Effect of annealing on the structural properties of spin-coated $Ba_{0.7}Sr_{0.3}TiO_3$ films

Zhimou Xu, Yuichiro Tanushi, Masato Suzuki, Keita Wakushima and Shin Yokoyama
Research Center for Nanodevices and Systems, Hiroshima University,
1-4-2 Kagamiyama, Higashi-Hiroshima 739-8527, Japan
Phone: 81-824-24-6265, Fax: 81-824-22-7185, Email: yokoyama@sxsys.hiroshima-u.ac.jp

1. Introduction

Ferroelectric thin film materials are very attractive due to their large electro-optic (E-O) coefficient and high transparent performance [1] making them useful for integrated opto-electronic devices such as E-O modulator, switch, and the optical waveguide. Recently, much attention has been also paid to $(Ba_xSr_{1-x})TiO_3$ (BST) films in integrated opto-electronic device applications as they have prominent properties such as large E-O coefficient and relatively low optical losses. Although many structural, electrical and optical data of BST thin films have been published, so far, there are only few data available for the structural properties of BST thin films directly deposited on SiO_2/Si or Si substrate. No data about optical properties of BST-based optical waveguide and switches directly formed on SiO_2/Si or Si substrate have been reported in detail. In this paper, the effect of annealing temperature and thickness on the structural properties of novel metal organic decomposition (MOD)-derived $Ba_{0.7}Sr_{0.3}TiO_3$ (BST0.7) films on a SiO_2/Si substrate is presented. The optical performance of BST0.7 E-O devices will be introduced in other papers.

2. Experiments

BST0.7 thin films were deposited on the Si substrate with 1.65 μm SiO_2 thermal oxide layer from metal organic solutions by spin-coating. The titanium tetra-n-butoxide ($Ti(C_4H_9O)_4$), strontium 2-caprylate ($Sr(C_8H_{15}O_2)_2$), Barium 2-caprylate ($Ba(C_8H_{15}O_2)_2$) and 3-methylbutyl acetate ($CH_3COOC_2H_4CH(CH_3)_2$) were used as the starting materials. Their appropriate molar ratio was satisfied with the composition of BST0.7. The precursor solution was spin coated, at 500 rpm/min for 10 s and 2000-2200 rpm/min for 20 s, on SiO_2/Si substrate. For about 180 nm to 500 nm thickness BST0.7 films, each wet layer was initially dried at 180°C to evaporate the solvent, rapidly prebaked at 450°C for 30min to remove residual organics. The desired thickness of the BST0.7 layer was achieved using multiple steps of spin-coating-prebaking process. For about 170 nm thickness BST0.7 films, each wet layer was initially dried at 180°C and the process was repeated three times to obtain about 170 nm thickness, then rapidly prebaked at 450°C for 30 min. The multilayer films of desired thickness were annealed at different temperature for 30 min in open air in a conventional box furnace. Heating and cooling rate were respectively kept at 5℃/min and 3 □/min. The structure of the BST0.7 thin films was analyzed by X-ray diffraction (XRD). The thickness of thin films was measured by Nanometrics (Nanospec/AFT 5000) machine and decided by SEM photographs of cross sections of samples.

3. Results and discussion

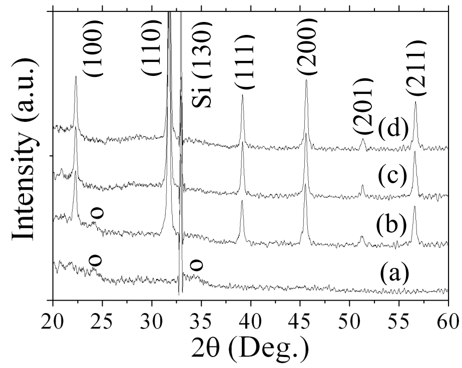

Fig.1 XRD patterns of 180 nm BST films postannealed at different temperature. The intermediate phases are marked with a hollow circle.

