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Phase Formations and Electrical Properties of Various $(Bi,La)_4Ti_3O_{12}$ Thin Films by Chemical Solution Deposition

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Abstract. The phase formation and electrical properties of $(Bi,La)_4Ti_3O_{12}$ (BLT) thin film and V-, Sm-doped BLT thin films prepared by the chemical solution deposition method on $Pt/TiO_2/SiO_2/Si$ substrates have been investigated. It was observed that the microstructure and electrical properties of BLT thin films dramatically varied with V- and Sm-doping. The crystallinity and grain size of BLT thin films were definitely increased by V- and Sm-doping into BLT films, which resulted in the enhancement of remanent polarization in doped BLT films. The remanent polarization (Pr) of Sm-doped BLT films annealed for 3 min by an RTA system was about 9 $\mu C/cm^2$. The V- and Sm-doped BLT films also exhibited good fatigue characteristics under bipolar stressing to 10^{10} cycles.

Keywords: $(Bi,La)_4Ti_3O_{12}$, doping, ferroelectrics, remanent polarization, leakage current

1. Introduction

Bismuth layer-structured ferroelectrics such as $SrBa_2Ta_2O_9$ and $Bi_{4-x}La_xTi_3O_{12}$ (BLT) thin films have recently attracted much attention for ferroelectric random access memory (FRAM) applications because they may probably be another promising candidate material due to good fatigue resistance and lead-free composition. In the viewpoint of process issue, recently reported BLT thin films have many advantages over SBT thin films. In particular, low process temperature of BLT films, yet maintaining relatively good ferroelectric properties is an attractive characteristic for the applications [1–4].

However, since BLT film has intrinsic strong anisotropic spontaneous polarization (P_r), crystallographic orientation of BLT films has been great concern to control polarization characteristics [5–8]. Furthermore, because BLT films have considerably lower P_r and somewhat higher processing temperature than those of Pb-based ferroelectrics, many researcher have still investigated to enhance the P_r value of BLT films at lower processing temperature. It is very important to maintain processing temperature of BLT films as low as possible, particularly in the FRAM device production, in that this achievement could provide a simplified electrode structure and diminish process steps. Therefore, ion substitution in BLT films has recently been attracted much attention as one of methods for improving the ferroelectric properties. Chon et al. reported that the fatigue-free samarium (Sm)-modified bismuth titanate ($Bi_{4-x}Sm_xTi_3O_{12}$) films capacitor exhibited the large spontaneous polarizations [9]. Wang et al. also investigated W- and Mo-doped bismuth lanthanum titanate films showing the larger P_r value and smaller coercive field (E_c) than that of bismuth titanate films [10].

In this study, we fabricated BLT and V-, Sm-doped BLT thin films prepared by the chemical solution deposition method on $Pt/TiO_2/SiO_2/Si$ substrates and then annealed three types of films by rapid thermal annealing (RTA) process. The variation of the crystallinity, the microstructure and electrical properties of $Bi_{3.15}La_{0.85}Ti_3O_{12}$ (BLT) films and V-, Sm-doped BLT films were investigated. In particular, the variation of Pr and leakage current in BLT thin films was observed with V- and Sm-doping. The fatigue characteristics in these films were also investigated under bipolar stressing.

2. Experimental

Various BLT thin films were prepared by alkoxide-carboxylate precursor solution. The preparation of BLT thin films is as follows; bismuth acetate, La(TMHD)$_3$, titanium isopropoxide, vanadium acetylacetonate and samarium acetate were chosen as precursors, and 2-methoxyethanol and butyl acetate were selected as solvents. The starting composition of various BLT solutions used in this study were $Bi_{3.15}La_{0.85}Ti_3O_{12}$ for non-doped BLT, $Bi_{3.15}La_{0.85}Ti_{2.99}V_{0.01}O_{12}$ for V-doped BLT and $Bi_{3.15}La_{0.85}Sm_{0.077}Ti_3O_{12}$ for Sm-doped BLT films, respectively. 5.5 mol% of excess Bi was added to compensate evaporation of Bi during the annealing. The solutions were spin-coated on Pt/TiO_2/SiO_2/Si substrates at a rate of 3000 rpm for 30 sec, and followed by a pyrolysis process at 300°C for 10 min. The RTA method was adopted for minimizing the thermal energy to degrade the Pt bottom electrode. The RTA process was done at 700°C for 1–3 min under oxygen environment. The thickness and microstructure of the films were investigated by scanning electron microscopy (SEM). The BLT films of 130 nm thickness were used in this study. The crystallinity and phases of the thin films were analyzed by X-ray diffraction (XRD). The diffraction patterns were recorded on a Regaku Rotaflex diffractometer using Cu K_α radiation (30 keV) at a scanning speed of 2°/min. Electrical measurements were conducted on films in a metal-ferroelectric-metal (MFM) configuration using Pt as the top and bottom electrodes. The Pt electrodes (area $= 1.0 \times 10^{-4}$ cm^2) were sputter-deposited and defined by a lift-off process. The films were then annealed at 600°C for 10 min after top electrode deposition to ensure good electrical contact. The polarization-electric field (*P-E*) curves and leakage current characteristics were measured using a RT66A ferroelectric tester and a HP 4145B semiconductor parameter analyzer, respectively.

