargement of the $R$–$T$ curve. (b) Phase diagram of FeSe$_{0.88}$ film deposition, with the empty square labeling which pure single-phased epitaxial films could be obtained, and the cross symbol, superconductivity detected. (c) Resistivity versus temperature for FeSe$_{0.88}$ film on LAO deposited under $3 \times 10^{-4}$ Pa at different temperatures. (d) Resistivity versus temperature for FeSe$_{0.88}$ film on LAO deposited at $620^\circ$C under different pressures.

Figure 3. SEM pictures of FeSe$_{0.88}$ films on LAO(001) deposited under $3 \times 10^{-4}$ Pa at (a) $610^\circ$C, (b) $620^\circ$C, and (c) $630^\circ$C. (d) Same surface as in (b), with higher magnification.

Figure 4. (a) Dependence of $T_{c,\text{onset}}$ and $T_{c,0}$ on the Se content for films deposited on LAO at $620^\circ$C under $3 \times 10^{-4}$ Pa. (b) Resistivity versus temperature in the external magnetic field. The zero-temperature upper critical field is $\sim 14.0$ T, as given in the inset of panel (b).

Acknowledgments

This work was supported by the MOST of China (2006CB921107 and 2004CB619004), the NSFC (10774165), and the BRJH of the CAS.

References


The shear strain determines the critical thickness and the film microstructures [21]. Furthermore, the phase transitions for LAO at $\sim 435$ °C and for $\alpha$-FeSe at $457$ °C may also influence the microstructure and morphology of the films.

The superconducting features of the FeSe$_x$ thin films with $x = 0.80, 0.84, 0.88$, and $0.92$ are shown in figure 4(a), in which the superconducting transition temperatures are summarized. It looks to have a dome-like feature with the highest critical temperature at $x = 0.88$. Therefore, we further made a study on the influence of magnetic field on superconductivity for FeSe$_{0.88}$ thin films which are deposited at $620^\circ$C under $3 \times 10^{-4}$ Pa. For this, magnetic fields up to $5$ T are applied along the $c$-axis, and the $R$–$T$ ($H$) data are shown in figure 4(b). The transition curve shifted to lower temperature while the field increased. As shown in figure 4(b), it can be seen that for the cuprate superconductor, the onset superconducting transitions are the same for all testing magnetic fields, and the broadening of the superconducting transition occurs with increasing magnetic field. This implies a mode of vortex motion similar to that for cuprate superconductor. By using the middle point of the superconducting transition temperature to determine $T_c$ for each field, the upper critical field $H_{c,2}(0)$ can be estimated to be $14.0$ T according to the WHH model [22], as shown in the inset of figure 4(b). This value is close to that obtained from the polycrystalline samples [10].

In summary, we deposited pure iron-based superconducting thin films, in particular, $c$-oriented iron selenide FeSe$_x$ films, on STO, LSAT, and LAO, with $x = 0.80, 0.84, 0.88$, and $0.92$. For $x = 0.88$, the films on LAO show $T_{c,\text{onset}}/T_{c,0}$ of $11.8$ K/$3.4$ K, and $H_{c,2}$ of $14.0$ T.

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References


3