Fig.1 shows the XRD patterns of BST0.7 films with 180 nm thickness postannealed at different temperature of (a) as deposited, (b) 550℃, (c) 600℃ and (d) 750℃. Generally, a higher postannealing temperature will result in better crystallinity. Fig.1 also presents this trend. As the postannealing temperature increased, the relative intensity of the XRD patterns of BST0.7 thin films increased. Any clear peaks belonging to crystalline BST0.7 did not appear for the as-deposited films prebaked for 30 min at 450℃, which demonstrates the amorphous nature of the films [curve (a) in Fig.1]. A complete pseudo-cubic perovskite phase of BST0.7 has already begun to appear at 550℃ only for 30 min-postannealing [curve (b) in Fig.1]. Although a little number of intermediate phases existed in BST0.7 films annealed at 550℃, it is expectable that they will disappear after prolonging the postannealing time. The crystallized temperature is relatively lower than that reported in other papers using the similar chemical solution-derived BST0.7 films methods such as sol-gel [2] and MOD [3] methods. One of the main reasons is the special precursor solution used in our experiments. The lower crystallized temperature for BST0.7 film is very helpful to be integrated in optoelectronic integrated circuits

(OEICs). The peaks of the perovskite phase became sharper with the increase of postannealing temperature from 550℃ to 750℃ while having no preferential orientation [curve (b) to (d) in Fig.1]. For the intermediate phases, our results demonstrated that they（Fig.1 (a)) have already showed-up in as-deposited BST0.7 films prebaked at 450℃. It advanced the crystallized process of BST0.7 films at the following postannealing treatment. From the reported literatures [3], it can be recognized that the intermediate phase at $2\theta = 24.1^{\circ}$ and 34.2° are barium carbonate ($BaCO_3$). But the intermediate phase $(Ba,Sr)_2Ti_2O_5CO_3$ -related [3] was not found in our results.

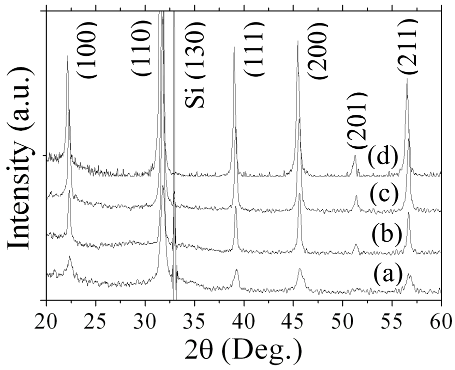

Fig.2 XRD patterns of BST films with different thickness postannealed at 750℃ for (a) 170 nm, (b) 180 nm, (c) 340 nm and (d) 500 nm.

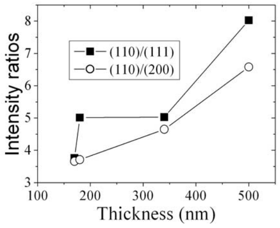

Fig.3 Intensity ratios for BST films with different thickness postannealed at 750℃.

Table 1 Dependence of the FWHM of the rocking curves on the BST film thickness.

Thickness (nm)	170	180	340	500
FWHM (Deg.)	0.68	0.32	0.36	0.35

In order to study the effect of film thickness on the structural quality, films with different number of spin-coated layers were fabricated. Fig.2 gives the XRD patterns of BST0.7 films with different thickness after post-annealing at 750℃ for (a) 170 nm, (b) 180 nm, (c) 340 nm and (d) 500 nm. It can be seen that the intensity of the spectra increases naturally with the film thickness. However, the (110) peak increases at a much faster rate. This is clearly illustrated in Fig.3, in which the intensity ratios of (110)/(111) and (110)/(200) are plotted against film thickness. Apparently, these ratios increase with film thickness especially for above 340 nm indicating that the (110) BST0.7 oriented growth is preferred. The rocking curves of the (200) peak were also measured. Table1 shows the dependence of the full width half maximum (FWHM) of the rocking curves on the film thickness. It is obvious that the FWHM of the rocking curves changed slightly as the thickness of BST0.7 films increased from 180 nm to 500 nm. However it increased sharply for the 170 nm thickness BST0.7 films. According to Scherrer's formula as shown Eq.1, the grain size of 170 nm BST0.7 films is smaller than those of other thickness BST0.7 films.

