Fabrication of STO Buffer Films on MgO Substrates by the MOD Method

T Uchida¹, S Watanabe¹, T Uchiyama², T Tachiki¹

¹Department of Electrical and Electronic Engineering, National Defense Academy, 1-10-20 Hashirimizu, Yokosuka, 239-8686 Japan
²Department of Physics, Miyagi University of Education, 149 Aramaki-aza-Aoba, Aoba-ku, Sendai 980-0845 Japan

E-mail:uchida@nda.ac.jp

Abstract. We fabricated SrTiO₃ (STO) thin films, which are expected to be used as buffer layers on MgO substrates, by the metal-organic decomposition (MOD) method, and evaluated the properties of the films. By introducing a 2-step heat treatment and optimizing the precursor temperature, we could improve the full width at half maximum (FWHM) values of the rocking curves up to 1.81 deg in the X-ray diffraction (XRD) measurements of the STO films on MgO substrates. The minimum FWMH value of the in-plane rocking curves of the films was 2.60 deg and the films had a cube-on-cube structure on the MgO substrates. Furthermore, the root mean square (rms) roughness values of the surfaces of the STO thin films derived from atomic force microscopy (AFM) were 2.11-5.37 nm.

1. Introduction

To fabricate a high quality superconducting film on a substrate, the introduction of a buffer layer is a very effective method. A MgO substrate that has a low dielectric constant and low dielectric loss is suitable for applications in the high frequency range. However, the lattice-mismatch between a MgO substrate and Bi₂Sr₂CaCu₂O₉ (Bi-2212) and YBa₂Cu₃O₇ (Y-123) high-Tc superconducting (HTS) films is about 9.2% and 7.9%, respectively, resulting in low crystal quality. However, the lattice-mismatch between SrTiO₃ (STO) and Bi-2212 and Y-123 is about 2% and 0.6%, respectively. Furthermore, STO has a perovskite structure and good chemical stability. Therefore, the STO thin film can be expected to be used as a buffer layer on MgO substrates [1]-[4]. With regard to growth techniques, pulse laser deposition (PLD), sputtering and molecular beam epitaxy (MBE) have all been utilized for the superconducting and buffer layers. However, all of these methods require a vacuum system and have high cost. Compared to these methods, the metal-organic decomposition (MOD) method has advantages of low cost and the ability to fabricate large-area films. Recently, the MOD method has been attracting significant attention as a very useful method for preparing superconducting and buffer layers [5]-[6].

Previously, we have reported the fabrication of STO thin films on MgO substrates by the MOD method [7]. The films were fired using rapid thermal processing (RTP), and the values of the full width at half maximum (FWHM) of the rocking curves were 3 ~ 3.5 deg in the X-ray diffraction (XRD) measurements. These values are still large, and in addition, further improvements in the crystal
quality are necessary. In the present study, we fabricated STO thin films by the MOD method with a 2-step heat treatment consisting of a preparation process of the STO precursor films and a subsequent firing process [8]. The properties of the films were then evaluated by rocking curve and in-plane rocking curve measurements using an XRD method and evaluated by the root mean squared (rms) roughness values of the surfaces of the STO thin films derived from atomic force microscopy (AFM) measurements.

2. Experimental procedure
The STO thin films were fabricated using a metal-organic solution (ST-06, Kojyundo Chemical Labs). The STO solution was coated directly onto the MgO (100) substrates by a spin coating method. The MgO (100) substrates were ultrasonically cleaned in trichloroethylene and in acetone for 10 min, respectively. The spinning rates used were 500 rpm for 10 sec and 2000 rpm for 20 sec. After drying on a hot plate at 120°C for 2 min, the samples were annealed in a tubular furnace for the 2-step heat treatment. Figure 1 shows the temperature profile of the 2-step heat treatment. In the first step, the samples were directly inserted into the furnace, maintained at the precursor temperature ($T_p$), and annealed for 15 min in an O$_2$ atmosphere. $T_p$ was varied from 350 to 500°C. The furnace was then cooled to room temperature with a cooling rate of 20°C/min. STO precursor films were fabricated in the first step. In the second step, the precursor films were installed into the furnace at room temperature, and the temperature of the furnace was increased up to the firing temperature ($T_f$) of 875°C with a heating rate of 7°C/min. After maintaining the temperature for 2 h in the O$_2$ atmosphere, the furnace was cooled to room temperature with a cooling rate of 20°C/min. The STO thin films were fabricated in the second step. During the second step, a face-to-face annealing method was used for firing the precursor films [9]. In this method, two STO precursor films on substrates fabricated in the first step were prepared, and one precursor substrate was placed face-to-face on the other substrate. The two precursor films were then fired. The thickness of STO thin films obtained was approximately 40 nm.

![Figure 1. Temperature profile of the 2-step heat treatment](image)

3. Experimental results and discussion
The $T_p$ dependence of the FWHM values ($\Delta \omega$) of the STO (200) thin films obtained from the XRD rocking curve measurements is shown in Fig. 2. Measurements on the STO thin films were carried out after the STO precursor films were annealed at 875°C for 2 h. The FWHM values for $T_p$ of 350 ~ 410°C were 3.5 ~ 4.0 deg. However, these values were reduced suddenly when $T_p$ exceeded 425°C. Furthermore, the values suddenly increased again above 475°C. The best value obtained in this study was 1.81 deg for a $T_p$ of 430°C. By introducing the 2-step heat treatment, we could improve the value
Figure 2. Precursor temperature dependence of the FWHM values (\(\Delta \omega\)) of the rocking curves for STO (200) thin films up to 1.81 deg. This value of 1.81 deg is almost the same as the value for STO thin films on MgO substrates fabricated by the sputtering method [2]. From this experimental result, it was found that the crystal quality of the STO thin films was strongly affected by the precursor temperature, and the optimum temperature for fabricating the STO precursor was 430ºC. We have investigated the reasons for the strong dependence of the FWHM values of STO (200) thin films on \(T_p\) in our previous study [10]. The large values of 3.5 ~ 4.0 deg for \(T_p\) of 350 ~ 410ºC are probably due to the residual carbonate impurities in the STO precursor films. The large values of about 4.0 deg for \(T_p\) of 475 ~ 500ºC is probably due to the random nucleation of crystals in the STO precursor films.

