A trial of Fe(Se$_{1-x}$Te$_x$) thin film fabrication by pulsed laser deposition using ArF excimer laser

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Abstract. We fabricated Fe(Se$_{1-x}$Te$_x$) thin films on LSAT(100), MgO(001), R-Al$_2$O$_3$ substrates by ArF excimer pulsed laser deposition (ArF-PLD) and investigated pulse repetition rate dependence on film growth of Fe(Se$_{1-x}$Te$_x$) thin films in ArF-PLD. Through x-ray diffraction measurements of Fe(Se$_{1-x}$Te$_x$) thin films grown by ArF-PLD, 00l peaks of Fe(Se$_{1-x}$Te$_x$) were confirmed in Fe(Se$_{1-x}$Te$_x$) thin films grown by pulse repetition rate of 10 Hz but the 00l peaks were not confirmed in Fe(Se$_{1-x}$Te$_x$) thin films grown at 5 Hz. Atomic force microscopy (AFM) revealed that 100 ~ 250 nm sized grains were formed on surface of the thin films grown at 10 Hz. It was found that the thin films grown at 5 Hz were formed thinner than those grown at 10 Hz, in spite of the same pulses. Energy dispersive x-ray spectroscopy (EDX) analysis revealed that composition elements of the thin films grown at 5 Hz were re-evaporated from them more than those grown at 10Hz. In $\rho$-T measurements of the thin films grown at 10 Hz, it was confirmed that the thin films has $T_{\text{ onset}} = 6.5 \sim 10.5$ K and $T_C$ of the Fe(Se$_{1-x}$Te$_x$) thin film on an MgO substrate is 3.9 K.

1. Introduction

LaFeAsO$_{1-x}$F$_x$ superconductors were reported by Hosono’s group in 2008 [1]. The superconductors are different from metal and copper-oxide based superconductors on main composition elements. Since the discovery of LaFeAsO$_{1-x}$F$_x$ superconductors, iron based superconductors related new superconducting materials have been aggressively researched by many researchers all over the world.

Recently, researches of iron based superconducting thin films are also advanced. The researches are very important for investigation of basic properties and devices applications such as junctions and SQUID. Now, pulsed laser deposition (PLD) is used as a typical method to fabricate iron based superconducting thin films. A few reports have been reported on the thin films fabricated by PLD using Nd:YAG (laser wavelength of 532nm), XeCl (308nm) or KrF (248nm) lasers [2-8]. Growth mechanism of thin films fabricated by PLD depends on used substrates, substrate temperatures during film growth, growth time etc. and relates to qualities of the thin films. Especially, wavelength of used laser is one of important factors for fabrication of thin films with high qualities. From there are exactly no reports about iron based superconducting thin film fabrication by PLD using lasers with shorter
wavelength. Then it is necessary to investigate film growth mechanism by using short wavelength. In order to investigate details of film growth mechanism of iron based superconducting thin films grown by PLD using lasers with shorter wavelength, we tried fabricating the thin films by PLD using ArF (193nm) excimer laser.

2. Experimental details

2.1. Selection of material for iron based superconducting thin film fabrication by ArF-PLD

For fabrication of iron based superconducting thin films by ArF-PLD, we focused on FeSe family thin films. Iron-based superconductors can be classified into 4 types of crystal structure [7]. The FeSe family superconductors have an 11-type crystal structure, which is the simplest among the crystal structures. In addition, composition elements in FeSe family superconductors are fewer than others. From the reasons, it is thought that fabrication of FeSe family thin films by ArF-PLD and analysis of the films are easier than the others. It was also reported that $T_c$'s of FeSe superconductors increase by replacing a part of Se to Te, recently [8-9].

We tried fabricating Fe(Se$_{1-x}$Te$_x$) thin films by ArF-PLD and investigated on pulse repetition rate dependence of the thin films.

2.2. Fabrication of Fe(Se$_{1-x}$Te$_x$) targets for PLD

First of all, we fabricated Fe(Se$_{1-x}$Te$_x$) targets for PLD. We mixed Fe, Se and Te powders (in the proportional ratios of Fe : Se : Te = 1 : 0.5 : 0.5 in mol). Next, the mixed powder was enclosed into quartz tubes and sintered at 400 $^\circ$C for 12 hours in a furnace. Then, they were re-grained into powders and pressed into Fe(Se$_{1-x}$Te$_x$) targets with a diameter of 15 mm and thickness of 4 mm. Finally, we obtained Fe(Se$_{1-x}$Te$_x$) targets for PLD by sintering them at 400 $^\circ$C for 12 hours.

2.3. Fabrication of Fe(Se$_{1-x}$Te$_x$) thin films by ArF-PLD

Fe(Se$_{1-x}$Te$_x$) thin films were grown on LSAT(100), MgO(001), R-Al$_2$O$_3$ substrates by ArF-PLD. The ArF excimer laser energy was 400 mJ/pulse. The laser energy density was about 1.5 J/cm$^2$. The substrate temperature was fixed at 375 $^\circ$C. The laser repetition rate was 10 Hz and 5 Hz. The film growth times were set as the thin films have the same thickness. We used Ar as background gas. The pressure of Ar gas was 1 Torr.

