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Crystallized SrFeO_{3-x} films deposited by pulsed laser ablation without in-situ substrate heating

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Abstract

Crystallized SrFeO_{3-x} ($0 \leq x \leq 0.5$) films were deposited by pulsed laser ablation without in-situ substrate heating with the third harmonic of a Nd:YAG laser and off-axis configuration. The crystallinity of SrFeO_{3-x} films strongly depended on the ambient pressure of Ar gas. The films deposited are amorphous below 10 Pa, and crystalline from 10 to 200 Pa. The films deposited at 30 Pa have the optimum stoichiometry of Sr to Fe, approximately 1.05. A stoichiometric and well-crystallized SrFeO_3 film with a smooth surface was fabricated by post-annealing (300 °C in air) the amorphous films deposited at 1 Pa.

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Keywords: Laser ablation; SrFeO_3 ; Thin films; Crystallization

1. Introduction

Perovskite-type oxides exhibiting ionic and/or electronic conductivity are interesting for their potential applications, such as high-temperature solid oxide fuel cells, battery electrodes, sensor materials [1,2], and colossal magnetoresistance effect [3–5]. SrFeO_3 perovskite oxide has recently received special attention since SrFeO_{3-x} (SFO, hereafter) exhibits a wide range of non-stoichiometry ($0 \leq x \leq 0.5$). This large non-stoichiometry is caused by the equilibrium compositional change with temperature and oxygen partial pressure, and the high oxygen mobility in the crystal lattice [6–9]. Electric, magnetic and optical properties vary remarkably with the change in oxygen content in SFO [10–12]; hence, the gas-sensing properties are also studied [13–15]. Thin films are expected to have a rapid response of various properties originating from the large non-stoichiometry and are also highly desirable for integration as functional components with silicon mon-

oliths. To meet these demands, a low-temperature thin-film processing technique is important.

Pulsed laser deposition (PLD) has proven highly successful in growing thin films of complex oxides with perovskite or perovskite-related structures. This technique has also been used to prepare epitaxial SFO films [10,15–17]. To change the oxygen content and crystallographic texturing of the SFO epitaxial films, various kinds of single crystal substrates, deposition atmospheres and pressures, cooling atmospheres, and post-annealing conditions have been examined. However, the substrate temperature for SFO film deposition (640 to 700 °C) is common in these experiments. Therefore, the substrate temperature plays an important role for SFO epitaxial film growth. Furthermore, oxygen or ozone ambient during cooling or post-annealing is also required for obtaining highly oxidized SrFeO_3 films.

We investigated oxide thin film preparation techniques through nanoparticle-aggregated films by PLD with an inert gas ambient and in an off-axis configuration. In this case, an oxide target is ablated, mostly in Ar, and hence the target itself provides the oxygen. Therefore, the confinement of the ablated species in a small space is very important for promoting nanoparticle formation

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Fig. 1. Schematic diagram of off-axis configuration for pulsed laser deposition.

and simultaneous oxidation in the vapor phase. Argon has more confining power than oxygen, because the energy of the ejected species from the target is easily dissipated by the oxygen ambient through rotational energy excitation of diatomic oxygen molecules. By adopting this technique, we successfully obtained crystallized nanoparticle aggregated oxide films of Co_3O_4 , Fe_2O_3 , LaFeO_3 and BaTiO_3 without any in-situ substrate heating [18–20]. However, a suitable pressure range exists for obtaining fully oxidized phase. In this article, we report the deposition of crystallized SFO films at room temperature by PLD. We also demonstrate well-crystallized film preparation by post-annealing an amorphous film at a relatively low temperature deposited just below the crystallization pressure range.

2. Experimental details

Laser deposition was performed using the third harmonic of a Nd:YAG laser with a wavelength of 355 nm, pulse width of 5–7 ns, and repetition rate of 10 Hz. The laser beam was focused on the target surface at an incidence angle of 45° . The beam spot diameter was approximately 2 mm on the target surface. The target was mounted in a rotating holder placed in a vacuum chamber evacuated to a base pressure below 5.5×10^{-4} Pa. The films were 600 to 700 nm thick after 20 min deposition. A rotating quartz substrate was placed in an off-axis position, perpendicular to the target at a distance of 16 mm, as illustrated in Fig. 1. Argon gas was introduced into the chamber and the pressure was kept constant at the selected value between 1 to 200 Pa during deposition. All the films were deposited at room temperature without any in-situ substrate heating. For comparison, the as-deposited films were post-annealed in air for two hours and then cooled naturally to room temperature.

