Linear correlation between the c-axis lattice constant and superconducting critical temperature in FeSe$_{0.5}$Te$_{0.5}$ thin films

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Keywords: pulsed laser deposition, FeSe$_{0.5}$Te$_{0.5}$, films, buffer layers, superconductivity

Abstract

Using x-ray diffraction, scanning electron microscopy, transmission electron microscopy, and electrical resistance analyses, we investigate structural and superconducting properties of FeSe$_{0.5}$Te$_{0.5}$ films deposited by pulsed laser deposition on TiO$_2$-buffered (CeO$_2$-buffered) SrTiO$_3$ substrates with the buffer film thickness varying from 0 to several tens of nanometers. It is found that the SrTiO$_3$ / TiO$_2$ (or CeO$_2$) / FeSe$_{0.5}$Te$_{0.5}$ film in a proper thickness range of the buffer film shows a higher superconducting transition temperature ($T_c$) than the SrTiO$_3$ / FeSe$_{0.5}$Te$_{0.5}$ film without buffer layer, indicating that the buffer layer can enhance $T_c$. Both $T_c$ and the c-axis lattice constant of FeSe$_{0.5}$Te$_{0.5}$ films increase first and then decrease with the buffer film thickness, each exhibiting its maximum at a particular buffer film thickness, and both of them show an almost linear correlation.

1. Introduction

The 11 type iron-based superconductor (FeSe$_{1-x}$Te$_x$) have drawn much attention in basic research and applications, especially in superconducting mechanism exploration [1, 2], because of their simplest crystal structure and non-toxic properties [3, 4]. The bulk FeSe showed a superconducting transition temperature ($T_c$) of about 8K [5], and the superconductivity onset in α-FeSe was reported to attain a broad maximum of 37 K under 7 GPa hydrostatic pressure [6]. Since Ginzburg and Kirzhnits in 1964 predicted that $T_c$ of low-dimensional superconductors would be continuously reduced with decreasing film thickness. Experimentally, superconductivity is widely believed to be suppressed in reduced dimensionality and is strongly surface/interface dependent as well, such as the recent research about unsupported ultrathin superconducting (110)-oriented Nb and (0001)-oriented NbSe$_2$ nanoplates [7]. However, it was found that a monolayer FeSe film grown on SrTiO$_3$ substrate by MBE has a very high $T_c$ (above 65K) [8–10]. This amazing discovery has made 11 type Iron chalcogenides a super-high-$T_c$ superconductor potentially.

Recently, a considerable amount of researches have done in FeSe$_{1-x}$Te$_x$ (FST) film deposited on different substrates, which can introduce compression or tension between FST films and substrates [11], to find out the key factors that affect superconducting properties. Imai et al [12, 13] investigated the crystal structures and superconducting properties of thin films of FeSe$_{0.5}$Te$_{0.5}$ grown on eight different substrates and suggested that there is a strong effect of substrate materials and the c-axis length on the superconducting properties. They concluded that superconductivity is not correlated with the lattice mismatch, but with the degree of in-plane orientation and with the lattice parameter ratio c/a. Yuan et al found that superconducting properties of FST film grown on three different substrates are quite different, though the in-plane lattice parameter of these substrates [La$_{0.16}$Sr$_{0.82}$Al$_{0.39}$Ta$_{0.41}$O$_3$ (LSAT), CaF$_2$-buffered LSAT and bare CaF$_2$ substrates] are almost identical [14, 15]. Thus they held the view that superconductivity of FST film is highly affected by thermal expansion.
mismatch between the film and substrate. Furthermore, Bellingeri et al. reported that the critical temperature of FST film is strongly correlated with substrate lattice constant, which can introduce strain and enhance $T_c$ [16–19]. However, there has still been a debate how the change in lattice parameters of FST film affect its superconductivity.

In all of these studies, application of different substrates introduces multiple variables, including lattice mismatch and thermal expansion mismatch between FST and substrate, which will bring ambiguity to physical analysis. In this work, in replacement of the traditional method of trying different substrates, we use a new idea of varying the thickness of buffer layer between the FST film and substrate to study the correlation between the lattice parameter of the FST and its superconductivity, which is more continuously adjustable. By growing a range of different thicknesses of (CeO$_2$ or TiO$_2$) buffer layers, followed by depositing the FST films with a thickness of 65 nm, we present a study of the strong correlation between the $c$-axis lattice constant and superconducting transition temperature of the FST film. It is found that both of them exhibit an almost linear relationship. We further propose a scheme for tuning the $c$-axis lattice constant and so enhancing $T_c$ of FST by varying the buffer layer thickness.

