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Effects of Processing Conditions on the Properties of Fe(Se,Te) Thin Films Grown by Sputtering

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***Abstract*— We studied the effects of processing conditions on the properties and microstructure of $Fe_y(Se_{1-x}Te_x)$ thin films grown on MgO substrates by RF sputtering. The thin films were grown in two ways; in-situ deposition onto heated substrates and deposition onto cold substrates followed by ex-situ annealing processes. Various properties of the deposited Fe(Se,Te) thin films including the phase, texture, surface morphology, composition and superconducting properties were investigated. The results showed that in-situ sputtering leads to higher quality films, e.g. smoother surface, pure phase, more uniform composition and better crystallographic alignment. For the ex-situ grown films, depending on the annealing conditions, phase separation, appearance of the impurity phases such as hexagonal Fe(Se,Te), poor texture, higher Fe-content, non-uniform composition and rough surfaces are developed in the films.**

***Index Terms*—Fe(Se,Te), Microstructure, Sputtering, Thin films.**

I. INTRODUCTION

Among the many Fe-based superconducting materials, the FeSe 11-phase has attracted considerable interest for the study of the mechanism of superconductivity in Fe-based superconductors due to its simple crystal structure, a stack of superconducting Fe_2Se_2 layers along the *c*-axis with no extra atoms/layers [1], [2]. Even though the transition temperature of FeSe is as low as 8 K [2], it can be substantially increased either by the application of pressure [3] or by chemical doping (chemical pressure effect) [4]. For example, T_C can be increased up to ~15 K by partial substitution of Te for Se for $FeSe_{1-x}Te_x$ compounds ($0.3 \leq x \leq 0.7$) [4]. By applying an external pressure of about 8.9 GPa, an enhancement of T_C up to 36.7 K can be also achieved for pure FeSe [3]. Another T_C enhancement option is via the epitaxial strain effect, where a maximum T_C of 21 K can be obtained in $FeSe_{0.5}Te_{0.5}$ thin film through lattice mismatch with different substrates [5]. From this point of view, thin films of Fe(Se,Te) are of great interest for both theory and experiment and have been extensively studied [5]-[9]. Most of these thin films are deposited by pulsed laser deposition [5]-[9] and molecular beam epitaxy [10]. The aim of this work is using sputtering to produce thin films of Fe(Se,Te). The sputtering process is usually performed in two different ways; in-situ and ex-situ [11]. For the in-situ process, the films are deposited onto heated substrates, while for the ex-situ process, the substrates are at room temperature when the films are deposited onto cold substrates and the correct phase is formed using a post-annealing process [11]. Here, we report the potential of in-situ and ex-situ processes for the epitaxial growth of Fe(Se,Te) thin films. Moreover, the effects of different annealing processes for the ex-situ grown films are also discussed.

II. EXPERIMENTAL METHODS

$Fe_y(Se_{1-x}Te_x)$ thin films with a thickness of 70 nm were deposited on MgO single-crystal substrates by RF magnetron sputtering under an Ar pressure of 2×10^{-2} mbar from a 2-inch target with the nominal composition of $Fe_{0.95}Se_{0.6}Te_{0.4}$. The sputtering target was made by mixing a required amount of high purity Fe, Se and Te powder, ball milling for 24 hrs and cold pressing. Two sets of films were deposited; in-situ grown films (referred as In-situ films) where the substrates are at high temperature (315°C) during film deposition, and ex-situ grown films, deposition of the film onto the cold substrate followed by annealing at 400°C for 2hrs. The annealing processes were performed in two different ways, inside sputtering chamber (at Ar) immediately after deposition (referred as Ex-situ (Ar)) and in a vacuum quartz tube in a furnace (referred as Ex-situ(V)).

The phase purity of the deposited thin films was examined by X-ray diffraction (XRD) using a Philips x-ray diffractometer. A Philips X'Pert MRD system was used to study the orientation of the film, and pole figures of the (101) plane of the tetragonal 11-phase were constructed to show the epitaxial alignment. The surface morphology and composition of the films were characterized using scanning electron microscope (SEM) and energy-dispersive x-ray (EDX) respectively. The superconducting properties were investigated by measuring magnetization using a SQUID system.