3. Results and Discussion

It is important to investigate the crystallographic orientation of BLT films because of its intrinsic anisotropy in spontaneous polarization. We observed that BLT thin films showed significant differences depending on intermediate RTA temperature and excess Bi content in BLT films in the previous report [11, 12]. Therefore, in this study, the composition of excess Bi was maintained to 5.5 mol% and an intermediate RTA process was not used for all samples. Figure 1 shows X-ray diffraction patterns of BLT film and V-, Sm-doped BLT films, which were RTA-processed at 700°C for 1 min in oxygen ambient. While the BLT films RTA-processed at 700°C for 1 min displayed a poorly crystallized phase, V- and Sm-doped BLT films exhibited well-crystallized phase and there were no observable secondary phases present in the XRD patterns of the films indicating complete phase formation. In V- and Sm-doped BLT thin films, ⟨117⟩ orientation indicating the growth with random crystallographic orientation was observed.

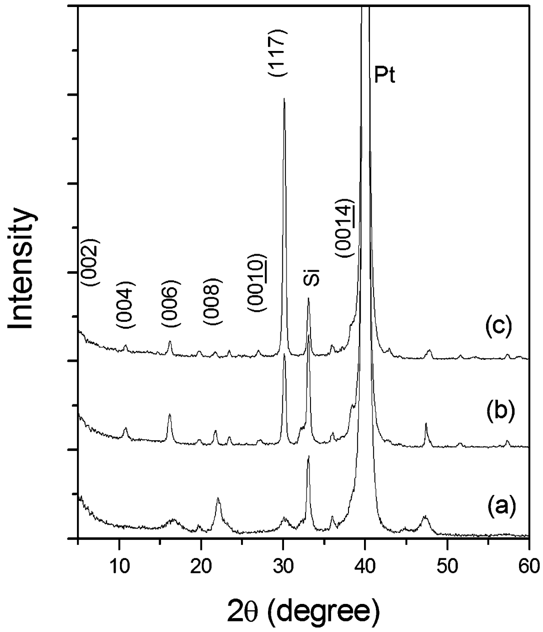

Fig. 1. XRD patterns of (a) BLT, (b) V-doped BLT and (c) Sm-doped BLT thin films on Pt/TiO_2/SiO_2/Si substrate. All films were annealed at 700°C for 1 min in oxygen atmosphere using an RTA system.

The morphological changes of various BLT thin films with dopant and RTA time were analyzed by scanning electron microscopy (SEM). Various BLT thin films RTA-processed have shown dense microstructures, in all conditions of Fig. 2. The grain size definitely increased with increasing RTA time on three different types of films and grains of BLT films showed quite different morphologies depending on V- and Sm-doping. The Sm-doped BLT thin films exhibited the maximum size at any identical RTA time. It was well