The thickness of obtained films was measured with a profilometer (Tencor alpha-step profiler 300). The crys-

Fig. 2. XRD spectra of SFO films deposited on quartz glass substrates at 200 mJ/pulse under different pressures of Ar. The spectrum of the ceramic SrFeO_3 target is also shown.

tal structure of the films was analyzed by X-ray diffraction (XRD, Rigaku RAD-C) using $\text{Cu-K}\alpha$ radiation. The surface morphology of the films was observed by a scanning electron microscope (SEM, Hitachi S-800). The atomic ratio of Sr to Fe in the films was determined by X-ray fluorescence measurement (XRF, Seiko SEA2010).

3. Results and discussion

3.1. Crystal structure and oxygen stoichiometry

Figs. 2 and 3 present the XRD patterns of a series of samples deposited at different pressures and laser ener-

Fig. 3. XRD spectra of SFO thin films deposited on quartz glass substrates at 10 Pa of Ar under different laser energies.

Fig. 4. Enlarged XRD spectra of the SrFeO_3 (110) peak from SFO films at 200 mJ/pulse under different pressures of Ar.

gies. XRD spectra with indexes shown at the top in these figures are from the ablation target that was used and coincide well with cubic perovskite SrFeO_3 [21]. Fig. 2 shows that the crystallinity of SFO films strongly depends on the ambient pressure of Ar gas. The sample deposited at 1 Pa exhibited no diffraction peaks and was amorphous. Just one weak peak near the (110) peak of the target appeared in the sample prepared at 10 Pa. At pressures from 30 to 200 Pa, strong but broad diffraction peaks comprising a few components were recorded at the lower angle side of the (110) peak from the target. Very weak and broad peaks were also detected near the (200) and (211) peaks of the target. Fig. 3 shows that the peak intensity increased with the laser energy, indicating that the film crystallinity was improved at the higher energies. The film deposited using 300 mJ/pulse irradiation had almost a cubic perovskite structure.

Fig. 4 illustrates the enlarged spectra in the region corresponding to the SrFeO_3 (110) peak in Fig. 2. At least three components were observed from most of the spectra. Increasing the ambient pressure reduced the intensity of the component at approximately 32.8° , although the components near 32.2° and 31.6° became more evident. Three bars near the spectrum at 30 Pa in Fig. 4 indicates the peak position and relative intensity

of the orthorhombic brownmillerite $\text{SrFeO}_{2.5}$ phase in the JCPDS database [22]. These three peaks, from the lower angle side, correspond to (200), (141) and (002) reflections from $\text{SrFeO}_{2.5}$. The peak splitting and shifting to lower angles by reduction of SrFeO_3 are due to loss of symmetry caused by oxygen vacancies and the resultant cell volume expansion that is as large as 7% [16].

SrFeO_{3-x} exhibits a wide range of non-stoichiometry ($2.5 \leq 3-x \leq 3.0$). Within this range, there are four phases at approximately $3-x$ (2.50 (brownmillerite, orthorhombic), 2.75 (orthorhombic), 2.87 (tetragonal) and 2.97 (cubic)) [7,9]. The intermediate $3-x$ value corresponds to the coexistence range of the closest end components at both sides. Nemudry et al. studied the electrochemical oxidation reactions of $\text{SrFeO}_{2.5}$ in detail and monitored XRD spectrum variations with charge transfer to the sample [7]. Initially, only the three peaks plotted as bars in Fig. 4 were observed in the same angle range. Along with the electrochemical oxidation, the intensity of these three peaks relative to the peak at 32.8° changed monotonically, and finally, when fully oxidized, only the peak from SrFeO_3 (110) remained. This monotonic change can thus be utilized to estimate the non-stoichiometric value $3-x$ of our samples from the XRD spectra shown in Fig. 4, though our samples have broader peaks due to the small size of constituent particulates in the films. The $3-x$ values estimated were 2.74 (10 Pa), 2.65 (30, 50 and 100 Pa), and 2.62 (200 Pa). As the deposition pressure increases from 10 to 200 Pa, the product gradually changes to a less oxidized composition.