$$D = \frac{0.94\lambda}{FWHM \times \cos\theta} \qquad (1)$$

where D is the grain size, λ is the wavelength of X-ray radiation used ($\lambda = 1.54\,\overset{\circ}{A}$) and θ is the peak position angle. One of main reasons is the change of spin-coating and prebaking process. For 170 nm thickness BST0.7 films, the prebaking process was completed after spin-coated 170 nm thickness BST0.7 films and the total prebaking time was only 30 min. The intermediate phases growth and the removal of residual organics were not adequate postponing the initial crystallization and grain growth process during the postannealing treatment. Additionally, Comparing the intensity ratios of (110)/(111) and (110)/(200) both 170 nm and 180 nm thickness BST0.7 films, the adequate prebaking process is favorable for crystallization and oriented growth. These results clearly suggest that enhanced (110) BST0.7 orientation was obtained by the increase of the BST0.7 film thickness and the adequate prebaking process. However the grain size of BST0.7 films changed slightly with the increase of thickness from 180 nm to 500 nm.

4. Conclusions

In summary, the crystalline BST0.7 films have been grown directly on SiO_2/Si substrate by novel MOD technique with relatively lower postannealing temperature 550℃. The lower crystallized temperature for BST0.7 film is very helpful to be integrated in OEICs. Enhanced (110) orientation was obtained by the increase of the BST0.7 films thickness and the adequate prebaking process.

References

[1] D. Kip., Applied Physics B, 67, p.131, (1998)
[2] Xiaofeng Chen et. al., Surface and Coatings Technology, 167, p.203, (2003)
[3] San-Yuan Chen et. al, Materials Chemistry and Physics, 77, p.632, (2002)

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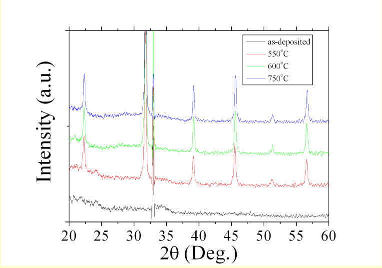
Objectives:

- The crystalline $Ba_{0.7}Sr_{0.3}TiO_3$ (BST0.7) films is grown directly on SiO_2/Si substrate by novel metal organic decomposition (MOD) technique with lower postannealing temperature 550℃.
- The effect of annealing temperature and thickness on the structural properties of MOD-derived BST0.7 films on a SiO_2/Si substrate is presented.
- The BST films are studied for the application to the electro-optic materials of the microring-resonator optical switch.

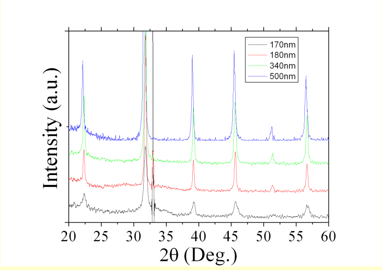
Experiments:

- BST films are formed by spin-coating method.
- The multilayer films of desired thickness were annealed in open air in a conventional box furnace.
- The phase structure was analyzed by X-ray diffraction (XRD). The surface morphology was measured by AFM.

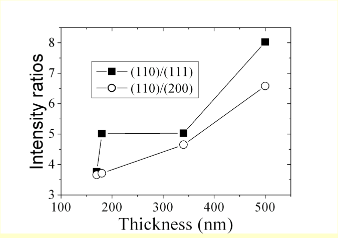
Phase development:



XRD patterns of 180 nm BST films postannealed at different temperature.



XRD patterns of BST films with different thickness postannealed at 750℃.