2. Methods

2.1. Synthesis of FST target

The target FeSe$_{0.5}$Te$_{0.5}$ was synthesized by solid state reaction method with a two-step process. In the first step, high purity Fe, Se and Te powders were weighed with stoichiometric molar ratio of Fe:Se:Te = 1:0.5:0.5 and thoroughly grinded using an agate mortar. Then, these milled powders were pressed into cylindrical pellets with thickness of 3 mm and diameter of 3/4 inch under a uniaxial pressure of 10 MPa, and sealed in an evacuated quartz tube. The sample was sintered at 700°C for 24 h and cooled to room temperature at the cooling rate of 30°C/h. In the second step, the pre-sintered sample was thoroughly grinded again and pressed under uniaxial pressure of 15 MPa, followed by sealing and sintering process just like the first step. All the weighing and grinding steps were performed in an argon atmosphere protected glove box with less than 1 ppm O$_2$ and H$_2$O.

2.2. Film deposition

CeO$_2$ (or TiO$_2$) buffer layers with different thickness were deposited on single crystal STO (001) substrates at 650°C (or 600°C) by pulsed laser deposition (PLD) with 10$^{-3}$ mbar O$_2$ atmosphere. Afterwards, the buffer films were annealed in 10$^{-3}$ mbar O$_2$ atmosphere and cooled down at the rate of 10°C/min, which is essential for avoiding oxygen deficiency in oxides [20]. Finally, FST films were deposited at 300°C by PLD and cooled down to room temperature at the rate of 5°C/min. All the thicknesses of deposited films were calibrated by the cross-sectional SEM image and expected to increase linearly with increasing deposition time. In this work, the thickness of the FST film was fixed at 65 nm. The PLD system provided a high vacuum chamber with less than 8 × 10$^{-9}$ mbar residual gas at room temperature and less than 10$^{-7}$ mbar during deposition. The working parameters of laser beam (248 nm) were fixed at an energy density of 2 J cm$^{-2}$ and a repetition rate of 2 Hz during the buffer and FST deposition. And the distance between target and substrate was 7 cm. Growth parameters, especially the buffer and FST deposition temperature, have been optimized for multiple times to get high $T_c$ FST films.

2.3. Characterizations

The method of $θ$–2$θ$ scan performed on x-ray diffraction (XRD) with Cu Kα($λ = 1.54056$ Å) radiation was used to characterize the as-grown films and so obtain their lattice parameters. The resistance of the films was measured by the standard four-probe method in a Physical Property Measurement System (PPMS-16T). Cross section was characterized by field emission scanning electron microscope (FESEM, ZEISS ULTRA55) and double spherical aberration corrected transmission electron microscopy (TEM, Titan G2 60-300).

3. Results and discussion

3.1. FST films deposited on STO substrate with 0–60 nm thickness of CeO$_2$ buffer

The XRD patterns are shown in figure 1 for FST films deposited on STO substrate with 0–60 nm thickness of the CeO$_2$ buffer. As shown in figure 1(a), only (00l) diffraction peaks of FST films, CeO$_2$ buffers and substrates are present for all films, indicating the perfect $c$-axis growth orientation of films and the high purity of phase. Figures 1(b) and (c) show the enlarged views of the (001) and (002) peaks of FST films. The shift in FST peaks can be clearly seen, which means that the FST lattice constants change continuously with varying the thickness of CeO$_2$ buffer. The FST $c$-axis lattice constant is found in the range of 5.81–5.98 Å, which is derived from (001) peaks by using the Bragg’s Law $2d \sinθ = n\lambda$ with $d$ as the interplanar distance, equal to the $c$-axis lattice
constant in this case ($n = 1$). The FST $c$-axis lattice parameter increases with increasing CeO$_2$ buffer thickness up to 45 nm and then decreases for greater thickness, which will be shown in figure 3 below.

Figure 2 shows the resistance versus temperature curves for FST films deposited on CeO$_2$-buffered STO substrate. Superconducting transition temperature ($T_c$) is defined as the onset temperature of zero resistance. Different thicknesses of CeO$_2$ buffer from 0 nm to 60 nm lead to different $T_c$ of FST films. When the films are directly grown on the bare STO substrate, the $T_c$ value of FST is only 6.9 K. It is found that the addition of the buffer layer significantly increases the $T_c$. As the CeO$_2$ thickness increases, the FST $T_c$ value first increases to its maximum $T_c$ of 15 K at CeO$_2$ buffer thickness of 45 nm and then rapidly drops to 4.1 K. It is worth noting that the electrical resistance shows the same dependence on the CeO$_2$ buffer thickness as the $c$-axis lattice constant, which will be shown below.