2.4. Estimations of Fe(Se$_{1-x}$Te$_x$) thin films grown by ArF-PLD

Preferred orientations of the Fe(Se$_{1-x}$Te$_x$) thin films were determined by measuring the 0/20 scan of the films by x-ray diffraction (XRD) with Cu-K $\alpha$ radiation. C-axis lengths of the Fe(Se$_{1-x}$Te$_x$) thin films were estimated by a Nelson-Riley function [10] using 00l peaks of Fe(Se$_{1-x}$Te$_x$). The film crystallinity was estimated by full width at the half maximum of the rocking curve using the 001 peak of the Fe(Se$_{1-x}$Te$_x$). The in-plane orientations of the Fe(Se$_{1-x}$Te$_x$) thin films were evaluated by x-ray $\phi$ scan (in-plane rotation) using the (101) plane of the Fe(Se$_{1-x}$Te$_x$). Surface of the Fe(Se$_{1-x}$Te$_x$) thin films was observed by atomic force microscopy (AFM). Thickness of the Fe(Se$_{1-x}$Te$_x$) thin films was confirmed by scanning electron microscopy (SEM). Energy dispersive x-ray spectroscopy (EDX) analysis was carried out to investigate compositional ratios of the thin films. The critical temperature ($T_c$) of the Fe(Se$_{1-x}$Te$_x$) thin films were measured by a four-probe method.

3. Results and discussion

3.1. XRD structural analysis of Fe(Se$_{1-x}$Te$_x$) thin films grown by ArF-PLD

Figure 1 shows typical XRD patterns of Fe(Se$_{1-x}$Te$_x$) thin films grown at 10 Hz and 5 Hz. Through the structural analysis of x-ray 0/20 diffraction, we confirmed 00l peaks of Fe(Se$_{1-x}$Te$_x$), indicating that the thin films grown at 10 Hz are $c$-axis oriented. However, the 00l peaks were not detected in the thin films grown at 5 Hz. It was estimated by a Nelson-Riley function using 00l peaks of the Fe(Se$_{1-x}$Te$_x$) that $c$-axis length of the thin films grown at 10 Hz is 5.92 ~ 5.94 Å. It was reported that $c$-axis length
of FeSe is 5.53 Å and that of Fe_{0.99}Se_{0.49}Te_{0.51} is 6.069 Å [11]. From the estimations, it was suggested that composition elements were re-evaporated from the thin films. Full width at the half maximum of a rocking curve using the 001 peak of the Fe(Se_{1-x}Te_{x}) shows that the thin films have Δω of 2.49 ~ 2.70 degrees. However, no clear in-plane orientations of the thin films were observed from x-ray φ scan measurements using the (101) plane of the Fe(Se_{1-x}Te_{x}).

3.2. Surface morphology of the Fe(Se_{1-x}Te_{x}) thin films
Figure 2 shows AFM images of the Fe(Se_{1-x}Te_{x}) thin films grown at 10 Hz and 5 Hz. In the thin films grown at 10 Hz, 150 ~ 200 nm sized grains were observed on the surface of them. The grains were not formed on the surface of the thin films grown at 5 Hz.

3.3. Cross-sectional observation of the Fe(Se_{1-x}Te_{x}) thin films by SEM
Figure 3 shows cross-sectional SEM images of the Fe(Se_{1-x}Te_{x}) thin films grown at 10 Hz and 5 Hz. The film thickness of the thin films grown at 10 Hz and 5 Hz is 150 ~ 240 nm and 75 ~ 100 nm.
respectively. From this result, it was confirmed that the thin films grown at 5 Hz was formed thinner than those grown at 10 Hz. We guessed that it was caused because composition elements of the thin films grown at 5 Hz were re-evaporated from the thin films more than those of the thin films grown at 10 Hz. It was also observed that the thin films were partly peeled from the substrates as shown in the cross-sectional SEM images. We guessed that it was caused because chemical connectivity between the Fe(Se\textsubscript{1-x}Te\textsubscript{x}) films and the substrates was weak. To obtain epitaxial Fe(Se\textsubscript{1-x}Te\textsubscript{x}) thin films, improvements of chemical connectivity of films to the substrates and more suitable substrates would be needed.

3.4. EDX analysis of the Fe(Se\textsubscript{1-x}Te\textsubscript{x}) thin films

Figure 4 and table 1 show EDX spectrum data recorded from the Fe(Se\textsubscript{1-x}Te\textsubscript{x}) thin films grown at 10, 5 Hz and compositional ratios in mol of them, respectively. Through the results of compositional ratios in the thin films by EDX analysis, it was revealed that composition elements of the thin films grown at 5 Hz were re-evaporated from them more than those grown at 10 Hz.