Intensity ratios for BST films with different thickness postannealed at 750℃.

Explanation:

- For phase structure, the **temperature dependence** divided **three** parts :

(1) A higher postannealing temperature will result in better crystallinity;

(2) A complete pseudo-cubic perovskite phase of BST0.7 has already begun to appear at 550℃ only for 30 min-postannealing. The lower crystallized temperature for BST0.7 film is very helpful to be integrated in optoelectronic integrated circuits (OEICs).

(3) The intermediate phases have already showed-up in as-deposited BST0.7 films prebaked at 450℃. This advanced the crystallized process of BST0.7 films at the following postannealing treatment.

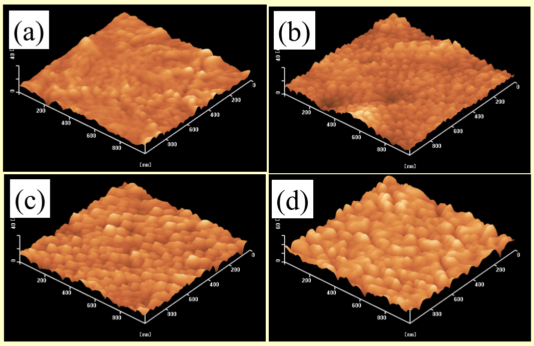
- For phase development, the **thickness dependency** is as follows.

(1) The intensity of the XRD spectra increases naturally with the film thickness;

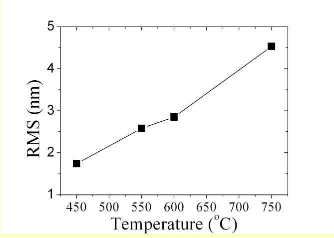
(2) Enhanced (110) BST0.7 orientation was obtained by the increase of the BST0.7 film thickness and the adequate prebaking process;

(3)The grain size of BST0.7 films changed slightly with the increase of thickness from 180 nm to 500 nm.

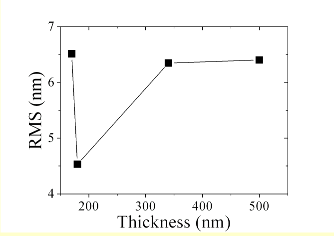
Surface morphology:



AFM surface morphology of BST films with 180 nm thickness after post-annealing at different temperature for (a) as deposited, (b) 550℃, (c) 600℃, and (d) 750℃.



RMS roughness of BST films with 180 nm thickness after post-annealing at different temperature



RMS roughness of BST films with different thickness after post-annealing at 750℃

Explanation:

- For surface morphology, the **temperature dependence** divided **two** parts :

(1) The surface roughness of the films is strongly affected by the annealing temperature ;

(2) The as-deposited film surface was comparatively smooth and the RMS roughness was about 1.74 nm. However, after postannealed, the RMS roughness of BST0.7 films increased almost linearly even at lower temperature of 550℃ and 600℃. .

- For surface morphology, the **thickness dependency** is as follows.

(1)The RMS roughness changed sharply when the thickness of BST0.7 films increased from 180 nm to 340 nm;

(2) In comparison with 170nm BST0.7 films, the RMS roughness was as larger as 340 nm to 500 nm BST0.7 film. It demonstrates that the adequate prebaking process which products the intermediate phases and remove the residual organics are necessary to fabricate BST0.7 optical waveguide films by MOD method.

Conclusion

① The crystalline BST0.7 films have been grown directly on SiO2/Si substrate by novel MOD technique with relatively lower postannealing temperature 550℃. The lower crystallized temperature for BST0.7 film is very helpful to be integrated in OEICs.

② Enhanced (110) orientation was obtained by the increase of the BST0.7 films thickness and the adequate prebaking process.

③ The RMS roughness of BST0.7 films increased almost linearly with the increase of postannealing temperature. The adequate prebaking process which reduced the final RMS roughness values was necessary to fabricate BST0.7 optical waveguide films by MOD method.