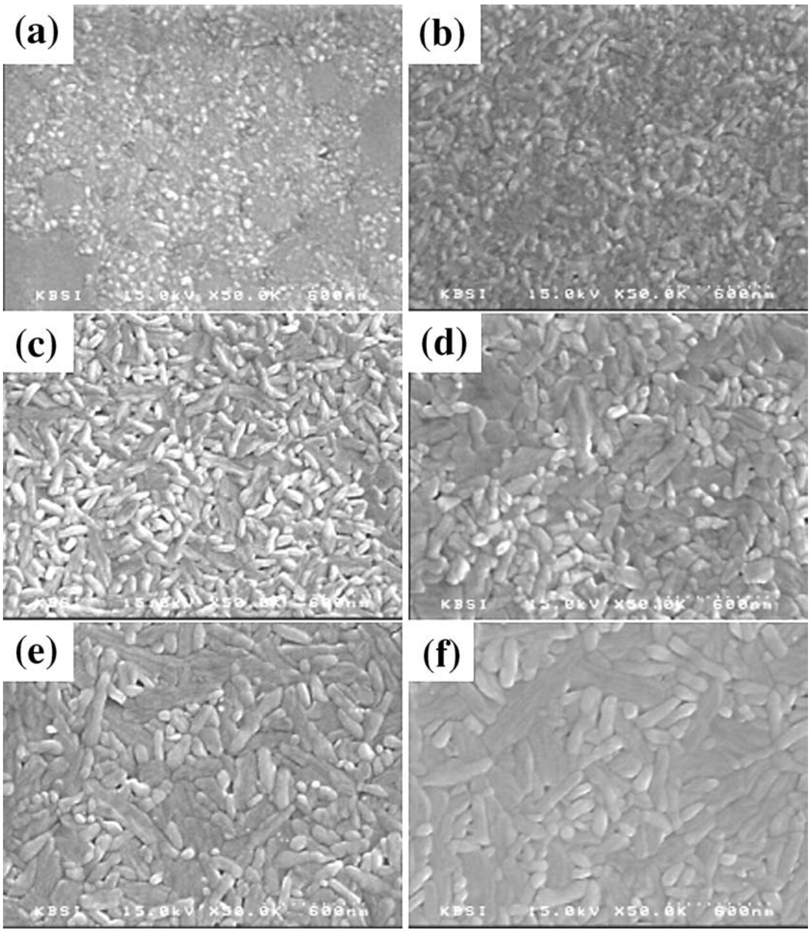

Fig. 2. Surface morphologies of various BLT thin films annealed at 700°C with rapid thermal annealing (RTA) time in oxygen atmosphere. BLT films: (a) for 1 min, (b) for 3 min, V-doped BLT films, (c) for 1 min, (d) for 3 min, and Sm-doped BLT films (e) for 1 min, and (f) for 3 min.

known that BLT films having random crystallographic orientation have uniform grain sizes and the shape of each grain in BLT films is rather rod-like compared with that having *c*-axis preferred orientation. These results were in accordance with previous morphologies [11]. However, at this moment, the exact mechanism of the doping effect on the grain growth has been still in the investigation.

Ferroelectric hysteresis measurements were conducted on various BLT thin films on $Pt/TiO_2/SiO_2/Si$ substrates at room temperature using a standardized RT66A ferroelectric tester. The doping effect on *P-E* hysteresis loops of BLT films prepared with two different RTA time is shown in Fig. 3. The ferroelectric properties of BLT thin films was improved by adding a small amount of *V* or Sm in BLT films and the P_r value of Sm-doped BLT films is higher than that of V-doped

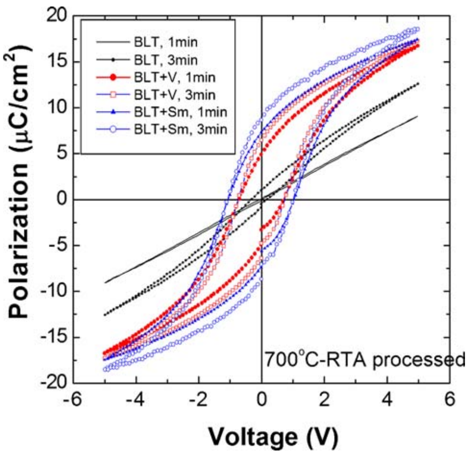

Fig. 3. Hysteresis characteristics of various BLT films prepared on $Pt/TiO_2/SiO_2/Si$ structure.

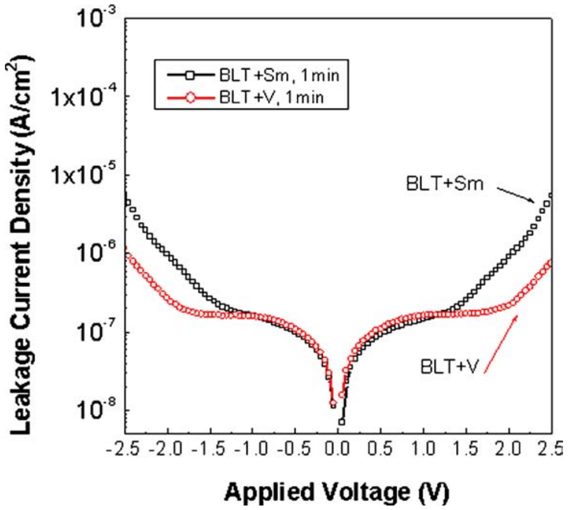

Fig. 4. Leakage current densities of *V* and Sm-doped BLT films on $Pt/TiO_2/SiO_2/Si$ substrate. BLT films was RTA-processed at 700°C for 1 min.