Figure 3 show the \(T_f\) dependence of FWHM values (\(\Delta \omega\)) of the STO (200) thin films obtained from the XRD rocking curve measurements when the STO precursor films were annealed at 430ºC for 15 min. The value of the FWHM value for a \(T_f\) of 750ºC was about 3.2 deg. The values gradually reduced with increasing \(T_f\). The best value obtained in this experiment was 1.81 deg for a \(T_f\) of 875ºC, when \(T_f\)
was varied from 750 to 885°C. This indicates that the crystal quality of the STO thin films improves with increasing $T_f$. We have previously reported that some capillary crystals appeared on the surface when $T_f$ exceeded 850°C with the rapid thermal processing [7]. However, no capillary crystals were observed up to a $T_f$ of 875°C in this study by using the face-to-face method. However, some capillary crystals were observed on the surfaces of films fired at 885°C.

![Intensity vs. Degree](image1)

**Figure 4.** $\phi$ scans of STO (110) and MgO (220)

The in-plane orientation is important for utilizing the STO films as buffer layers on MgO substrates. We therefore evaluated the in-plane-orientation properties for the STO thin films on MgO substrates. Prior to the XRD in-plane rocking curve measurements, we confirmed that the clear STO ($h00$) diffraction peaks were only observed from the measurements of the XRD $2\theta/\theta$ scans. Typical $\phi$-scans of a STO thin film on a MgO substrate are shown in Fig. 4. As can be seen from the figure, a cube-on-cube textured growth of STO [100] // MgO [100] was clearly observed in the $\phi$-scans of STO (110) and MgO (220). All the STO thin films showed a cube-on-cube structure on the MgO substrates.

![FWHM vs. Precursor Temperature](image2)

**Figure 5.** Precursor temperature dependence of the FWHM values ($\Delta\phi$) for the in-plane rocking curves
Figure 5 shows the $T_p$ dependence of the FWHM values ($\Delta \phi$) of the STO thin films obtained from the XRD in-plane rocking curve measurements. The measurements on the STO thin films were carried out after firing the STO precursor films at 875ºC for 2 h. The FWHM values for $T_p$ of 350 ~ 410ºC were 4.0 ~ 4.8 deg. The values suddenly reduced when $T_p$ exceeded 425ºC. The values then suddenly increased again above 475ºC. The best value obtained in this study was 2.60 deg. This precursor temperature dependence of $\Delta \phi$ was almost the same as the dependence of $\Delta \omega$ shown in Fig. 2. STO thin films which had a narrow $\Delta \omega$ (1.81-2.21 deg) showed good in-plane crystallinity. From these experimental results in Figs. 2 and 5, it was found that the angle distribution ($\Delta \phi$) for the in-plane orientation had a strong relationship with the distribution ($\Delta \omega$) for the c-axis orientation.

Finally, the rms roughness values of the surfaces of the STO thin films derived from the AFM observations were evaluated. Figure 6 shows the $T_f$ dependence of the rms values when the STO precursor films were annealed at 430ºC for 15 min. The rms values were calculated over an area of 1 $\mu$m$^2$. The rms values became large with increasing $T_f$. Circular grains, with a diameter of about 0.1 $\mu$m, were observed in the AFM images for the STO film fired at 800ºC. On the other hand, the grain diameter was about 0.3 $\mu$m for the film fired at 875ºC. The grain size became larger with increasing $T_f$. The increase in the grain size caused an increase in the rms values. As shown in Fig. 3, the crystal quality of the STO thin films improved with increasing $T_f$. In contrast, the surface roughness of the films increased with increasing $T_f$. The rms value of the STO film ($\Delta \omega = 2.39$ deg) fired at 800ºC was 2.23 nm. This value is suitable for further deposition of other superconducting films. However, the surface roughness suddenly increased above 825ºC and the rms of the STO film ($\Delta \omega = 1.81$ deg) fired at 875ºC was 5.37 nm.

Figure 6. Firing temperature dependence of the rms values of the surface of STO thin films derived from the AFM images

4. Conclusions
STO buffer films on MgO substrates were fabricated by the MOD method. By introducing a 2-step heat treatment and by optimizing the temperature of the precursor fabrication, we could improve the FWHM values of $\Delta \omega$ and $\Delta \phi$ up to 1.81 deg and 2.60 deg, respectively. The films showed only a cube-on-cube structure on the MgO substrates. Furthermore, the rms value of the surface for the STO film with a $\Delta \omega$ of 2.39 deg was 2.23 nm. This value is suitable for further deposition of other superconducting films. However, the value for the film with a $\Delta \omega$ of 1.81 deg was 5.37 nm. This value
is relatively large and further improvement in the surface morphology can be expected by optimizing the fabrication conditions, such as the firing time and the atmosphere used.

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