In order to analyze the correlation between the FST film lattice parameters and $T_c$, we compare the $c$-axis lattice constant and the superconducting transition temperature of the FST for different buffer layer thicknesses. A strong correlation between $T_c$ and FST $c$-axis lattice constants can be seen in figure 3. Both $T_c$ and $c$-axis lattice constant show the same dependence on the buffer layer thickness. Therefore, we conclude that the $T_c$ value of the FST film is strongly associated with its $c$-axis lattice constant.
3.2. FST films deposited on STO substrate with 0–220 nm thickness of TiO2 buffer

Table 1 shows the in-plane lattice mismatch, which is defined as the percentage difference in in-plane lattice parameters between the FST bulk and substrate (STO and CeO2-buffered STO). For the CeO2-buffered STO substrate, the in-plane lattice mismatch is 0.7%, much smaller than 2.8% for the STO substrate without buffer layer. At the same time, $T_c$ shows a great enhancement when the FST/STO interface is inserted by a CeO2 buffer layer with an appropriate thickness. Thus, it can be reasonably expected that the smaller the in-plane lattice mismatch, the higher the $T_c$ value of the FST film has.

In what follows TiO2 buffer is selected to investigate the buffer effect and verify our points mentioned above, since there is an extremely small in-plane lattice mismatch (0.4%) between FST and TiO2. Moreover, TiO2 buffer and TiO2-terminated STO have shown exciting results in single-layer FeSe film with high-temperature superconducting performance [8, 22].

Figure 4 displays the XRD patterns for FST films deposited on STO with the TiO2 buffer of 0–220 nm thickness. As shown in figure 4(a), all the films also have a perfect c-axis growth orientation and high purity of phase. Figures 4(b) and (c) show the enlarged views of the (001) and (002) peaks of FST films. Since the FST peaks shift continuously with the change of the TiO2 thickness, the same as the CeO2 buffer, the c-axis lattice constant of the FST film varies with the TiO2 buffer thickness, which will be shown in figure 7.

SEM image in figure 5(a) exhibits a cross-sectional image of the STO/TiO2/FST structure with TiO2 buffer layer of 220 nm thickness, which is the thickest in this series of experiments. As shown in figures 5(b) and (c), the interfaces between STO/TiO2 and TiO2/FST are very clear and smooth, and the atomic alignments are perfect, with almost no defects. From the microstructure characterizations of TEM, it follows that our epitaxial films have excellent crystalline quality.

Figure 6 shows the plots of resistance as a function of temperature for FST films deposited on TiO2-buffered STO substrate. Interestingly, the TiO2 buffer leads to a stronger superconductivity enhancement than the CeO2 buffer. The addition of 17 nm TiO2 buffer layer strikingly improves the FST film $T_c$ to 12.9 K, which is 6 K higher than the STO/FST system without buffer layer. While the FST film grown on a 15 nm CeO2-buffered STO only exhibits a 0.4 K $T_c$ improvement than bare STO. And a maximum $T_c$ of 14.4 K is obtained in FST film with a 50 nm TiO2 buffer layer. After then, the $T_c$ value declines slowly as the TiO2 thickness continue to increase.

The lattice constant and the $T_c$ value of the FST film as functions of the thickness of the TiO2 buffer are plotted in figure 7, from which one sees a strong correlation between $T_c$ and FST c-axis lattice constant. Such a

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**Table 1. In-plane lattice mismatch between the FST bulk and substrate.**

|        | STO [11] | CeO2 [21] | TiO2 [22] |
|--------|----------|-----------|-----------|
| a-axis value ($Å$) | 3.905    | 3.825     | 3.782     |
| lattice mismatch with FST bulk (3.798 Å) [23] | 2.8%     | 0.7%      | 0.4%      |

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Figure 3. The c-axis lattice constant of FST and its $T_c$ versus the CeO2 buffer thickness for FST films grown on CeO2-buffered STO substrate.
correlation suggests that the c-axis lattice constant is the crucial factor for changing the superconducting properties of the FST film.

Comparing the $T_c$ dependence on the buffer thickness in figures 3 and 7, one sees that after $T_c$ reaches its maximum, with further increasing the buffer thickness, $T_c$ decreases rapidly for the CeO$_2$ buffer layer but very slowly for the TiO$_2$ buffer layer. As shown in figures 8 and 7, $T_c$ still remains above 10 K as the TiO$_2$ buffer thickness reaches 220 nm. It shows that the FST film deposited on the STO/TiO$_2$ substrate has a much wider platform with high $T_c$ than that deposited on the STO/CeO$_2$ substrate. This behavior is most like due to the fact that the in-plane lattice constant of the TiO$_2$ buffer layer is very close to that of the FST, and the in-plane lattice mismatch on the TiO$_2$/FST interface is lower than that on either CeO$_2$/FST interface or STO/FST interface, as shown in table 1. To see clearly such a slow decrease of $T_c$ with the buffer thickness, the thickness range of the TiO$_2$ buffer was extended to 0–220 nm.

