Fabrication of tetragonal FeSe–FeS alloy films with high sulfur contents by alternate deposition

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We report the synthesis of tetragonal FeS$_{x}$Se$_{1-x}$ films ($x \leq 0.78$) by pulsed-laser deposition. To fabricate tetragonal alloy films with tetragonal FeSe and hexagonal FeS targets, we adopted an alternate deposition technique with an FeS$_{x}$ buffer layer on MgO(001). The overall film composition is controlled by the thickness ratio of FeS/FeSe layers. The out-of-plane lattice parameter of the films follows Vegard’s law, demonstrating homogeneous alloying by interdiffusion. The sulfur solid solubility reaches $x = 0.78$ in the FeS$_{x}$Se$_{1-x}$ films, which is by far higher than $x \sim 0.40$ in bulk governed by the tetragonal phase instability.

Fig. 1. (Color online) (a) Schematic of alternate deposition of FeS/FeSe stacked films by pulsed-laser deposition. The films were deposited on 2-nm-thick FeS$_{x}$ buffer/MgO(001) substrates. (b) Chemical composition analysis results for (S + Se)/Fe and S/(S + Se) as a function of FeS thickness ratio. Error bars for S/(S + Se) are smaller than the symbols.

Table I. Thicknesses of FeS and FeSe used for alternate deposition. The number of alternate deposition cycles was set to 6. The total film thickness including the FeSe buffer thickness (~2 nm) was approximately 15 nm. See text for the definitions of the FeS thickness ratio and sulfur content $x$.

| FeS layer thickness (nm) | FeSe layer thickness (nm) | Number of cycles | FeS thickness ratio | Sulfur content, $x$ |
|-------------------------|--------------------------|------------------|--------------------|--------------------|
| 0.50                    | 1.70                     | 6                | 0.20               | 0.24               |
| 1.01                    | 1.19                     | 6                | 0.40               | 0.44               |
| 1.26                    | 0.94                     | 6                | 0.50               | 0.53               |
| 1.52                    | 0.68                     | 6                | 0.60               | 0.66               |
| 1.77                    | 0.43                     | 6                | 0.70               | 0.78               |
| 2.03                    | 0.17                     | 6                | 0.80               | 0.89               |

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PbO-type tetragonal FeSe is the simplest compound among Fe-based superconductors, showing superconductivity at a critical temperature ($T_c$) of 8 K.\(^1\) Since its tetrahedrally coordinated Fe plane is the common structural unit of Fe-based superconductors, the electronic structure and paring mechanism of FeSe\(^2,3\) have been one of the central topics in superconductivity research. In addition, the formation of an electronic nematic phase\(^4\) and, more recently, the emergence of high-$T_c$ superconductivity under 1-unit-cell (u.c.)-thick\(^5,6\) and ultrathin-film conditions\(^7,8\) have raised further interest in FeSe. The simple crystal structure is also suitable for investigating the effects of chemical substitution on the structural and electronic properties. In particular, alloy systems with related chalcogenide compounds\(^9\) have been studied intensively.\(^10-14\) Tetragonal alloy films with isostructural FeTe have been fabricated by pulsed-laser deposition (PLD)\(^15\). $T_c$ was found to increase to 23 K for FeSe$_x$Te$_{0.2}$ on a CaF$_2$ substrate where the phase separation inherent in bulk samples is effectively suppressed by PLD.\(^16\)

Although PbO-type FeSe can be obtained by a hydrothermal method ($T \sim 5$ K),\(^17\) the sulfur solid solubility as tetragonal FeS$_{x}$Se$_{1-x}$ bulk alloy is as low as $x \sim 0.40$.\(^10,18\) This is primarily due to the existence of a thermodynamically stable hexagonal FeS phase, which gives rise to a structural deformation at a higher $x$.\(^19\) In this study, we demonstrate that tetragonal FeS$_{x}$Se$_{1-x}$ can be stabilized up to $x = 0.78$ by PLD.

