研究

Fabrication and Properties of $(\text{Bi},\text{La})_4\text{Ti}_3\text{O}_{12}$ Thin Films through Metal-Organic Compounds

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SYNOPSIS

$(\text{Bi},\text{La})_4\text{Ti}_3\text{O}_{12}$ thin films of Bi-layered perovskite structure were fabricated on $\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$ substrates by chemical solution deposition (CSD) method. The crystallization and microstructure of the $(\text{Bi},\text{La})_4\text{Ti}_3\text{O}_{12}$ thin films markedly depended upon the kind of used La-sources when the precursor solutions were prepared. Synthesized $\text{Bi}_{3.35}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ (BLT) thin films from the precursor solution using a $\text{La}(\text{O}^i\text{Pr})_3$ as a starting material revealed (00 l) preferred orientation and anisotropic grain growth. On the other hand, BLT thin films using a $\text{La}(\text{OAc})_3$ as a La-source showed random orientation with a strong (117) reflection and homogeneous microstructure. This is due to the difference in the pyrolysis and crystallization behaviors of the precursor films. The BLT thin films exhibited the well-saturated ferroelectric P-E hysteresis loops. The BLT thin film prepared from a La-acetate showed the Pr value of $15.6\ \mu\text{C}/\text{cm}^2$, which was higher than that of the BLT thin films from a La-alkoxide.

KEY WORDS

$(\text{Bi},\text{La})_4\text{Ti}_3\text{O}_{12}$, thin film, lanthanum source, chemical solution deposition, ferroelectric properties

1 Introduction

Ferroelectric thin films have been receiving great attention for various applications, such as ferroelectric random access memories (FeRAMs). FeRAMs are extremely attractive memories because of their nonvolatility, lower working voltage and higher access speed¹. Ferroelectric thin films for FeRAMs are required to have excellent ferroelectric properties, such as large remanent polarization (Pr) and fatigue-free properties.

As candidate materials for FeRAMs, $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) and $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) thin films have been studied extensively^{1,2}. Although PZT thin films have many advantages such as large remanent polarization, PZT thin films on Pt electrodes are known to show ferroelectric fatigue². In addition, PZT thin films contain a toxic and volatile element (Pb). Although SBT thin films have excellent fatigue-free properties², SBT films easily crystallize to an undesirable crystallographic phase during the crystallization process. Also, the crystallization temperature of SBT is not sufficiently low for fabrication on Si substrates.

Among other candidates of ferroelectric materials, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) attracts significant attention. Similar to SBT, BIT has a layered perovskite structure consisting of

triple TiO_6 octahedra in perovskite-like layers separated by Bi_2O_2 layers. Although BIT has a large crystallographic anisotropy, BIT exhibits a large remanent polarization and high Curie temperature. Furthermore, BIT thin films are known to crystallize at a lower temperature compared to SBT thin films. Substitution of rare earth ion (such as La^{3+}) for Bi site, especially in the perovskite block of BIT structure, is known to be effective in improving its properties³⁻⁸. This result can be explained by the fact that the stabilization of unstable Bi^{3+} ion in the perovskite block of BIT structure was enhanced by the substitution of nonvolatile rare earth ion³.

On the other hand, a chemical solution deposition (CSD) method is suitable for the fabrication of ferroelectric thin films, because this process has several advantages over the other fabrication methods, such as ease of precise control of composition, high purity, good homogeneity, low processing temperature and lower equipment cost^{4,6-10}. In the CSD process, the fabrication of high-quality films depends strongly upon the preparation of an appropriate precursor solution as well as upon the crystallization condition to the desired crystallographic phase.

In this study, the fabrication of $(\text{Bi},\text{La})_4\text{Ti}_3\text{O}_{12}$ thin films on $\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$ substrates by the CSD method using

two types of metallo-organic precursor solutions was performed. The pyrolysis behavior of the precursor and crystallization of the precursor films were examined. The ferroelectric properties and microstructures of synthesized $(\text{Bi,L a})_4\text{Ti}_3\text{O}_{12}$ films were also evaluated.