III. RESULTS

A. *Phase analysis*

Fig. 1 shows theta-2theta XRD patterns of the deposited films before and after annealing process. The cold-deposited film shows only MgO peaks with no trace of tetragonal-Fe(Se,Te) phase. The phase purity and crystallographic alignment are influenced by the annealing process. For the Ex-situ (Ar) film, in addition to the (*00l*) peaks corresponding to

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the β-Fe(Se,Te) phase (tetragonal structure), the (101) peak can be also observed indicating that the sample is not perfectly c-axis aligned and there are some off-axis grains. Moreover, all the peaks are split into two sets implying coexistence of two structurally similar phases with a slight difference in lattice parameters. Both of these two phases are possibly the 11-phase with different Se/Te ratios leading to two different sets of lattice spacings.

For the Ex-situ(V) film, no peak splitting is observed, but in addition to the (*00l*) peaks of β-Fe(Se,Te), a number of weak peaks corresponding to the high-temperature δ-Fe(Se,Te) hexagonal structure appear in the XRD pattern. The presence of only (*00l*) peaks of β-Fe(Se,Te) indicates that the film is strongly c-axis aligned, in contrast with the Ex-situ (Ar) where (101) peak is also detected.

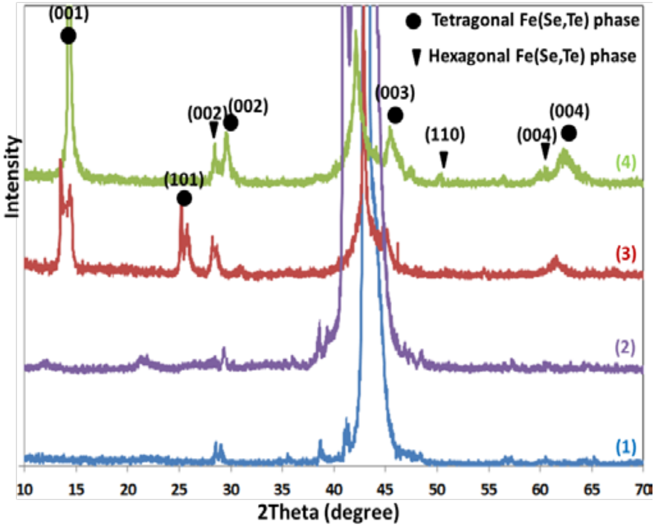

Fig. 1. XRD patterns of Fe(Se,Te) thin films grown on MgO substrate for 1hr in different conditions; (1) MgO substrate, (2) Cold-sputtered film, (3) Ex-situ (Ar) and (4) Ex-situ(V).

B. Texture analysis

Annealing process under different conditions leads to various degrees of crystallographic alignment in the deposited films. (101) pole figures of the grown films in different processing conditions are shown in Fig. 2. The In-situ film shows a strong alignment, both in-plane and out-of-plane, i.e. the epitaxial growth via in-situ process leads to an almost single crystal film. However, the texture of the ex-situ grown films is not as perfect as that of the In-situ film. Annealing in the furnace in an evacuated quartz tube leads to a good c-axis alignment, but random in-plane orientation. When annealing is performed inside sputtering chamber under Ar, the film shows some preferred texture but with a greater proportion of off-axis aligned grains as can be seen in Fig. 2c. These results are in agreement with the theta-2theta XRD data discussed earlier.

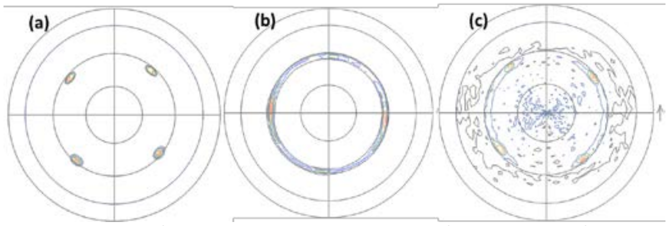

Fig. 2. (101) pole figures obtained by texture XRD from (a) In-situ film, (b) Ex-situ(V) film, (c) Ex-situ (Ar) film.

C. Compositional analysis

Chemical compositions of the grown films by different processing conditions are presented in Fig. 3. Due to different sputtering rates for different elements, the compositions of the films are different from that of the target [11]. The films contain less Te compared to the target because Te is the heaviest element in the target resulting in the lowest sputtering rate for Te. After annealing the films show even less Te and higher Fe compared to those of the cold-deposited film. This is because of the re-evaporation of the volatile elements e.g. Te from the substrates at high temperatures. Due to a large difference between the vapor pressures of Se and Te and that of Fe, a considerable re-evaporation of Se and Te happens at high temperatures leading to a higher Fe content in the films. It can be also seen that the In-situ film and the cold-deposited film are more chemically homogenous. This uniform composition is an advantage of sputtering deposition over other methods [11]. However, after annealing, due to the phase separation, there is considerably more chemical inhomogeneity consistent with the XRD data where peak splitting was observed after annealing.

