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Processing and properties of ferroelectric (Bi, La)$_4$(Ti, Ge)$_3$O$_{12}$ thin films by chemical solution deposition

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Abstract

Ferroelectric (Bi, La)$_4$(Ti, Ge)$_3$O$_{12}$ thin films have been prepared on Pt/TiO$_x$/SiO$_2$/Si substrates using metal–organic precursor solutions by the chemical solution deposition (CSD). The Bi$_{3.25}$La$_{0.75}$Ti$_{2.9}$Ge$_{0.1}$O$_{12}$ (BLTG) precursor films were found to crystallize into the Bi layered perovskite Bi$_4$Ti$_3$O$_{12}$ (BIT) as a single phase. The synthesized BLTG films revealed a random orientation having strong 0 0 *l* reflections. The BLTG thin films prepared at 700 °C showed a well-saturated P–E hysteresis loop with a remanent polarization, P_r of 12 μC/cm^2 and a coercive field, E_c of 66 kV/cm at an applied voltage of 5 V. The surface morphology of the BLTG thin films was greatly improved by germanium (Ge) doping compared with that of nondoped Bi$_{3.35}$La$_{0.75}$Ti$_3$O$_{12}$ (BLT) films.

Keywords: Films; Sol–gel processes; Ferroelectric properties; Titanates

1. Introduction

Bismuth titanate, Bi$_4$Ti$_3$O$_{12}$ (BIT) is one of the most important lead-free ferroelectric materials and its thin films have been receiving considerable attention for their potential applications in nonvolatile ferroelectric random access memories (FeRAMs). Compared with SrBi$_2$Ta$_2$O$_9$ and its related materials, BIT thin films are known to have a large remanent polarization (P_r), a high Curie temperature and lower crystallization temperatures. However, BIT contains volatile Bi ions, which are easily evaporated during heating. The volatility of Bi ions enhances the formation of oxygen vacancies, which leads to degrade the ferroelectric and fatigue properties. Bi^{3+} ions in the BIT structure can be substituted by rare earth ions for the improvement of its properties.[1–5] As a representative example, (Bi, La)$_4$Ti$_3$O$_{12}$ has been intensively investigated as a promising ferroelectric material for memory devices because of its excellent properties.[1–3] However, the fabrication of high-density FeRAMs is still difficult, because of problems such as insufficient microstructure and ferroelectric properties. Recently, silicon (Si)-substituted BIT thin films with good surface morphologies were reported by Kijima and Ishiwara.[6] Since several properties of germanium (Ge) are quite similar to Si, Ge-doped BIT-based thin films are expected to exhibit excellent properties with a good surface morphology.

On the other hand, the chemical solution deposition (CSD) process using metal–organic compounds is useful for the precise control of the chemical composition of desired thin films with reducing the equipment costs. This paper focuses on the processing of (Bi$_{3.25}$La$_{0.75}$)(Ti$_{2.9}$Ge$_{0.1}$)O$_{12}$ (BLTG) thin films through the CSD method using metal–organic precursor solutions. The effects of Ge doping into (Bi, La)$_4$Ti$_3$O$_{12}$ on the crystallization of precursor films and the surface morphol-

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ogy of crystallized films were investigated. The ferroelectric properties were also evaluated.

2. Experimental procedures

$Bi(O^tC_5O_{11})_3$, $Ti(O^iC_3H_7)_4$, $Ge(OC_2H_5)_4$ (Kojundo Chemical, Japan) and $La(CH_3COO)_3{\cdot}3/2H_2O$ (Mitsuwa Chemical, Japan) were used as starting materials for the preparation of (Bi, La)$_4$(Ti, Ge)$_3O_{12}$ precursor solutions. $La(CH_3COO)_3{\cdot}3/2H_2O$ was heated at 110 °C under vacuum for 4 h, yielding anhydrous $La(CH_3COO)_3$. 2-Methoxyethanol as a solvent was dried over a molecular sieve and distilled prior to use. The desired amounts of $Bi(O^tC_5O_{11})_3$, $Ti(O^iC_3H_7)_4$, dehydrated $La(CH_3COO)_3$ and $Ge(OC_2H_5)_4$ corresponding to a $Bi_{3.35}La_{0.75}Ti_{2.9}Ge_{0.1}O_{12}$ (BLTG) composition (with 3% of excess Bi) were dissolved in absolute 2-methoxyethanol, and acetylacetone was then added to the solution as a stabilizing agent. The molar ratio of acetylacetone to BLTG precursor was set at 6. Since the starting materials are extremely sensitive to moisture, the entire procedure was carried out in a dry N_2 atmosphere. The solution was refluxed for 18 h, yielding a homogeneous solution. The precursor solutions were concentrated to approximately 0.1 M by the removal of the solvent by vacuum evaporation.

