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2012 Supercond. Sci. Technol. 25 105013

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A novel approach for preparing Fe(\(\text{Te}_x\text{S}_y\)) superconducting films: solid phase epitaxial growth from amorphous precursors

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Received 25 June 2012, in final form 2 August 2012
Published 6 September 2012
Online at stacks.iop.org/SUST/25/105013

Abstract

Fe(\(\text{Te}_x\text{S}_y\)) films were fabricated on (100) \(\text{SrTiO}_3\) substrates from Fe(\(\text{Te}_{0.65}\text{S}_{0.16}\)) amorphous precursors by a solid phase epitaxial growth process under various background atmospheric conditions. Structural analysis by x-ray diffraction showed strong peaks corresponding to Fe(\(\text{Te}_x\text{S}_y\)) phases, when the amorphous precursors were heated with Fe(\(\text{Te}_{0.8}\text{S}_{0.2}\)) sintered pellets. The crystallinity of the films deteriorated at longer periods of heating but the compositional shifts were found to have decreased. Consequently, the critical temperature, \(T_{c_{\text{zero}}}\), of the Fe(\(\text{Te}_x\text{S}_y\)) film with minimum compositional shift was found to be 9.0 K and critical current density, \(J_C\), of the film was about \(1.4 \times 10^4\) A cm\(^{-2}\).

(Some figures may appear in colour only in the online journal)

1. Introduction

Since the discovery of LaFeAsO\(_{1-x}\)F\(_x\) superconductors by Hosono \textit{et al} in 2008 [1], a large number of researchers have fabricated and investigated Fe-based superconductors [1–5]. Currently, Fe-based superconductors are categorized into five main families: 1111 family [1], 21113 family [2], 111 family [3], 122 family [4] and 11 family [5]. Among these families, 11 family superconductors have tetragonal structure and it is the simplest crystal structure and composition, so that their crystal growth and the superconducting properties have been intensively examined [6–18].

Among many other fabrication processes available, a pulsed laser deposition (PLD) method has always been the best choice of fabricating 11 family films due to its ease of controlling the growth conditions such as Fe(\(\text{Se}_{1.9}\text{Te}_y\)) [6–14] and Fe(\(\text{Te}_x\text{S}_y\)) [15–18] films. In general, the PLD process requires heating of substrates during the crystallization procedure of the film, which would cause the unsteady composition of the film due to it containing highly volatile elements such as Se, Te and S [9, 14–16, 18]. This heating process results in compositional shifts, so that the superconducting properties of the fabricated film became unstable [14, 18]. Therefore optimization of PLD processes and novel fabrication methods have always been sought to suppress the compositional shift, for example by controlling background gas pressure [14] and by using targets with high concentration for highly volatile elements [12, 18].

In this paper, a solid phase crystal growth process with various conditions was applied to fabricate Fe(\(\text{Te}_x\text{S}_y\)) films...
Structural analyses of Fe(100) SrTiO$_3$ (STO) substrates of about 3 $\times$ 10 mm$^2$ by PLD using a Nd:YAG laser (wavelength = 532 nm) at 5 Hz, whose energy and laser spot size were 30 mJ/pulse and 2.54 mm$^2$, respectively. Ar gas was introduced to the vacuum chamber at 3.0 $\times$ 10$^{-5}$ Torr pressure. The substrate temperature was kept at room temperature to suppress the volatilization of Te and S from deposited precursors. The deposition period was set for 2 h to obtain about 60 nm thick Fe(100) SrTiO$_3$ amorphous precursors. An Fe$_{0.65}$S$_{0.16}$ target was used for fabrication of the Fe(100) SrTiO$_3$ amorphous precursors. The target-substrate distance was maintained at 55 mm.