In order to show the correlation between the c-axis values and superconducting properties, we plotted $T_c$ as a function of the c-axis lattice constant for FST films grown on different substrates in figure 8. The c-axis values of FST are in the range of 5.81–5.98 Å, smaller than its bulk value (6.024 Å) [23]. An almost linear relationship between $T_c$ and FST c-axis lattice constants can be observed. The closer to its bulk value the c-axis lattice constant
Figure 6. The resistance versus temperature of FST films deposited on STO substrate with different thickness of TiO$_2$ buffer.

Figure 7. The $c$-axis lattice constant of FST and its $T_c$ versus the TiO$_2$ buffer thickness for FST films grown on TiO$_2$-buffered STO substrate.

Figure 8. Superconducting transition temperature versus $c$-axis lattice constant of FST. The dashed line is the fitted curve.
of the FST film, the higher the $T_c$ value shows. These results strongly suggest that the c-axis lattice constant of FST is the crucial factor affecting the superconducting properties of FST films.

Finally, we wish to make some discussion about the related physical mechanism. The film growth under stress is a complex problem. In the absence of buffer layer, the FST is subjected to a relatively larger tensile stress, because the in-plane lattice constant of the STO substrate is 2.8% larger than that of the bulk FST crystal. In this case, there is a larger in-plane lattice mismatch and a shorter c-axis lattice constant. Inserting an ultrathin CeO$_2$ or TiO$_2$ buffer film at the interface between STO and FST can decrease the tensile stress because the in-plane lattice constant of the buffer layer is smaller than that of the STO, so that the in-plane lattice mismatch is decreased and the c-axis lattice constant of FST film is increased. It is easy to understand that the tensile stress decreases with increasing the ultrathin buffer thickness.

After the tensile stress is decreased to its minimum and the c-axis lattice constant of FST is close to its bulk value, the tensile stress can increase again with further increasing the buffer thickness. This behavior can be attributed to complex dependence of strain on the film thickness by taking the Volmer-Weber growth mode and strain relaxation mechanism into account [24–30]. For a metal or metallic compound, a typical behavior is that the magnitude of strain can change non-monotoically with film thickness, usually a large tensile strain appears. This effect was used to enhance the critical temperature of MgB$_2$ thin films due to the effect of softening of the $E_{2g}$ Phonon mode by tensile strain [18, 31]. For STO/CeO$_2$ (or TiO$_2$)/FST, the increasing tensile strain in thick CeO$_2$ (or TiO$_2$) buffer layer directly affects the tensile strain of the FST film, which plays a decisive role in the decreasing of c-axis lattice constant of FST film. For this reason, the FST films show a maximum of the c-axis lattice parameter at a particular buffer film thickness.

As regards the enhanced $T_c$, it is a pending problem, for the physical mechanism of iron-based superconductors is still a controversial issue. Either electron-electron correlations or electron-phonon coupling, or both, were suggested as possible mechanism. In any case, they are closely related to the strain on the FST film. In this paper, our experimental results are consistent with the general understanding that strain effect playing a great impact on FeSe$_{1-x}$Te$_x$ superconducting performance, i.e., compressive strain would enhance superconductivity and tensile strain would suppress superconductivity [11, 16–18]. The strain on the film is a type of internal pressure, and it will greatly affect the electronic structure as well as phonon spectra of the FST film. The c-axis lattice constant can characterize the magnitude and sign (tensile or compressive) of the strain. It is expected that the approximate linear correlation between $T_c$ and the c-axis lattice constant observed in the FST film will provide valuable information for its superconducting mechanism.

4. Conclusions

In summary, we have prepared the high-crystalline-quality FST thin film deposited on the STO substrate with CeO$_2$ or TiO$_2$ buffer layer, whose thickness can be quasi-continuously adjustable in the range of tens of nanometers. From the experimental measurement, we get three meaningful findings. The first is that the buffer layer inserted between the FST and STO substrate can enhance the superconductivity. The STO/CeO$_2$ (or TiO$_2$)/FST film in a proper thickness range of the buffer film shows a higher $T_c$ than the STO/FST film without buffer layer. A maximum $T_c$ value of 15 K (4.4 K) is obtained in FST film with a 45-nm-thick CeO$_2$ (50-nm-thick TiO$_2$) buffer film. The second is that the change in the buffer thickness can adjust the lattice matching on the STO/FST interface, the latter being characterized by the change of the c-axis lattice constant of the FST film. The third is that there is an almost linear correlation between the c-axis lattice constant and $T_c$ in FST thin films. Therefore, we propose a new approach of varying the buffer thickness to enhance $T_c$ of the FST thin film, in replacement of the traditional method of trying different substrates.

Acknowledgments

This work was supported by the Ministry of Science and Technology of China (2017YFA0303200) and the National Natural Science Foundation of China (11671203). P. Wang was supported by the National Natural Science Foundation of China (11874199).

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