Films were deposited on MgO(001) substrates at 300 °C in a vacuum (a base pressure of the order of 10⁻⁶ Torr), with tetragonal FeSe and hexagonal FeS polycrystalline targets supplied by Kojundo Chemical Laboratory. Our preliminary attempts to grow tetragonal FeS directly on MgO(001) at various temperatures, and on other substrates, LaAlO$_3$(001), SrTiO$_3$(001), (La,Sr)(Al,Ta)O$_3$(001), and TiO$_2$(001), were not successful. We therefore employed a 2-nm-thick FeS$_{x}$ buffer and subsequent FeS/FeSe alternate deposition technique to stabilize the tetragonal phase with high sulfur content, as schematically shown in Fig. 1(a). Each layer thickness was tuned by the number of laser pulses irradiated to FeS and FeSe targets. As listed in Table I, the thickness ratio of FeS over the entire film (denoted as the FeS thickness ratio hereafter) was varied from 0.2 to 0.8 while keeping each thickness at a value less than 2.2 nm (~4 u.c.) to suppress the hexagonal phase formation of FeS. The total film thickness was approximately 15 nm.

We first evaluated the sulfur content of the as-grown FeS/FeSe stacked films by electron probe microanalysis. Figure 1(b) shows the chemical composition ratios, (S + Se)/Fe and S/(S + Se), as a function of FeS thickness ratio. The stacked films are slightly anion rich, with approximately 10 ± 5 at.% excess anions against Fe cations. This might be due to the composition deviation in the ablation\(^19\) of FeS.
because the ratio for FeSe is close to unity. In this work, we focus on the substitution of S for Se; we simply express the film composition as FeS$_{x}$Se$_{1-x}$ and define $x$ as the S atomic fraction in the anions, i.e., \( S/(S+Se) \). Table I and Fig. 1(b) demonstrate that the x of the films can be controlled by the FeS thickness ratio.

Figure 2(a) shows out-of-plane X-ray diffraction (XRD) patterns for FeSe and FeS/FeSe stacked films. The FeSe ($x = 0$) single layer exhibits an intense (001) peak at 16.1° associated with clear thickness fringes. In FeS/FeSe stacked films, peaks appear between 16.1° for FeSe(001) and 17.6° for tetragonal FeS(001), and at higher angles with increasing $x$ and disappear at $x = 0.89$. No peaks assignable to secondary phases as well as peak splitting indicative of phase separation are discerned. The absence of crystalline peaks for $x = 0.89$ implies that it is hard to grow a tetragonal or hexagonal FeS single layer on an FeSe buffer layer. The lattice parameter calculated from those peaks is in good agreement with c-axis lengths of bulk tetragonal FeS$_{x}$Se$_{1-x}$ ($x \leq 0.4$) (Ref. 10) as well as Vegard's law between bulk values of tetragonal FeSe and FeS (Ref. 17), as plotted in Fig. 2(b). It is therefore reasonable that c-axis-oriented FeS$_{x}$Se$_{1-x}$ isostuctural to tetragonal FeSe is formed in our films. The linearly decreasing lattice constant holds up to $x = 0.78$ in the FeS$_{x}$Se$_{1-x}$ alloy films. This is in stark contrast to the bulk result, which clearly deviates from the relation above $x = 0.40$. These observations suggest that the FeS$_{x}$Se$_{1-x}$ alloy films are obtained from the alternately deposited FeSe and FeS stacked films owing to an interdiffusion, which likely occurs during deposition at 300°C. Measurements of in-plane lattice parameters and rotational symmetry with much thicker films in future works will further support the observations.

By in situ annealing FeS$_{x}$Se$_{1-x}$ films for 30 min at 450°C, we examined the stability of tetragonal alloy films for $x$ below and above the bulk solubility limit. Figure 2(c) shows XRD patterns for the annealed FeS$_{x}$Se$_{1-x}$ films with $x = 0.28$ and 0.44. Even after annealing, the diffraction peak position for $x = 0.28$ remains unchanged [also see Fig. 2(b)], evidencing the formation of a thermodynamically stable tetragonal phase at a low $x$. No additional annealing effect also corroborates the completion of interdiffusion during deposition. In contrast, the disappearance of the (001) peak for $x = 0.44$ indicates that the high-$x$ alloy decomposes, presumably owing to the thermodynamically unfavorable tetragonal phase. Thus, the nonequilibrium process of PLD is beneficial for stabilizing the tetragonal phase with high sulfur content.