Previously, in our studies on the preparation of nanoparticle-aggregated films by laser ablation, we found similar pressure dependences for simple oxides, such as cobalt oxide or iron oxide, under the same configuration for deposition without any substrate heating [18,19]. At low pressure, the products were amorphous. With pressure increase, a crystalline film of Co_3O_4 or Fe_2O_3 (the same composition as the target) formed concurrently with nano-sized particulates. Further pressure increases resulted in products with mixtures of Co_3O_4 and CoO , or of Fe_2O_3 and FeO , i.e. a less oxidized composition. For SFO, the product changed from amorphous to crystallized $\text{SrFeO}_{\sim 2.74}$, and finally to crystallized $\text{SrFeO}_{\sim 2.62}$, with the pressure increase, though the product at 10 Pa was not the same composition as the target. This is probably because the higher oxidation state of tetravalent iron (Fe^{4+}) is unstable [10,11,23,24], and, therefore, an oxygen deficiency is inevitably introduced for SFO perovskite thin films without a strongly oxidizing environment [16].

3.2. Sr-to-Fe stoichiometry

Figs. 5 and 6 present the $[\text{Sr}]/[\text{Fe}]$ atomic ratio by XRF analysis in the films deposited at different Ar

Fig. 5. Argon pressure dependence of [Sr]/[Fe] atomic ratio for the deposited SFO films by 200 mJ/pulse irradiation.

pressures. The film stoichiometry is closely related to the ambient pressure. Analysis by XRF indicated that the films deposited at 30 Pa have optimum stoichiometry, i.e. an atomic ratio of [Sr]/[Fe] close to unity (1.05) irrespective of the laser energy. The atomic ratio [Sr]/[Fe] exceeded 1.1 below 10 Pa, and was less than 0.9 above 50 Pa. The Sr deficiency in the film arose from the deposition process. This Sr deficiency could be different from the Li deficiency due to the high Li volatility during deposition of LiNbO_3 films [25]. Resputtering, another possible mechanism resulting in non-stoichiometric products of metallic components, is not considered since this is generally observed in UV laser ablation under high vacuum with very high laser fluence [26]. In our previous study on LaFeO_3 and BaTiO_3 perovskite film preparation by laser ablation [20], the heavy A-site ions (La, Ba) became rich compared to the light B-site ions (Fe, Ti) in the deposited films at lower pressures (approx. 1 Pa). This trend was also observed for SFO films, as shown in Fig. 5. Even with a change in laser energy, this phenomenon is still almost the same, as shown in Fig. 6 where similar Sr/Fe ratios are evident. Monte Carlo simulation of the laser deposition process [27] suggests that this could be due to the mass difference between Sr and Fe. The vaporization process played a crucial role in determining the film microstructure and stoichiometry of complex oxides during the deposition. The ambient gas pressure affects the kinetic energy of the species arriving on the substrate surface due to the collision of ablated species, including atoms, ions, molecules and nanoparticles in the gas phase. High ambient gas pressure results in a small plume and low kinetic energy of the species in the

plume due to the successive collisions between species. Conversely, at low pressure, fewer collisions occur in the larger plume, and the lighter species travel further without collision. Collision between flying species plays an important role in stoichiometry of thin films prepared by pulsed laser ablation [28]. There is thus an optimum pressure range for fabricating crystalline films with the appropriate stoichiometry between A and B ions. From these results, this pressure range is from 30 to 50 Pa for deposition of stoichiometric SrFeO_{3-x} films.

3.3. Film morphology

All the deposited films were brownish yellow, though they varied from transparent to opaque as the Ar pressure increased. This reflected the aggregate formation at higher pressure. Fig. 7 presents SEM photographs of the SFO film surfaces deposited at 10 Pa at different laser pulse energies. Many particles were observed, though the number of particles decreased as the laser energy decreased. The particles observed on thin films deposited by pulsed laser ablation originated mainly from two sources: the droplets directly dislodged in liquid phase from the target and the particles segregated from the thin film matrix on the substrate. The amount of droplets can be easily decreased by using a lower laser energy, because there is generally a threshold laser fluence below, which the droplets are scarcely observable [29]. The particles observed in Fig. 7 were mainly droplets coming from the target, though they disappeared below 150 mJ/pulse and a smooth surface was obtained.