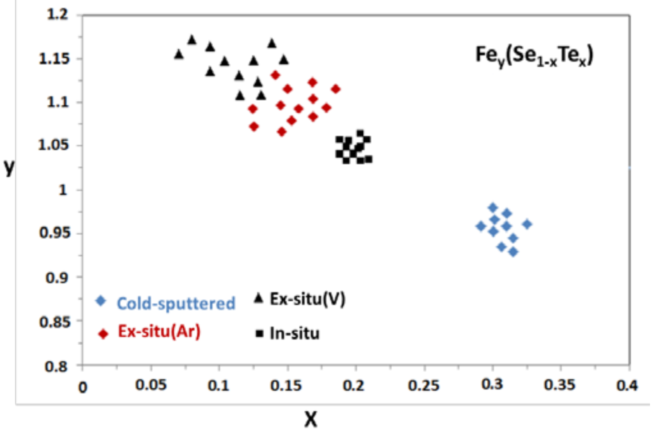

Fig. 3. Chemical composition of the films grown in different conditions; cold-sputtered film, In-situ film, Ex-situ (Ar) film and Ex-situ(V) film. Each point in the graph is the result of the point SEM-EDX analysis over the films. This spot analysis was done in different regions over the sample in order to investigate chemical homogeneity.

D. Surface morphology

SEM analysis of the grown thin films (see Fig. 4) shows that the cold-deposited film and the In-situ film have a relatively smoother surface compared to the surface of the annealed samples which contain many defects such as holes, cracks and impurities. Backscattered SEM micrograph of the Ex-situ(V) film shows two contrasts; a dark contrast in the matrix with a large number of regions in a brighter contrast. High magnification imaging of one of these regions (Fig. 4e-f) along with the EDX mapping (Fig. 4f-j) reveals that there are some surface defects and compositional variations in these regions. The distribution of Fe and Se is relatively uniform, but the Te content considerably increases in these bright regions where the Mg content seems low. It can be suggested that during annealing Te evaporates in the quartz tube, and when the sample is cooled down to room temperature Te is re-deposited on the surface especially in preferential places where surface defects exist. Therefore annealing leads to more surface defects, loss of Te and re-deposition of the Te atoms around the defects.

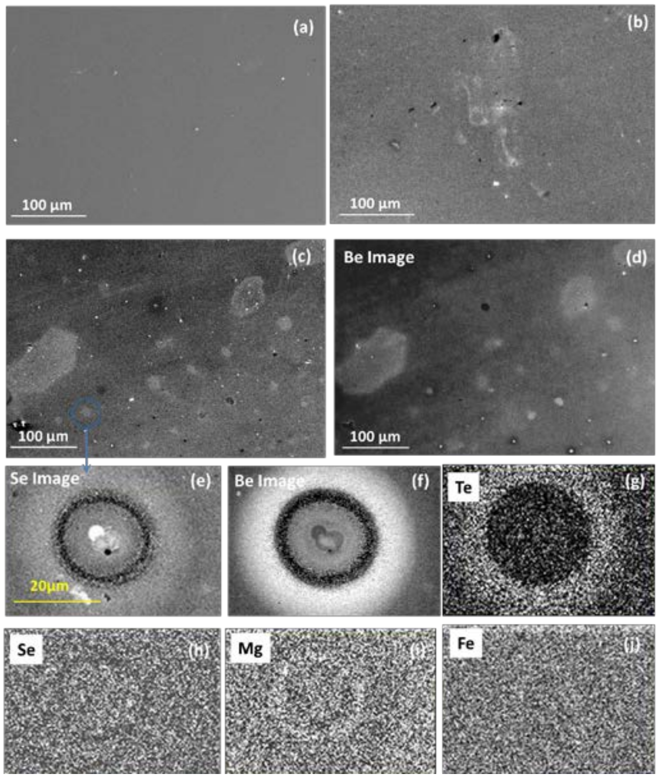

Fig. 4. SEM micrographs of (a) cold-sputtered film, (b) Ex-situ (Ar) film, (c and d) Secondary electron and back-scattered electron images of the Ex-situ(V) film, (e-j) Elemental mapping data of the indicated region.