2 Experimental procedure

$\text{Bi}(\text{O}^i\text{Am})_3$, $\text{Ti}(\text{O}^i\text{Pr})_4$, $\text{La}(\text{O}^i\text{Pr})_3$ [Kojundo Chemical, Japan] and $\text{La}(\text{OAc})_3 \cdot \text{H}_2\text{O}$ [Mitsuwa Chemical, Japan] were selected as starting materials for preparing $(\text{Bi,L a})_4\text{Ti}_3\text{O}_{12}$ precursor solutions. $\text{La}(\text{OAc})_3 \cdot \text{H}_2\text{O}$ were dehydrated at 110°C for 4 h under vacuum yielding anhydrous $\text{La}(\text{OAc})_3$. 2-Methoxyethanol was dried over a molecular sieve and distilled prior to use. Since the starting metal-organic compounds are extremely sensitive to moisture, the entire procedure was carried out in a dry N_2 atmosphere. The required amounts of $\text{Ti}(\text{O}^i\text{Pr})_4$ and $\text{Bi}(\text{O}^i\text{Am})_3$ with 3% Bi excess composition and $\text{La}(\text{O}^i\text{Pr})_3$ or $\text{La}(\text{OAc})_3$ were dissolved in 2-methoxyethanol. The effect of excess Bi on the fabrication of $(\text{Bi,L a})_4\text{Ti}_3\text{O}_{12}$ thin films has been reported by the authors⁶. Acetylacetone was added to the solution as a stabilizing agent. Then, the mixed solution was refluxed for 20 h yielding a 0.1 M homogeneous precursor solution.

Films were fabricated using the precursor solution by spin-coating on $\text{Pt}(200\text{nm})/\text{TiO}_x(50\text{nm})/\text{SiO}_2/\text{Si}$ substrates. As-deposited precursor films were dried on a hot plate at 150°C for 5 min and calcined at 500°C for 10 min in an O_2 flow, and then annealed at temperatures between 600°C and 700°C for 30 min in an O_2 flow by rapid thermal annealing (RTA) at $150^\circ\text{C}/\text{min}$. The thickness of $(\text{Bi,L a})_4\text{Ti}_3\text{O}_{12}$ films was adjusted to be approximately 200 nm by repeating the coating / calcining cycle.

To study the pyrolysis behavior of the metallo-organic precursors, differential thermal analysis and thermogravimetry (DTA-TG) [Rigaku, Tas-300] were conducted in an O_2 atmosphere from room temperature to 700°C with a temperature ramp rate of $10^\circ\text{C}/\text{min}$. The prepared thin films were characterized by X-ray diffraction (XRD) [Rigaku, RAD 2X] analysis using $\text{CuK}\alpha$ radiation by a monochromator. The surface morphology of the thin films was observed using an atomic force microscope (AFM) [Seiko Instruments, SPI 3800HV]. The electrical properties of films were measured using a Pt top electrode deposited by RF sputtering onto the surface of $(\text{Bi,L a})_4\text{Ti}_3\text{O}_{12}$ films followed by annealing at the crystallization temperature for 30 min. The Pt layer of the $\text{Pt}/\text{TiO}_x/\text{SiO}_2/\text{Si}$ substrate was used as a bottom electrode. The ferroelectric properties of films were evaluated using a ferroelectric test

system [Aix ACCT. Inc., TFA-Analyzer 2000] at 100 Hz and room temperature. The current pulse was applied on the film in a vertical direction through the bottom and top electrodes using a microprobe system [Signatone, S-1060].

