Fabrication of FeSe superconducting films with chemical transport deposition process

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Abstract. FeSe Superconducting films were fabricated with a chemical transport deposition process. During the fabrication process, Fe foils were adopted as substrates and Se powders were put at one end of the tube furnace. During the heating process, Se powders were vaporized, and vaporized atoms were carried by Ar flow and deposited on the Fe substrates. With a heat treatment process under proper temperature, superconducting tetragonal $\beta$-FeSe phase can be obtained. The effects of key parameters, including the sintering temperatures and the distances between Fe substrates and Se source on the phase composition and morphology of the obtained films were systematically investigated. The superconducting transition temperature of 7.8 K was obtained on the optimized film. By further optimization of the heat treatment process, it is promising to fabricate FeSe films with higher superconducting phase content and better superconducting properties.

1. Introduction

In 2008, the superconducting transition with critical temperature $T_c$ of ~8 K was discovered in tetragonal $\beta$-FeSe system by Hsu et. al. [1]. Then in the following decades, it attracted more and more attentions from the standpoints of both fundamental researches and practical applications. FeSe based superconductors, known as “11” systems, exhibit the simplest lattice structures among all the superconductors, which is only composed of -Fe-Se- layers as superconducting layers with no blocking layers. Based on the similar Fe₂Se₂ layer structures, FeSe₁₋ₓTeₓ, and FeTe₁₋ₓSₓ also register their distinct presence in this iron chalcogenide system, with both $T_c$ values of ~15 K. It is interesting that the $T_c$ values of FeSe system is quite tunable. It can be greatly enhanced up to 37 K under high pressure [2] and to 65 K by preparing unit cell FeSe ultrathin films [3-6]. At the same time, the advantages such as high upper critical field, $H_{c2}$ of ~47 T [7], low cost and low toxicity of starting materials compared to FeAs-based superconductors all suggest their potentials in practical applications.

Recently, aiming at practical applications, many researchers paid attentions to the fabrication of FeSe wires or tapes [8]. However, although the current carrying density of FeSe (or FeSe,Te) single crystals and films can all reach as high as $10^5$ Acm⁻² at 4.2 K [9-11], that of FeSe wires still remains only about 100 Acm⁻² [12-16]. The main factor which limits the current transport is the intergrain weak link. Both the low superconducting filaments density and the existence of secondary phase are responsible for the intergrain weak links. The fabrication of thin films is a possible way to realize practical applications of superconductors, such as YBCO coated conductors [17]. Recently, the developments of FeSe thin film fabrication techniques are mostly focused on either pulsed laser
deposition (PLD) [11, 16, 18, 19] or Molecular Beam Epitaxy (MBE) method for the fabrication of single layer thin films [3, 6, 20-22], which are both very costly. Electrochemical deposition is a potential low-cost method. However, the crystallization of obtained films is not good enough [23-25]. Thus it is necessary to develop a new method for the fabrication of β-FeSe thin films with high transport properties.

In this study, chemical transport deposition (CTD) method is designed and optimized for the preparation of β-FeSe superconducting films. The effects of key processing parameters, including the sintering temperatures and the distances between Se source and Fe substrates on the phase composition and morphology of obtained films are investigated. β-FeSe superconducting film with the critical temperature of 7.8 K is obtained, which suggests the potential of this method on the fabrication of β-FeSe films in an industrial scale.

2. Experimental
Foils with the purity of 99.9% were carefully washed by ethanol and deionized water and punched into small rectangular pieces with the dimension of 1.5×1.0 cm² as substrates. During the fabrication process, high purity elemental Se (99%) powders (from Alfa Aesar) were adopted as starting materials and put on one end of the tube furnace, where the temperature is ~100 °C lower than that at the center of the furnace. And Fe substrates were put at the center of the tube furnace with the distance carefully measured as d. The change of distances between Fe and Se was realized by changing the positions of Fe. Ar flow with the flowing rate of 1 L/min was adopted as the carrying gas. The sintering process was performed by heating these substrates up to $T_{\text{max}}$ with $T_{\text{max}}$ = 500 and 600 °C and kept for 12 h, respectively, then slowly cooling to room temperature with the cooling rate of ~25 °C/h.

Phase composition of all the obtained thin films was determined by X-ray diffractometer (XRD, Bruker D8 Advance) with CuKα ($\lambda$=1.5406 Å) radiation. And a phase purity parameter, $F_{\beta-\text{FeSe}}$ related to the tetragonal phase content ratio was calculated as,

$$F_{\beta-\text{FeSe}} = \frac{\sum I_{\beta-\text{FeSe}}}{\sum I_{\beta-\text{FeSe}} + \sum I_{\delta-\text{FeSe}}} \times 100\%$$

Eq.1

where $I_{\beta-\text{FeSe}}$ and $I_{\delta-\text{FeSe}}$ represent for the diffraction peak intensities of β-FeSe and δ-FeSe phase, respectively. The morphologies of thin films were characterized by scanning electron microscopes (SEM, JEOL-6390A). And the superconducting critical temperature was measured by magnetization method, which was carried out on Superconducting Quantum Interference Device (SQUID, MPMS-XL-7) with the applied field of 10 Oe from 4.2 K to 30 K.