BLT, which could be explained by the grain size difference, shown in Fig. 2. The measured coercive field of 130 nm-thick films was 57 kV/cm in V-doped BLT and 73 kV/cm in Sm-doped BLT, respectively, which is slightly lower than the previously reported value [11].

The leakage current densities of V- and Sm-doped BLT films prepared on $Pt/TiO_2/SiO_2/Si$ substrate are shown in Fig. 4. The I-V curve was obtained at a 0.02 s delay time during the measurement, because of the appearance of a switching current in doped-BLT ferroelectrics. Two doped BLT films have no polarity dependence upon an applied voltage. However, the leakage current density of Sm-doped BLT films showed almost same values as that of the V-doped BLT to the applied electric field of 100 kV/cm and then increased more rapidly than that of the V-doped BLT films above 100 kV/cm. The relatively low leakage current in V-doped BLT films at high electric field could be considered that some oxygen vacancies in V-doped BLT films, in our study can be removed by B-site substitution, as other work reported [10]. The leakage current density of doped BLT films is $\sim 1 \times 10^{-7}$ A/cm^2 at the applied field of 100 kV/cm.

Polarization fatigue endurance of BLT films having random crystallographic orientation as a function of switching cycle was recorded using a RT66A ferroelectric tester. The applied bipolar stress was a square wave of 4 V amplitude and 1 MHz frequency. In Fig. 5, P^*r and $P^\wedge r$ refer to the switched and nonswitched remanent polarizations, respectively and $P^*r - P^\wedge r$ is nearly equivalent to $2P_r$, where P_r is the remanent polarization. The observed polarization loss after 10^{10}

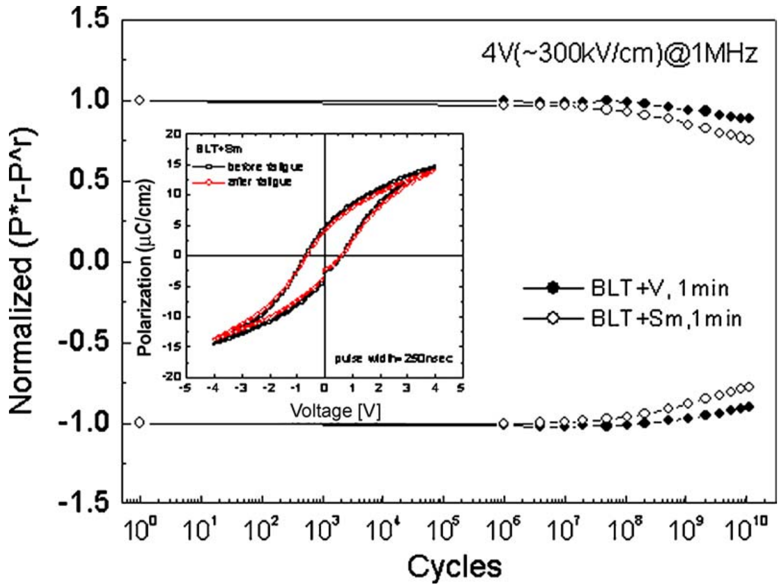

Fig. 5. Polarization fatigue endurance of *V* and Sm-doped BLT thin films as a function of bipolar switching cycle using a 1 MHz bipolar square wave of 4 V (∼300 kV/cm) amplitude.

switching cycles was less than 10% of the initial value. Moreover the shapes of the hysteresis curve before and after the bipolar switching cycles do not change significantly suggesting that V- and Sm-doped BLT thin films are promising materials for FRAM devices.

4. Conclusions

The $(Bi,La)_4Ti_3O_{12}$ (BLT) thin film and V-, Sm-doped BLT thin films were prepared by the chemical solution deposition method on $Pt/TiO_2/SiO_2/Si$ substrates. The crystallinity and microstructure of BLT thin films dramatically varied with V and Sm doping. The remanent polarization (Pr) of doped BLT films was definitely higher than that of non-doped BLT film, which could be induced by the enhancement of crystallinity and grain size in doped BLT films. The Pr of Sm-doped BLT films annealed for 3 min by RTA was 9 $\mu C/cm^2$. The V and Sm-doped BLT films also exhibit good fatigue characteristics under bipolar stressing to 10^{10} cycles, indicating that V- and Sm-doped BLT thin films are promising materials for FRAM devices.

Acknowledgments

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