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Preparation and Dielectric Properties of $SrBi_2Ta_2O_9$ Thin Films by Sol–Gel Method

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Abstract

Ferroelectric $Sr_{0.7}Bi_{2.2}Ta_2O_9$ (SBT) thin films were prepared at 600 and 750°C for 1 h using SBT precursor solutions of metal alkoxides with and without an addition of acethylacetone (acac), respectively. Crystalline SBT thin films were successfully prepared at 600°C from precursor solutions without an addition of acac. SBT thin films prepared at 750°C exhibited a high (105) diffraction intensity with random orientation, and exhibited a bimodal grain structure consisting of stone wall-like grains of 500–860 nm and small grains of 100–300 nm. The addition of acac to precursor solutions promoted a c*-axis preferred orientation of SBT. SBT thin films with a* c*-axis preferred orientation showed a bimodal microstructure which consisted of large grains of 200–300-nm and small grains of about 50 nm. SBT thin films prepared at 750°C from precursor solutions without an addition of acac exhibited ε_r of 119, P_r of 3·1 $\mu C\ cm^{-2}$ and E_c of 65·1 $kV\ cm^{-1}$, while those prepared at 750°C from precursor solutions containing acac exhibited ε_r of 205, P_r of 7·2 $\mu C\ cm^{-2}$ and E_c of 53·3 $kV\ cm^{-1}$.* © *1999 Elsevier Science Limited. All rights reserved*

Keywords: acethylacetone, films, mixing, sol–gel processes, ferroelectric properties.

1 Introduction

Recently, a significant amount of research and development has focused on ferroelectric thin films for nonvolatile memory applications. Bismuth layer-structured ferroelectric (BLSF) materials such as $SrBi_2Ta_2O_9$, $SrBi_2Nb_2O_9$, $SrBi_4Ti_4O_{15}$ have attracted great interest as a promising nonvolatile random access memory (NvRAM) applications.[1–4] Among them, $SrBi_2Ta_2O_9$ (SBT) is the most promising candidate for nonvolatile memory applications, because of non-fatigue nature and possibility of low polarization switching voltage. Furthermore, this material has the potential to be used to realize a highly integrated nonvolatile memory. Therefore, various investigations have been carried out using solution processing. Among them, in the case of sol–gel method using alkoxides,[5–8] bismuth, tantalum and strontium sources are a very important factor in the control of crystal orientation of SBT thin films. We reported[7] that the crystal orientation and the microstructure of sol–gel-derived SBT thin films depended upon the process by which the metal alkoxides were mixed and the addition of acac to the solution. However, the addition of acac to the solution prevented crystallization of SBT thin films and deteriorated ferroelectric properties.

This paper describes the preparation of SBT thin films from precursor solutions which were obtained by mixing strontium di-n-butoxide, bismuth tri-i-propoxide and tantalum pentaethoxide at room temperature. In this work, the precursor solutions of mixed metal alkoxides in solvent were not refluxed. Crystal orientation, surface morphology and dielectric properties of SBT thin films were investigated.

2 Experimental

Figure 1 shows the method of preparing solution of SBT thin films by sol–gel method. Strontium di-n-butoxide, bismuth tri-i-propoxide and tantalum pentaethoxide were used as starting materials. The solvent used was 2-methoxyethanol.

It has been reported[7–9] that a double alkoxide ($Sr[Bi(OR)_4]_2$) formed when bismuth alkoxide was mixed with strontium alkoxide in the solvent. Thus, in this work at first strontium di-n-butoxide

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and bismuth tri-i-propoxide were mixed together in 2-methoxyethanol at room temperature for 1 h, and then the solution was added to tantalum ethoxide, and finally stirred for 2 h at room temperature. The final concentration of SBT precursor solutions was about 10 wt%. In some SBT solutions, acac was added as a chelating agent to Sr, Bi and Ta-containing solutions. The molar ratio of acac/Bi in the SBT precursor solutions were 0·44. The main composition of SBT thin films used in this study was $Sr_{0.7}Bi_{2.2}Ta_2O_9$.

SBT gel thin films were prepared by spin-coating technique on Pt(111)/Ti/SiO_2/Si substrates. Gel thin films were dried at 150°C for 5 min and heated at 400°C for 30 min and then heated at 500–750°C for 5 min by rapid thermal annealing (RTA) in an O_2 atmosphere. The above-mentioned process was repeated several times. SBT thin films were finally heated at 500–750°C for 1 h by RTA.