Precursor films were prepared using the BLTG precursor solutions by spin-coating onto Pt (200 nm)/TiO_x (50 nm)/SiO_2/Si substrates. As-deposited precursor films were dried on a hot plate at 150 °C for 5 min, and then calcined at 500 °C for 10 min in an O_2 flow followed by crystallization at 700 °C for 30 min at a rate of 150 °C/min using rapid thermal annealing (RTA) in an O_2 flow. The thickness of BLTG films was adjusted to be approximately 200 nm by repeating the coating/calcining cycle.

Powder sample was also prepared from the precursor solution by the removal of the solvent to study the crystallization of the precursor. The precursor powder was heat-treated at 800 °C in an O_2 flow for 1 h.

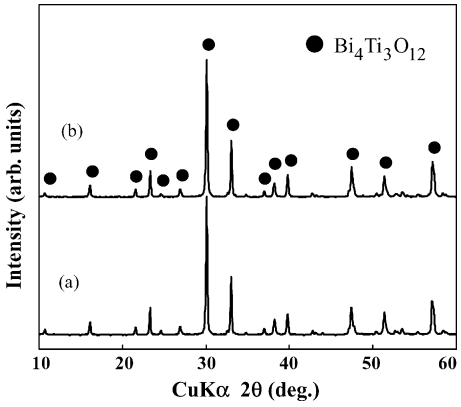

Fig. 1. XRD patterns of: (a) $Bi_{3.35}La_{0.75}Ti_3O_{12}$ (BLT) and (b) $Bi_{3.35}La_{0.75}Ti_{2.9}Ge_{0.1}O_{12}$ (BLTG) powders crystallized at 800 °C.

The crystallographic phases of the powders and the films on substrates were characterized by X-ray diffraction (XRD) analysis using Cu Kα radiation with a monochromator and by Raman microprobe spectroscopy. The surface morphology of the synthesized films was observed using an atomic force microscope (AFM). After film deposition, platinum top electrodes were deposited onto the surface of the films by rf sputtering for electrical measurement, followed by annealing at the crystallization temperature for 30 min. The ferroelectric properties of the films were evaluated using a ferroelectric test system at 100 Hz and room temperature.

3. Results and discussion

3.1. Crystallization of precursor powders and thin films

In this study, the amounts of La for the Bi site of (Bi, La)$_4$(Ti, Ge)$_3O_{12}$ and excess Bi were set at the same values as those in the previous work.[3] The Ge amount of BLTG was determined based upon the most effective amount for (Bi, Nd)$_4$(Ti, Ge)$_3O_{12}$ thin films reported by the authors.[7] The crystallization of $Bi_{3.35}La_{0.75}Ti_{2.9}Ge_{0.1}O_{12}$ precursor powder was investigated prior to the fabrication of ferroelectric Bi-layered perovskite BLTG films. Fig. 1 illustrates XRD patterns of $Bi_{3.35}La_{0.75}Ti_3O_{12}$ (BLT) and BLTG precursor powders after heat treatment at 800 °C. In order to clarify the effect of Ge doping in the $Bi_4Ti_3O_{12}$ structure on the crystallographic phase of resultant powders, the crystallization temperature was selected to be 800 °C. The BLT and BLTG precursor powder crystallized in the single-phase BIT, because no diffraction corresponding to the second phase was observed. Further investigation for the crystallographic phase of BLTG powders was performed by Raman spectroscopy. Fig. 2 shows Raman spectra of BLT and BLTG powders heat-treated at 800 °C. The Raman spectrum of BLTG was consistent with that of BLT. The characteristic Raman scatterings of BLT were assigned to the reported modes[8] from A to D as shown in Fig. 2. No scattering of Bi–Ge–O compound, such as $Bi_4Ge_3O_{12}$[9] was observed for the BNTG powder shown in Fig. 2b. It turned out from Figs. 1 and 2 that BLTG precursor powder was

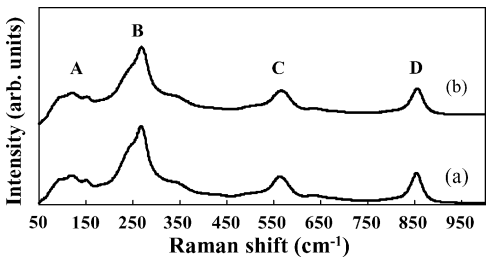

Fig. 2. Raman spectra of crystalline: (a) BLT and (b) BLTG powders prepared at 800 °C. (A) Vibration of Bi (A site)-O bonds; (B) TiO_6 stretching and vibration modes; (C) vibration in a pseudo-perovskite layer; and (D) vibration of Bi (A site)-O bonds.