Figure 1 and table 1 show a schematic diagram of a sample enclosed in a quartz tube for the heat treatment and the conditions in the quartz tubes during the heat treatment of the amorphous precursors, respectively. Three different conditions were examined in order to investigate the effect of background atmosphere on the crystallization, condition 1 in quartz tubes, condition 2 in quartz tubes with powdered pellets composed of Te:S = 1:1, condition 3 in quartz tubes with sintered pellets of Fe$_{0.65}$S$_{0.16}$. Powdered pellets and sintered pellets were pressed into a pellet shape with a diameter of 9 mm and a thickness of about 1 mm. The length of the enclosed quartz tubes was 10–12 cm. The inside and outside diameters of the quartz tubes were 10 mm and 12 mm, respectively. The enclosed capacity of the quartz tubes was 7.9–9.4 cm$^3$ in volume. The distance from the sample to the powdered pellet or sintered pellet was maintained at about 1.5 cm. The inside of the quartz tubes was substituted by Ar gas before closing and an Ar gas pressure of about 75 Torr was applied. Heating temperature was fixed at 600$^\circ$C and three different heating periods were selected, 10, 120 and 240 min.

Table 1. Conditions in quartz tubes during heat treatment.

<table>
<thead>
<tr>
<th>Condition no.</th>
<th>Pellets enclosed in quartz tubes with Fe(100) SrTiO$_3$ amorphous precursors</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nothing</td>
</tr>
<tr>
<td>2</td>
<td>Powdered pellets composed in Te:S = 1:1</td>
</tr>
<tr>
<td>3</td>
<td>Sintered pellets of Fe$<em>{0.65}$S$</em>{0.16}$</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Crystal growth and background atmospheric conditions

Figure 2 shows XRD $\theta$/2$\theta$ patterns of Fe(100) SrTiO$_3$ films heated for 120 min under three different conditions. In the case of condition 1, the color of Fe(100) SrTiO$_3$ films turned colorless from light black after the heat treatment, which suggests a noticeable compositional shift from Fe:Te:S = 1:0.65:0.16 to Fe:Te:S = 1:0.00:0.09 during the heat treatment. Condition 1 was therefore not suitable for crystallization of Fe(100) SrTiO$_3$ amorphous precursors. On the other hand, the surface of films was covered by a large quantity of S after the
heat treatment under condition 2. The composition of the film was measured as Fe:Te:S = 1:0.02:1.81. A weak peak was recognized at 33.17° in figure 2, which did not correspond to the Fe(3e,S) phase. It is thought that the peak is related to phases composed by Fe and S or only S elements. The saturated vapor pressures in 600°C of Te and S are 5 Torr and 2000 Torr, respectively [20]. On the other hand, the Ar gas pressure is estimated as 75 Torr in enclosed quartz tubes at room temperature, and it may become 220 Torr at 600°C. It can easily be assumed that S became volatilized from the powdered pellets composed of Te and S, which caused the increase of partial pressure of S inside quartz tubes at 600°C. Volatilized S atoms in the atmosphere adhered on the surface of the film during the cooling process. Consequently, condition 2 was therefore not suitable for crystallization of Fe(3e,0.65S0.16) amorphous precursors, either.

In contrast to conditions 1 and 2, the intensity of the 00ℓ reflection peak was clearly visible from the films prepared via condition 3. The bonding of Fe–Te and Fe–S in sintered pellets was possibly decomposed thermally by the heat treatment, in the case of the films prepared via conditions 1 and 2. In this case, it is assumed that Te and S were volatilized from the sintered pellets in 600°C and filled the quartz tubes. Quantities of volatilized Te and S were reflected in partial pressures of Te and S in the quartz tubes, and it was suggested that Fe(3e,0.65S0.16) amorphous precursors were crystallized by suppling Te and S and suppressing the volatilization of Te and S from the amorphous precursors.

3.2. Dependence of crystal orientation and composition on heating period

Figure 3 shows XRD θ/2θ patterns of Fe(3e,S) films heated for three different periods, 10, 120 and 240 min under condition 3. The peak intensities were normalized by (200) reflection peak intensities of STO substrates for the comparison among peak intensities in each film.

structural analysis of the XRD θ/2θ-scan confirmed that the 00ℓ reflection peak intensity was recognizable in all samples. It was revealed that 00ℓ reflection peaks of the films shifted to higher angle with the increase of heating period, suggesting that the c-axis length of the films was shortened with the increase of heating period.

Figure 4 shows FWHM of rocking curves (δω) using (001) reflection peaks and that of (101) reflection peaks (δϕ) in Fe(3e,S) films heated for 10, 120 and 240 min under condition 3. The inset shows the XRD in-plane pattern of the film heated for 10 min.
Figure 5. Average compositions of Te and S within the Fe(Te,S) films heated for 10, 120 and 240 min under condition 3. The error bars show maximum and minimum of Te and S compositions.