The crystallization and the crystal orientation of SBT thin films were examined by X-ray diffraction (XRD). The microstructures of thin films were observed by field-emission scanning electron microscope (FE-SEM). Gold electrodes of 0·2 mm diameter were vacuum-deposited through a mask onto the surface of SBT thin films. The dielectric constant (ε_r) and the dielectric loss (tan δ) were measured using an impedance analyzer (YHP-4192A) at 1 kHz with a micromanipulator. P–E hysteresis loops were observed using RT-66A (Radiant Technologies, Inc.) at 1 kHz. The applied voltage was 5 V.

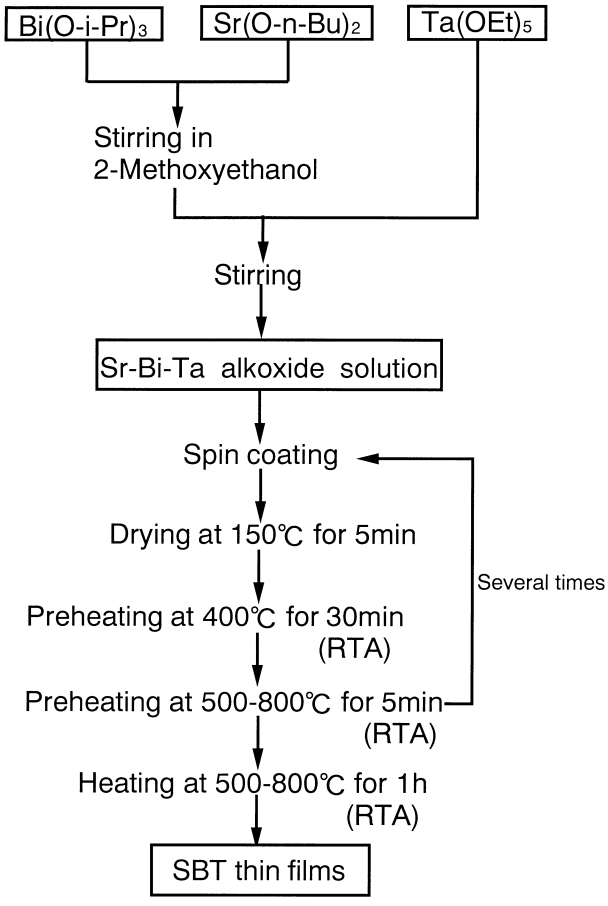

Fig. 1. Flow diagram for the preparation of SBT thin films.

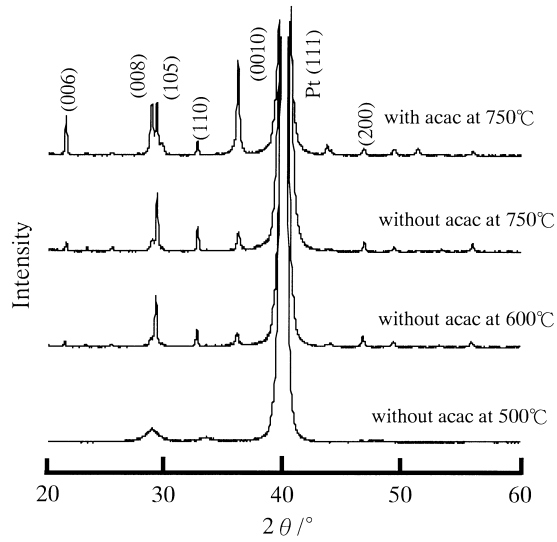

Fig. 2. XRD patterns of SBT thin films prepared from precursor solutions with and without acethylacetone.