Figure 3. Cross-sectional SEM images of the Fe(Se\textsubscript{1-x}Te\textsubscript{x}) thin films grown at 10 Hz and 5 Hz. The images of upper and lower show cross-section of Fe(Se\textsubscript{1-x}Te\textsubscript{x}) thin films grown at 10 Hz and 5 Hz, respectively. A bar indicates 100 nm.

Figure 4. EDX spectrum data recorded from the Fe(Se\textsubscript{1-x}Te\textsubscript{x}) thin films grown at 10 Hz and 5 Hz. The patterns of upper and lower show EDX spectrum data recorded from Fe(Se\textsubscript{1-x}Te\textsubscript{x}) thin films grown at 10 Hz and 5 Hz, respectively.
Table 1. Compositional ratios (in mol) of the Fe(Se_{1-x}Te_x) thin films grown at 10 Hz and 5 Hz.

| Film/substrate     | 10 Hz                  | 5 Hz                     |
|--------------------|------------------------|--------------------------|
| FeSeTe/LSAT        | Fe : Se : Te = 1 : 0.513 : 0.276 | 1 : 0.433 : 0.286         |
| FeSeTe/MgO         | 1 : 0.542 : 0.305      | 1 : 0.432 : 0.257         |
| FeSeTe/R-Al\textsubscript{2}O\textsubscript{3} | 1 : 0.515 : 0.276 | 1 : 0.402 : 0.272         |

3.5. $T_c$ measurements of the Fe(Se$_{1-x}$Te$_x$) thin films by a four-probe method

Figure 5 shows resistivity-temperature ($\rho$-T) curves of the Fe(Se$_{1-x}$Te$_x$) thin films grown at 10 Hz. The inset shows the magnified $\rho$-T curves of the thin films around 4 K. It was confirmed that the thin films has $T_{\text{C onset}} = 6.5 \sim 10.5$ K and $T_{(0)}$ of the Fe(Se$_{1-x}$Te$_x$) thin film on the MgO substrate is 3.9 K. The resistivity of the thin film is lower than those of the Fe$_{1.18}$(Se$_{0.5}$Te$_{0.5}$) thin films [3]. From this result, it was guessed that Fe-rich by re-evaporation of Te atoms were caused in our thin films and result in low $T_c$'s.

In this study, it was revealed that Fe(Se$_{1-x}$Te$_x$) thin films were able to be grown by ArF-PLD. Composition elements of films are thermal-evaporated in PLD with longer-wavelength and are resolved to atomic level in PLD with shorter-wavelength. In order to obtain Fe(Se$_{1-x}$Te$_x$) thin films with higher $T_c$’s by using ArF-PLD, it is thought that optimization of ArF-PLD conditions such as the ArF excimer laser energy, the substrate temperature, the pulse repetition rate, the pressure of Ar background gas, etc., is needed. Especially, growth conditions of ArF-PLD, which prevent Se and Te atoms from re-evaporating, is required. Otherwise, the problem may be solved by changing compositional ratios of Fe(Se$_{1-x}$Te$_x$) targets for PLD. We believe that Fe(Se$_{1-x}$Te$_x$) thin films with higher $T_c$’s are able to be grown by ArF-PLD.
4. Summary

We fabricated Fe(Se_{1-x}Te_x) thin films on LSAT(100), MgO(001), R-Al_2O_3 substrates by ArF excimer pulsed laser deposition (ArF-PLD) and investigated pulse repetition rate dependence on film growth of Fe(Se_{1-x}Te_x) thin films grown by ArF-PLD. Through x-ray diffraction measurements of the Fe(Se_{1-x}Te_x) thin films, 00l peaks of Fe(Se_{1-x}Te_x) were confirmed in Fe(Se_{1-x}Te_x) thin films grown by pulse repetition rate of 10 Hz. However, the 00l peaks were not confirmed in Fe(Se_{1-x}Te_x) thin films grown at 5 Hz. No clear in-plane orientations of the thin films grown at 10 Hz were observed from x-ray φ scan measurements using the (101) plane of the Fe(Se_{1-x}Te_x). It was observed by atomic force microscopy (AFM) that 100 ~ 250 nm sized grains were formed on surfaces of the thin films grown at 10 Hz. In the thin films grown at 5 Hz, the grains were not observed. Through cross-sectional scanning electron microscopy (SEM) observations of the thin films, it was found that the thin films grown at 5 Hz were formed thinner than those grown at 10 Hz, in spite of the same pulses. Energy dispersive x-ray spectroscopy (EDX) analysis revealed that composition elements of the thin films grown at 5Hz were re-evaporated from them more than those grown at 10 Hz. By ρ-T measurements of the thin films grown at 10 Hz, it was confirmed that the thin films has $T_{\text{onset}} = 6.5 ~ 10.5$ K and $T_c$ of the Fe(Se_{1-x}Te_x) thin film on the MgO substrate is 3.9 K. Through this study, it was revealed that Fe(Se_{1-x}Te_x) thin films can be also grown by ArF-PLD. We believe that Fe(Se_{1-x}Te_x) thin films with higher $T_c$’s are able to be fabricated by optimization of ArF-PLD growth conditions, which prevent Se and Te atoms from re-evaporating.

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