Table 2. Variation of c-axis and a-axis lengths of Fe(Te,S) films heated for 10, 120 and 240 min under condition 3. The c-axis length was estimated by the Nelson–Riley function using the 00ℓ reflections of the films. The a-axis length was calculated by using the equation \( \frac{1}{d_{101}^2} = \frac{1}{a^2} + \frac{1}{c^2} \). The error limits of c and a-axis lengths were ±0.0004 Å and ±0.009 Å, respectively.

<table>
<thead>
<tr>
<th>Heating period (min)</th>
<th>c-axis length (Å)</th>
<th>a-axis length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>6.198</td>
<td>3.837</td>
</tr>
<tr>
<td>120</td>
<td>6.197</td>
<td>3.868</td>
</tr>
<tr>
<td>240</td>
<td>6.196</td>
<td>3.850</td>
</tr>
</tbody>
</table>

10 min. The (101) reflection peaks of Fe(Te,S) shown in the inset of figure 4 were seen at every 90° interval in the ϕ-scan XRD, which indicated the in-plane orientations of the film with four-fold rotational symmetry. In addition, it was also observed in ϕ-scan XRD that the films heated for 120 and 240 min were in-plane orientated with four-fold rotational symmetry. The δϕ was almost the same at different heating periods, 1.65° for 10 min, 1.65° for 120 min and 1.75° for 240 min. From these results, it was revealed that the films became thermally decomposed and the crystal orientation deteriorated with the increase of heating period.

Figure 6. SEM surface images of Fe(Te,S) films heated for 10, 120 and 240 min under condition 3. It was obvious that the contents of volatile elements Te and S were smaller than those of amorphous precursors and decreased with the increase of heating period. The longer heating period caused the deterioration of the crystal orientation, as seen from structural analysis of the films in figure 4. It is thought that the volatilization of Te and S elements led to the deterioration of film crystal orientation.

As a result, the crystal orientation of the film was found to have deteriorated and the elements became volatilized further from the films at longer heating periods, seen from XRD structural analysis and compositional analysis by SEM-WDX. Namely, the optimum heating period for fabrication of Fe(Te,S) films should be determined from the viewpoints of both the crystal growth rate and the volatilization rates from the Fe(Te0.65S0.16) amorphous precursors.

3.3. Micro-structure of the films

Figure 6 shows SEM images of the Fe(Te,S) film surface heated for 10, 120 and 240 min under condition 3. Although
Figure 7. AFM surface images of Fe(Te$_x$S$_{y}$) films heated for (a) 10, (b) 120 and (c) 240 min under condition 3. AFM surface image (d) and cross-sectional profile (e) of the film heated for 240 h under condition 3, which contains some pores.

The difference of surface morphology was hardly seen in films heated for 10 and 120 min, some pores become present in the case of the film heated for 240 min. The holes ranged from several hundreds of nm to a few µm, which suggested the pores were caused by volatilization of Te and S elements from the film.

Figure 7 shows a set of AFM surface images and the cross-sectional profile of Fe(Te$_x$S$_{y}$) films heated under condition 3. Figures 7(a)–(c) are AFM surface images of the films heated for 10, 120 and 240 min, respectively. Figure 7(d) is an AFM surface image with some pores of the film heated for 240 min. The profile under the AFM image shows a cross-section on a line between A and B in the image of (d). A large number of grains several tens—hundreds nm in diameter started to appear on the surface of films heated for shorter heating periods, as shown in figures 7(a)–(c). On the other hand, the surface is very smooth for the case of film heated for 240 min. The surface morphology of the films was probably changed by the volatilization of elements due to the heating treatment. In addition, it was also obvious from the cross-sectional profile of figure 7(d) that the pores on the surface of film heated for 240 min were about 60 nm in depth, indicating that Fe(Te$_x$S$_{y}$) films were almost absent. In XRD crystal structural analysis and compositional analysis by SEM-WDX, it was shown that the films deteriorate with the increase of heating period. From the results, it is suggested that the pores occurred in thinner or crystallinity-lower parts by the heat treatment.