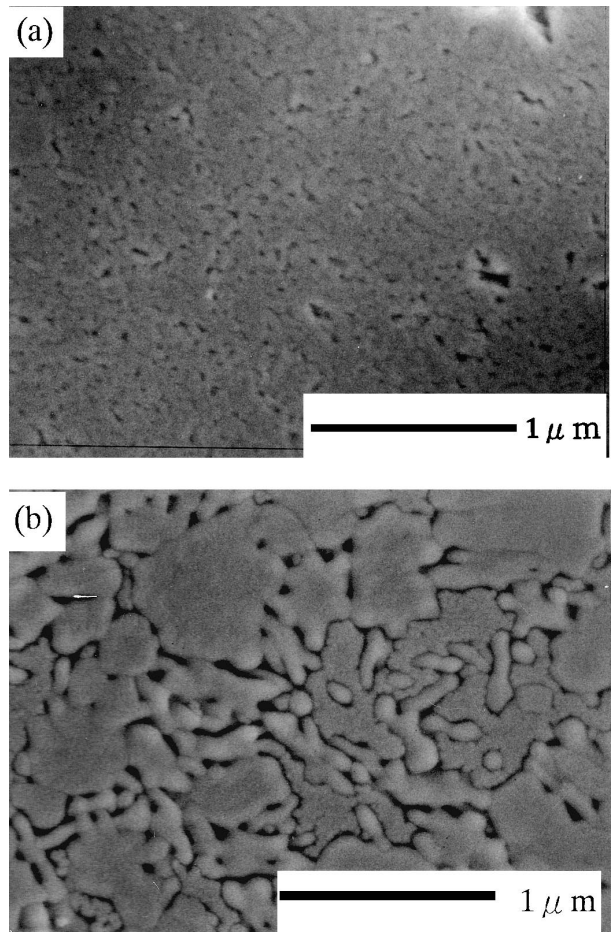

Fig. 3. FE-SEM micrographs of surfaces of SBT thin films prepared at different annealing temperatures without an addition of acac: (a) without acac at 600°C; (b) without acac at 750°C.

3 Results and Discussion

SBT precursor solutions prepared at room temperature exhibited relatively high stability toward hydrolysis with the moisture in atmosphere, even though acac was not added.

Figure 2 shows X-ray diffraction patterns of SBT thin films prepared from precursor solutions with and without an addition of acac. SBT gel thin films without an addition of acac started to crystallize at approximately 500°C. Crystalline SBT thin films with random orientation were prepared at 600°C as a single phase, but the crystallinity of the thin films was relatively low. However, SBT thin films prepared at 750°C showed a high (105) diffraction intensity. On the other hand, SBT thin films prepared from precursor solutions with an addition of acac were crystallized at 600°C. However, the thin films showed a very low crystallinity, compared to those prepared at 600°C from precursor solutions without an addition of acac. SBT thin films prepared at 750°C from precursor solutions with an addition of acac showed (00ℓ) preferred orientation along with a high (105) diffraction intensity. The crystallinity of the SBT thin films prepared in this work was higher, compared to SBT thin films prepared from precursor solution obtained under conditions of refluxing alkoxide solutions.[7]

Figures 3 and 4 show FE-SEM micrographs of SBT thin films. SBT thin films prepared at 600°C without an addition of acac exhibited a grain microstructure with small grains of 30–40 nm. But, SBT thin films prepared at 750°C exhibited porous bimodal grains microstructure consisting of a mixture of stone wall-like grains of 500–860 nm and small grains of 100–300 nm. On the other hand, SBT thin films prepared at 750°C with an addition of acac showed a bimodal microstructure that consisted of large grains of 200–300 nm and small grains of about 50 nm. SBT thin films of 380–420 nm thickness were obtained by repeating coating and heating process four times.

Table 1 and Fig. 5 show dielectric properties and P–E hysteresis loops of sol–gel-derived SBT thin films on $Pt/Ti/SiO_2/Si$ substrates. SBT thin films

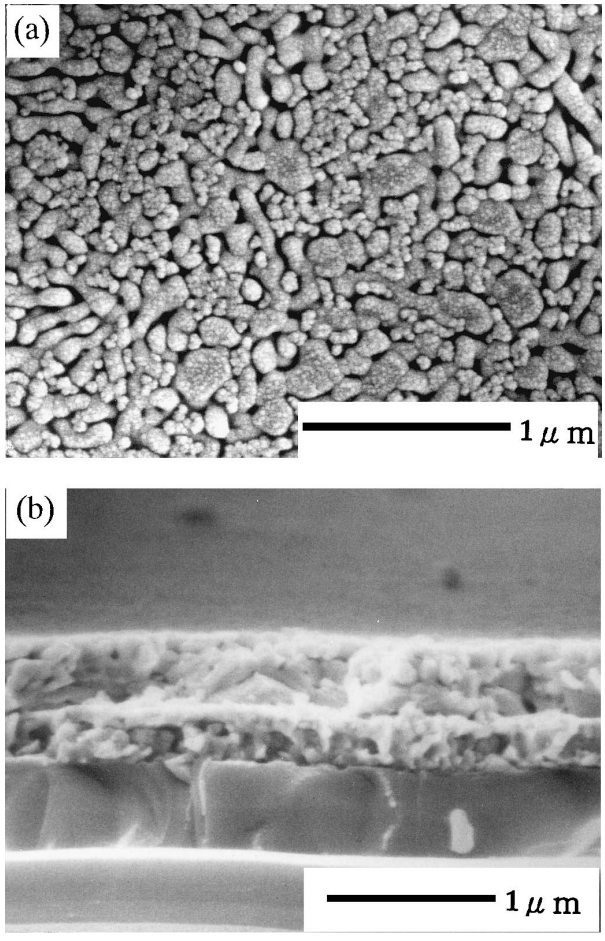

Fig. 4. FE-SEM micrographs of surface and cross section of SBT thin films prepared at 750°C with an addition of acac: (a) surface; (b) cross section of (a).