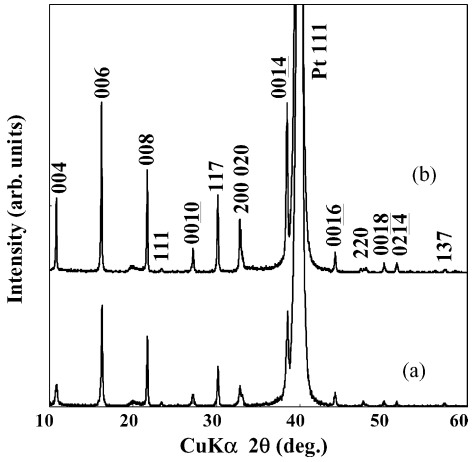

Fig. 3. XRD profiles of: (a) $Bi_{3.35}La_{0.75}Ti_3O_{12}$ (BLT) and (b) $Bi_{3.35}La_{0.75}Ti_{2.9}Ge_{0.1}O_{12}$ (BLTG) thin films on $Pt/TiO_x/SiO_2/Si$ substrates crystallized at 700 °C.

judged to crystallize in the BIT structure of single-phase BLT.

Fig. 3 illustrates the XRD profiles of BLT and BLTG thin films prepared at 700 °C on $Pt/TiO_x/SiO_2/Si$ substrates. These films crystallized into the BIT single phase and exhibited a random orientation with strong 00*l* reflections, because no change in diffractions with Ge doping was observed, as shown in Fig. 3a and b. The reason why these films crystallized with 0 0 *l* preferred orientation may be explained by the relation of the atomic alignment between *c*-plane of BLT and Pt(1 1 1) as reported by Yamada et al.[5] These films were also found to exhibit the same Raman spectra as powders shown in Fig. 2.

3.2. Surface morphology of BLTG thin films

Fig. 4 shows AFM surface images of BLT and BLTG thin films prepared at 700 °C on $Pt/TiO_x/SiO_2/Si$ substrates. BLT thin films prepared at 700 °C consisted of large grains as shown in Fig. 4a. The mean roughness values of BLT thin films prepared at 700 °C were about 20 nm. On the other hand, BLTG thin films showed a good surface morphology. The mean roughness values of BLTG thin films prepared at 700 °C measured to be below 10 nm. Also, the grain size and shape of BLTG thin films were relatively uniform compared with those of nondoped BLT thin films. As can be seen from Fig. 4, the nucleation and growth process in the BLTG thin film during heating could be optimized by doping of Ge for the BLT. This finding is important in fabricating thinner ferroelectric layers for thin film devices with low working voltages.

3.3. Ferroelectric properties of BLTG thin films

Fig. 5 shows P–E hysteresis loops of the BLT and BLTG thin films crystallized at 700 °C. These films are approximately 200 nm thick. P–E hysteresis measurements were performed at an applied voltage of 5 V and a frequency of 100 Hz. The remanent polarization and coercive field of BLT

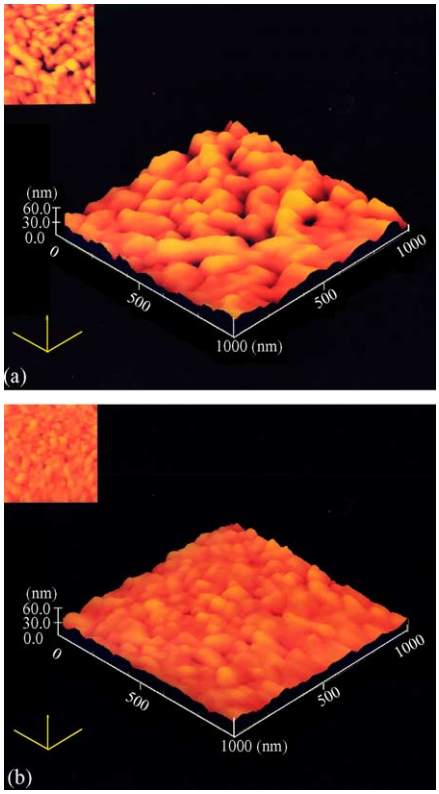

Fig. 4. AFM images of the surfaces of: (a) BLT and (b) BLTG thin films on $Pt/TiO_x/SiO_2/Si$ substrates prepared at 700 °C.