Figure 8 shows a cross-sectional TEM image and four diffraction patterns of the Fe(Te$_x$S$_{y}$) film heated for 10 min under condition 3. Figures 8(b)–(e) are the diffraction patterns obtained from regions I, II, III and IV in figure 8(a), respectively. Epitaxial growth of the film on the substrate was seen from figures 8(b) and (c). On the other hand, it was recognized from figures 8(d) and (e) that the film was not crystallized epitaxially. The difference of c-axis and in-plane orientations within films induces deterioration of superconducting properties such as current characteristics. It is therefore very important to arrange the crystal orientations in films to improve superconducting properties. It is suggested that optimization of film growth conditions, including the partial pressures of Te and S in quartz tubes, compositions of amorphous precursors, heating temperature and others, leads to control of crystal orientations within the films.

3.4. Superconducting properties

Figure 9 shows resistivity–temperature curves of the Fe(Te$_x$S$_{y}$) films heated for 10, 120 and 240 min under condition 3. $T_{\text{Conset}}$ of the films was almost the same, from 9.9 to 10.7 K. On the other hand, the influence of heating period on $T_{\text{Czero}}$ was clearly recognizable, 9.0 K for 10 min, 6.6 K for 120 min and 7.2 K for 240 min. The compositional shift in the film heated for 10 min was suppressed by more than 120 and 240 min, and the crystal orientation was the best quality, so that it is thought that $T_{\text{Czero}}$ of the film heated for 10 min was the highest among them.

Figure 10 shows that the $J_C$ values were measured at 2.0 K in self-field. The $J_C$ values of the films heated for 10 and 240 min were about 14 000 and 5670 A cm$^{-2}$, respectively. The c-axis and in-plane orientations within films are very important for superconducting properties such as current characteristics. $\delta \omega$ and $\delta \varphi$ of the films increased in
longer heating periods, as shown in figure 4. Further, it was obvious that the contents of volatile elements Te and S in the films decreased with the increase of heating period, as shown in figure 5. It is thought that the difference in the $J_C$ values was caused by crystallinity and compositional shift. It was also revealed that the $J_C$ value of the film heated for 10 min was higher than that of the film fabricated by PLD [16] and it shows the effectiveness of solid phase crystal growth in Fe(8$\text{Te}_x\text{S}_y$) film fabrication.

4. Summary

Fe(8$\text{Te}_x\text{S}_y$) films were grown by the solid phase crystal growth technique using Fe($\text{Te}_{0.65}\text{S}_{0.16}$) amorphous precursors in small quartz tubes as a novel approach filled in for a PLD process. Then crystal orientations, compositions and superconducting properties of the films were investigated. It was revealed that the amorphous precursors heated with the Fe($\text{Te}_{0.8}\text{S}_{0.2}$) sintered pellets were highly oriented. On the other hand, it was seen that the crystal orientation of films deteriorated and elements of both Te and S in the films decreased by thermal decomposition when the heating period was increased. It is thought that Te and S partial pressures of background atmosphere in quartz tubes and the heating period are the most important factors for the crystallization of Fe($\text{Te}_{0.65}\text{S}_{0.16}$) amorphous precursors and suppressing compositional shifts of Te and S by the heat treatment. $T_{Czero}$ of the Fe($\text{Te}_{0.57}\text{S}_{0.15}$) film with minimum compositional shift and the best crystal orientation was 9.0 K and the $J_C$ was about $1.4 \times 10^4$ A cm$^{-2}$. It is necessary to arrange the crystal orientations and suppress compositional shifts within films by optimizing the heating temperature, heating period and Te and S partial pressures, to achieve better superconducting properties.
Figure 9. Resistivity-temperature curves of the Fe(\text{Te},\text{S}) \text{S}_x films heated for 10, 120 and 240 min under condition 3.

Figure 10. A $T_{\text{Czero}}$-$J_C$ diagram of the Fe(\text{Te},\text{S}) \text{S}_x films heated for 10 and 240 min under condition 3. The square plot in the diagram was obtained from the report by Mele \textit{et al} [16]. The $J_C$ values were measured at 2.0 K in self-field.

Acknowledgments

This work was supported by Professor S Awaji (Tohoku University) and Mr K Konya (Kyushu University) for the current property measurement. The authors are deeply grateful to them.

References