3. Results and Discussions
The XRD patterns of obtained films with the sintering temperatures of 500 and 600 °C are plotted in Figure 1 (a) and (b), respectively. The films are named 500-1#–500-4# and 600-1#–600-4# based on the different distances from Fe substrates to Se source of d=30, 35, 40, and 45 cm, respectively. As shown in both figures, these thin films are all composed of tetragonal β-FeSe phase and hexagonal δ-FeSe phase. The small content of residual Se is due to the Se deposition during the cooling process. It is known that the tetragonal β-FeSe phase is the superconducting phase. Thus the contents of β-FeSe phase in all the films are estimated with the phase purity parameter $F_{\beta-\text{FeSe}}$ and plotted in each inset. It can be noticed that with the sintering temperature of 500 °C, the β-FeSe phase purity parameters are all smaller than 60%, suggesting that the sintering temperature of 500 °C is not high enough for the formation of β-FeSe phase. With the increase of sintering temperature to 600 °C, the β-FeSe phase content greatly increases, and the maximum phase purity parameter of 91% is achieved.

The distances between Se source and Fe substrates, d, also plays an important role for the film preparation. In both sintering process, with the increase of d, the β-FeSe phase purity parameter increases then decreases, and the optimized value is d=40 cm under both conditions. Considering that all the substrates are in the flat-temperature zone, with the temperature variation within ±1 °C, the
different phase purity parameters should be attributed to the different Fe:Se ratios on each film. Based on our previous study, the increase of Fe:Se ratio can lead to the increase of $\beta$-FeSe phase content [26]. The amount of Se that reaches Fe substrate mostly depends on the distances between the Se source and Fe substrates. Therefore, more Se can deposit on sample #1 with the shortest $d$ value. And under the same sintering condition, more hexagonal $\delta$-FeSe phase can be formed. The decrease of $\beta$-FeSe phase content in film 4# may be attributed to the larger cooling rate, considering that it is at the edge of our flat-temperature zone.

Figure 1. X-ray diffraction patterns of FeSe thin films sintered at different temperature of (a) 500 and (b) 600 °C, respectively. The red-purple and dark-green lines are standard diffraction lines of $\beta$-FeSe and $\delta$-FeSe from the JCPDS card of 85-0735 and 75-0608, respectively.

The obtained films are peeled off the substrates and the cross section images of the obtained films sintered under 600 °C at the position of 2, 3, and 4# are obtained as shown in Figure 2 (a~c). It can be observed that the thickness of each film is uniform with the variation within 3.0 μm. However, the thicknesses of films changes obviously with different $d$ values, which decrease from ~200 μm to ~165 μm. As discussed above, the different thicknesses should be attributed to the Se deposition content, that with the increase of $d$, less Se powders can be deposited on the Fe films. The top view morphology of film surface of film 600-3# is shown in Figure 2(d). The observed ripples and topographical irregularities are due to the unevenly deposition of Se. In Figure 2 (a~c), the formation of columnar grain can be observed on the top part of the films. And the grain size obviously decreases closer to the substrate. It is because the nucleation rate of FeSe grains is larger on the Fe substrates. And on the top of the film, more stress can be released, thus the grains can grow bigger.
The magnetization of obtained film 600-3# is measured after peeling off the film from Fe substrate as shown in Figure 3. The positive magnetization over the entire temperature range should be related to the residual Fe substrates on the film. The field cool and zero field cool (FC-ZFC) curves present a superconducting transition at 7.8 K, which should be the critical temperature of obtained β-FeSe phase. However, the small superconducting phase content can be attributed to both the existence of hexagonal δ-FeSe phase and the chemical composition off-stoichiometry of β-FeSe phase. Thus with further optimizations of both the deposition and heat treatment process, better superconducting property can be expected.

4. Conclusions
Chemical transport deposition technique for the fabrication of FeSe superconducting films has been successfully developed. The optimal key parameters, including the sintering temperatures and the distances between Fe substrates and Se source were obtained. It is concluded that within the flat-temperature zone, the increase of $d$ could lead to the decrease of Se deposition content. Thus the thickness and phase composition of the films were all changed. The optimized film with critical temperature, $T_c$ of 7.8 K was obtained with the sintering temperature of 600 °C and $d$ of 40 cm. Further optimization of the heat treatment process is on the way in order to obtain the films with higher superconducting phase content and better superconducting properties.

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