The temperature ($T$) dependence of resistivity ($\rho$) for the as-grown and annealed FeS$_{x}$Se$_{1-x}$ films is displayed in Fig. 3(a). As reported previously (Ref. 20) the thickness of 15 nm for FeSe is not thick enough to achieve metallic conduction and superconducting transition behavior in the as-grown state ($x = 0$ in the left panel); annealing induces metallic transport (right panel). A weak but definite $\rho$ decrease at a low $T$ in the annealed FeSe film can be considered as the onset of...
superconductivity. The relatively low onset superconducting critical temperature \( T_c \) of about 5 K and the incomplete superconducting transition are commonly observed for such thin films.\(^{3,8,20}\) In Fe\(_{1−x}\)Se\(_x\) alloy films \( x > 0 \), \( ρ−T \) curves are metallic with a relatively low \( ρ \) at a high \( T \) in the as-grown state, showing only a slight \( ρ \) upturn at a low \( T \). However, we did not detect the onset behavior in all as-grown samples. In the annealed Fe\(_{0.16}\)Se\(_{1−x}\) films, we observed an onset \( T_c \) of \( \sim 3 \) K under zero magnetic field [blue line in the inset of the right panel in Fig. 3(a)]. The suppression of the onset behavior as observed at 9 T is characteristic of superconductivity. The thermally activated transport in the as-grown Fe\(_{0.88}\)Se\(_{0.11}\) and annealed Fe\(_{0.44}\)Se\(_{0.56}\) films is likely caused by disorder, consistent with the decomposition revealed by XRD (Fig. 2).

Having observed the onset behavior in the annealed Fe\(_x\)Se\(_{1−x}\) films \( x = 0 \) and 0.16, we examined the role of annealing by Hall effect measurement. Figure 3(b) displays the \( x \) dependence of the Hall coefficient \( R_H \) at 50 K where normal state transport can be measured. In Fe\(_{0.16}\)Se\(_{1−x}\) samples \( x = 0 \), the negative \( R_H \) in the as-grown state becomes positive after annealing. According to the multiband model widely accepted for Fe\(_{1−x}\)Se [hole pocket at the \( \Gamma \) point and electron pocket at the M point as depicted in the Fig. 3(b) inset],\(^9\) the \( R_H \) variation corresponds to carrier-type crossover: the effective hole carrier density \( (n_h) \) predominates the electron carrier density \( (n_e) \), in association with the Fermi level shift. Previous works have shown that superconductivity in bulk Fe\(_{1−x}\)Se and thick Fe\(_{1−x}\)Se films favors slightly Fe-rich conditions,\(^{1,21,22}\) and positive \( R_H \) values at a low \( T \). In fact, two annealed samples \( x = 0 \) and 0.16 exhibiting the onset \( ρ−T \) behavior show positive \( R_H \) values. On the other hand, the \( R_H \) values of Fe\(_{1−x}\)Se\(_{1−x}\) alloy films \( x > 0.2 \) are close to zero, and there are no apparent variations caused by annealing. This result implies that the hole and electron carriers balance in Fe\(_x\)Se\(_{1−x}\) alloy films. Taking into account that metallic transport is already achieved in our alloy films with slightly Fe deficient compositions, it may be possible to induce superconductivity in the as-grown state by adjusting the stoichiometry, e.g., with a Fe-rich Fe\(_{1−x}\)Se target.\(^{1,21,22}\) Although there still remains such issues for further investigation, our films are expected to reflect different structural and electronic properties in high-\( x \) Fe\(_x\)Se\(_{1−x}\) alloy.

In summary, we have stabilized tetragonal Fe\(_{1−x}\)Se\(_{1−x}\) up to \( x = 0.78 \) by an alternate PLD technique. The effectiveness of alternate deposition in the expanded sulfur solid solubility would open a new way towards experiments on the Fe\(_x\)–Fe\(_{1−x}\) alloy system.

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