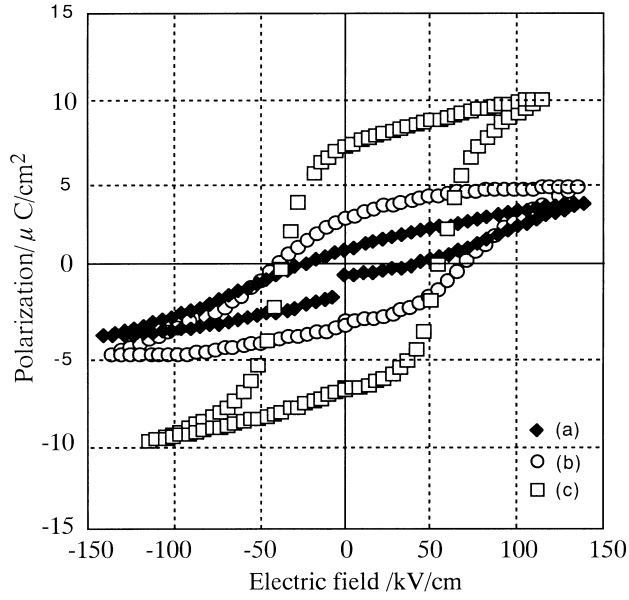

Fig. 5. P–E hysteresis loops of SBT thin films prepared by RTA: (a) without acac (600°C); (b) without acac (750°C); (c) with acac (750°C).

Table 1. Dielectric properties of SBT thin films

Annealing temperature (°C)	*acac/Bi alkoxide mol ratio*	*Thickness (nm)*	ε_r	*tan* δ *(%)*	Pr *(μC cm^{-2})*	E_c *(kV cm^{-1})*
600	0	380	126	7·3	1·1	25·7
750	0	370	119	8·4	3·1	65·1
750	0·44	420	205	8·5	7·2	53·3

heated at 600°C without an addition of acac showed ε_r of 126, a remanent polarization P_r of 1·1 μC cm^{-2}, and a coercive field, E_c of 25·7 kV cm^{-1}. And, SBT thin films heated at 750°C without an addition of acac showed ε_r of 119, a P_r of 3·1 μC cm^{-2}, and an E_c of 65·1 kV cm^{-1}. On the other hand, SBT thin films prepared at 750°C with an addition of acac/Bi = 0·44 molar ratio showed an ε_r of 205, a P_r of 7·2 μC cm^{-2}, and an E_c of 53·3 kV cm^{-1}.

SBT thin films prepared at 600°C exhibited a lower remanent polarization than that of the thin films prepared at high temperature. This may be attributed to a lower crystallinity and smaller grain sizes. A higher crystallization temperature made a coarser microstructure in the case of non-addition of acac. However, the addition of acac to alkoxide solutions made it possible to prepare SBT thin films with a homogeneous and dense microstructure at higher annealing temperatures.

SBT thin films have no or little polarization along the *c* axis. Polarization axis of SBT thin films have *a* or *b* axis. Thus, it is important to develop a process to control *a* or *b* axis preferred orientations of SBT thin films. For preparation of SBT thin films with *a* or *b* axis preferred orientation, it is desirable not to add acac to SBT precursor solution.

4 Conclusions

$Sr_{0.7}Bi_{2.2}Ta_2O_9$ thin films were prepared at 600 and 750°C for 1 h from alkoxide precursor solutions with and without an addition of acac, respectively, by sol–gel method.

In the case of non-addition of acac, SBT thin films were prepared as a single phase at 600°C. The thin films showed a low (105) diffraction intensity with random orientation, and the microstructure exhibited extremely small grains of about 30–40 nm, but SBT thin films prepared at 750°C showed as high diffraction intensity, and the microstructure exhibited bimodal grains consisting of stone wall-like grains of 500–860 nm and small grains of 100–300 nm. On the other hand, SBT thin films prepared at 750°C from precursor solutions with an addition of acac showed a high (00ℓ) preferred orientation with a high (105) diffraction intensity. The microstructure showed bimodal structure that consisted of large grains of 200–300 nm and small grains of about 50 nm.

SBT thin films prepared at 750°C from precursor solutions without acac exhibited an ε_r of 119, a P_r of 3·1 μC cm^{-2} and an E_c of 65·1 kV cm^{-1}, while SBT thin film prepared at 750°C from precursor solutions with acac exhibited an ε_r of 205, a P_r of 7·2 μC cm^{-2} and an E_c of 53·3 kV cm^{-1}.

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