The films deposited at 1 Pa were amorphous as shown in Fig. 2. SEM observation also revealed droplets on these films, indicating that the droplets on the films were not crystalline. Therefore, the droplets were not

Fig. 6. [Sr]/[Fe] atomic ratio in the deposited films vs. different laser energies for SFO films deposited at various Ar pressures.

Fig. 7. SEM images of SFO films deposited under 10 Pa of Ar at 250 mJ/pulse and 150 mJ/pulse.

produced directly from the original bulk material of the target, such as fragments, but due to modified material from the target during ablation. The crystallinity of SFO films obtained at higher pressures is thus not due to the particulates from the target.

3.4. Effect of post-annealing on crystal structure

Crystallized SFO films were obtained by laser ablation at pressures of 10 to 200 Pa of Ar without any in situ substrate heating or post-annealing. However, as shown in Fig. 2, the as-deposited films were not perfectly crystallized, because the film is a nanoparticle-aggregated film. To further promote crystallization of SFO films, we studied the effect of post-annealing on the films deposited at 1 Pa (amorphous) and 100 Pa (crystallized) with 200 mJ/pulse. The films were annealed in air for 2 h at 300 to 500 °C. Fig. 8 illustrates the XRD spectrum change caused by post-annealing of the amorphous films deposited at 1 Pa. The spectrum of the amorphous, as-deposited film was transformed to

that of a cubic perovskite structure even by annealing at 300 °C in air. When the film was annealed at 400 °C or higher, a small amount of SrCO_3 was generated due to the reaction of excess strontium oxide (Fig. 5) with carbon dioxide in air. The crystal structure of the main component in the annealed SFO films still corresponded to cubic perovskite.

Conversely, for the films deposited at 100 Pa, annealing at 300 °C did not lead to complete oxidation to cubic phase, and just a slight increase of the cubic component was observed. Further annealing at 400 or 500 °C yielded cubic phase as the main component, though the peak intensity was still very low compared to the case at 1 Pa, indicating less crystallinity. SrCO_3 was also generated and the peak became stronger with increasing annealing temperature. This clearly indicates that an amorphous iron component still remained in the film, since the Sr-to-Fe stoichiometric ratio is approximately 0.8. SFO films once crystallized in nanoparticles probably have to be annealed in oxygen or ozone at least at 600 °C to obtain crystalline films as in the bulk case [15,16].

By post-annealing at 300 °C, the amorphous film deposited at 1 Pa changed to the well crystallized SFO film while for the film deposited at 100 Pa the crystallization did not proceed further. As shown in Fig. 2, the pressure 1 Pa was just below the threshold pressure that determined whether the product would become an amorphous film or a crystallized nanoparticle-aggregated film. Therefore, the film deposited at 1 Pa might contain smaller nucleus-like substances that would act as nucleation sites and lower the activation energy for crystallization, resulting in the lower crystallization temperature.

Fig. 8. XRD patterns of the films deposited at 1 Pa using 200 mJ/pulse and post-annealed in air for 2 h at various temperatures.

Conversely, once larger crystallized nanoparticles were present and aggregated, as in the film deposited at 100 Pa, the crystallization process might be similar to the bulk case. The contrast of the post-annealing effect for the SFO films could be explained in this way.

4. Summary

In summary, we have successfully obtained crystalline SrFeO_{3-x} films by pulsed laser ablation without in-situ substrate heating or post-annealing. The crystallinity and stoichiometry of SrFeO_{3-x} films depends on the ambient pressure of the Ar gas. The product changed from an amorphous form to crystallized $\text{SrFeO}_{\sim 2.74}$, and finally to crystallized $\text{SrFeO}_{\sim 2.62}$, with the pressure increase. The films deposited at 30 Pa have the optimum stoichiometry with an atomic ratio of $[\text{Sr}]/[\text{Fe}]$ close to unity (approx. 1.05), irrespective of laser energy. Stoichiometric crystallized SrFeO_3 films with smooth surfaces can be fabricated by post-annealing the amorphous films at 300 °C in air. Regarding the morphology, particulates observed by SEM on surfaces of films deposited at laser energies above 200 mJ/pulse were not present below 150 mJ/pulse.

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