thin films prepared at 700 °C were 13 μC/cm^2 and 80 kV/cm, respectively. On the other hand, BLTG thin films exhibited a little lower P_r value of 12 μC/cm^2 with a lower E_c of 66 kV/cm. At lower crystallization temperature of 650 °C, the P_r of BLTG thin films was 12 μC/cm^2, which higher than that of BLT thin films (9.0 μC/cm^2) fabricated by the authors.[3] The P_r does not decrease in Ge-doped BLT films, even when the crystallization temperature is lowered by 50 °C. This tendency is consistent with Ge-doped $(Bi, Nd)_4Ti_3O_{12}$ thin films.[7] The lower P_r value of BLT thin films at lower tem-

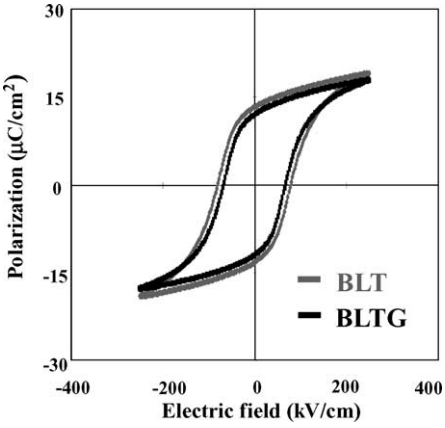

Fig. 5. P–E hysteresis loops of BLT and BLTG thin films on $Pt/TiO_x/SiO_2/Si$ substrates prepared at 700 °C.

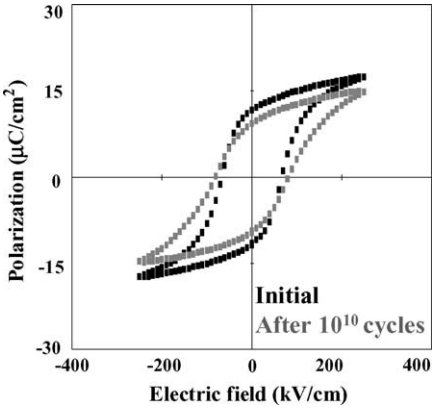

Fig. 6. P–E hysteresis loops of BLTG thin film on $Pt/TiO_x/SiO_2/Si$ substrate prepared at 700 °C before and after fatigue measurement of 10^{10} switching cycles at a frequency of 1 MHz.

peratures might be due to the inhomogeneous microstructure similar to the case of $(Bi, Nd)_4Ti_3O_{12}$ films.[7] On the other hand, BLTG thin films at 700 °C had dense and homogeneous and smooth surface morphologies (Fig. 4b). The surface morphology and ferroelectric properties will be improved by the further control of synthesis conditions such as optimization of the Ge content in BLTG, particularly for the case of thinner films prepared at lower temperatures.

3.4. Fatigue properties of BLTG thin films

Fig. 6 shows P–E hysteresis loops of BLTG thin film prepared at 700 °C before and after 10^{10} switching cycles at a frequency of 1 MHz under an applied voltage of 5 V. The P_r values of the BLTG thin film decreased by about 15% after the fatigue measurement (Fig. 6b). The fatigue of the BLTG thin film was found to begin at around 10^8 cycles. BLT thin films prepared at 700 °C also exhibited a similar fatigue endurance to the BLTG film shown in Fig. 6. The fatigue phenomena of the current films could be improved by V doping with higher valence to eliminate the defects in the films such as oxygen vacancy as in the case for the $(Bi, Nd)_4Ti_3O_{12}$ thin films.[10]

4. Conclusions

Ferroelectric Ge-doped $(Bi, La)_4Ti_3O_{12}$ thin films were successfully synthesized from metal–organic precursor solutions, and their crystallographic phase, crystal orientation, microstructure and ferroelectric properties were examined. $Bi_{3.35}La_{0.75}Ti_{2.9}Ge_{0.1}O_{12}$ precursor films on platinized silicon substrates crystallized into the $Bi_4Ti_3O_{12}$ single phase at 700 °C with $00l$ preferred orientation. The Ge doping into $Bi_{3.35}La_{0.75}Ti_3O_{12}$ was found to improve markedly the surface morphologies of resultant films. Ge-doped $Bi_{3.25}La_{0.75}Ti_3O_{12}$ thin films exhibited a well-saturated P–E hysteresis loop with a P_r of 12 μC/cm² and a E_c of 66 kV/cm at an applied voltage of 5 V. Ge-doped $(Bi, La)_4Ti_3O_{12}$ thin films developed in this study have a potential for application in the ferroelectric layer of FeRAM devices with high-density and low working voltages.

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