IV. Discussion

All of the SEM results along with XRD/texture data show that the overall quality of the films grown by ix-situ processing is notably higher than that of the ex-situ grown films in terms of phase purity, crystallinity, surface morphology and chemical homogeneity. In particular, the texture develops more perfectly in the In-situ films as the substrate is already heated when the sputtered atoms arrive to the surface and they can more easily form a unique crystalline structure. However, the post-annealing of an amorphous deposited film hardly leads to a perfect out-of-plane and in-plane alignment. This fact has been also reported for some other thin films grown by sputtering [11], [12]. Annealing at higher temperature may lead to better texture alignment, but, as observed above, at higher temperatures there is the possibility of the formation of the hexagonal phase which destroys superconductivity in β-FeSe in addition to compositional variations and growth of Te-rich regions on the surface.

Another important parameter affecting the overall properties of the films is the annealing conditions. Although both annealing processes were carried out at 400°C, for the Ex-situ (Ar) film, the substrate is heated by a heating element beneath the substrate. The temperature of the top surface on which the film is growing depends on thermal conductivity of the MgO substrate which is not very high especially at higher temperatures. The thermal conductivity of MgO single crystals hugely decreases with temperature. For example it is 38.1 $Wm^{-1}k^{-1}$ at 200°C, and 16.2 $Wm^{-1}k^{-1}$ at 400°C [13]. Therefore the real temperature of the film may be lower than 400°C (annealing temperature) for the Ex-situ (Ar) film resulting in a sample free of high temperature phases such as the hexagonal phase, the presence of off-axis grains and higher amount of volatile Se and Te. The higher annealing temperature for the Ex-situ(V) sample as well as the vacuum atmosphere in the quartz tube lead to a high evaporation of Se and Te and alteration of the composition of the sample.

The observation of peak splitting only for the Ex-situ (Ar) film indicates that phase separation occurs in this sample leading to the formation of two phases with different Se/Te ratio. This type of phase separation has been also reported in other work [14]-[16], but only for the $FeSe_{0.75}Te_{0.25}$ stoichiometry. For example, Fang et al studied the phase evolution of $FeSe_{1-x}Te_x$ over the compositional range $0 \leq x \leq 1$, and found peak splitting only in $FeSe_{0.75}Te_{0.25}$ [14]. They reported that this phase separation happens because the structure of $FeTe_{0.75}$ is essentially different from that of $FeSe_{0.75}$ even though both of them can be described by a similar tetragonal lattice. One of these structure is stable for $0 \leq x \leq 0.15$, while the other one is stable for $0.3 \leq x \leq 1.0$ and both structural phases coexist in the range $0.15 \leq x \leq 0.3$ [14]. The EDX data of the Ex-situ (Ar) film (Fig. 3) reveals $Fe_{1.18}Se_{0.83}Te_{0.17}$ as the average composition of this sample. The ratio of Se/Te for this sample is within the phase coexistence region although the ratio of Fe/(Se+Te) is different. It can be suggested that phase separation (peak splitting) happens in the Ex-situ (Ar) film as a result of local variations in Te/Se ratio, and possibly this phase separation is not highly sensitive to the Fe/Se ratio; however, the overall Se/Te ratio must lie in the range identified above. Moreover, as shown in Fig. 3, other thin films have different compositions, out of the co-existence compositional range, leading to absence of peak splitting and phase separation.

The difference in composition between these samples can be also supported by the peak shift towards larger angles (smaller c lattice parameter) for the sample annealed in the furnace. The evaporated Te and Se can be easily re-deposited around the defects on the surface after annealing resulting in a non-uniform and rough surface.

The magnetization measurement of these samples shows semiconducting behavior due to high amount of Fe. It has been reported that the T_C of Fe(Se,Te) phase is highly sensitive to Fe content, and even small amount of excess Fe can completely destroy superconductivity of Fe(Se,Te) compound [1]. Therefore it is necessary to precisely control the composition of the films deposited by sputtering to obtain superconducting phase.

V. CONCLUSION

We have investigated processing conditions of the sputtering method for the fabrication of Fe(Se,Te) thin films. High-quality epitaxial Fe(Se,Te) thin films can be grown by the in-situ sputtering process in terms of surface roughness, chemical homogeneity, phase purity and texture development. In comparison, ex-situ grown films show lower quality and depending on the annealing process, they develop phase separation, non-uniformity in composition, higher amount of Fe and very poor texture. Whether the annealing process is carried out inside sputtering chamber or in a quartz tube in a furnace makes a considerable difference in the properties of the films although the annealing temperature is the same.

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