3 Results and Discussion

3.1 Pyrolysis behavior of $(\text{Bi,L a})_4\text{Ti}_3\text{O}_{12}$ precursors

Homogeneous and stable $(\text{Bi,L a})_4\text{Ti}_3\text{O}_{12}$ precursor solutions were prepared by controlling the reaction of starting metallo-organic compounds in 2-methoxyethanol with a key additive of acetylacetone. The quality of the films prepared by the CSD method was affected by the decomposition and burn-out behaviors of organic species contained in the precursor film during heating. Therefore, the pyrolysis behaviors of two types of $(\text{Bi,L a})_4\text{Ti}_3\text{O}_{12}$ precursors prepared in this study were investigated by DTA-TG analysis. Fig. 1 illustrates DTA-TG curves of (a) BLT precursor prepared from a $\text{La}(\text{O}^i\text{Pr})_3$ and (b) BLT precursor from a $\text{La}(\text{OAc})_3$. The decomposition and burn-out behaviors of organic species of precursors were found to depend upon the kind of starting lanthanum (La) sources. When metal-alkoxide ($\text{La}(\text{O}^i\text{Pr})_3$) was used as a La-source, the precursors decreased in weight gradually with increasing temperature up to 600°C as shown in Fig. 1 (a). In the first stage, remaining solvents are evaporated at around $80 - 130^\circ\text{C}$, and then residual organic species are decomposed between 130°C and 550°C . The exothermic peaks at around $150 - 350^\circ\text{C}$ and $400 - 550^\circ\text{C}$ observed in DTA correspond to the combustion of organic species of precursors. The quite small exothermic peak at $550 - 600^\circ\text{C}$ is due to the crystallization and burn-out of residual organic species. On the other hand, the pyrolysis behavior of precursor formed from a lanthanum acetate ($\text{La}(\text{OAc})_3$) was quite different from those of the former BLT precursor. As shown in Fig. 1 (b), the two sharp exothermic peaks with rapid weight loss were observed at $200 - 270^\circ\text{C}$. In this stage, the decomposition and the burn-out of organics in the precursors occur simultaneously. The broad exothermic peaks followed by a gradual weight loss above 270°C in the BLT precursor are attributed to the combustion of residual organic species. The small exothermic peak at around $500 - 550^\circ\text{C}$ is considered to be due to crystallization. It is noteworthy that little weight loss was detected during crystallization in the BLT precursor above 500°C . The optimization of the molecular design of precursors is considered to be a key for the synthesis of high-quality $(\text{Bi,L a})_4\text{Ti}_3\text{O}_{12}$ ferroelectric films. The detail structures of these two types of precursors were now under investigation using NMR and IR spectroscopic analyses.

Fig.1 DTA-TG curves of (a) BLT (La-source: $\text{La}(\text{O}^i\text{Pr})_3$) and (b) BLT (La-source: $\text{La}(\text{OAc})_3$) precursors [Endo.: endothermic, Exo.: exothermic].

3.2 Synthesis of $(\text{Bi,L a})_4\text{Ti}_3\text{O}_{12}$ thin films

Based upon the data of pyrolysis behavior of precursors, BLT thin films were fabricated on $\text{Pt}/\text{TiO}_x/\text{SiO}_2/\text{Si}$ substrates. BLT thin films were found to crystallize into Bi-layered perovskite single-phase above 600°C . As the annealing temperature increased, the full-width at half maximum of each diffraction gradually decreased. This result indicates that the films increased in crystallinity. In order to clarify the effect of the difference in the precursor

Fig.2 XRD profiles of (a) BLT (La-alkoxide) and (b) BLT (La-acetate) thin films prepared at 700°C on $\text{Pt}/\text{TiO}_x/\text{SiO}_2/\text{Si}$ substrates.

solution on the microstructure and ferroelectric properties of resultant films, the full crystallization temperature was selected to be 700°C . Fig. 2 illustrates the XRD patterns of BLT thin films heat-treated at 700°C . The thin films showed different orientations with high crystallinity. BLT thin films prepared from the precursor solution using a $\text{La}(\text{O}^i\text{Pr})_3$ exhibited strong (00 l) diffractions, whereas BLT thin films from a $\text{La}(\text{OAc})_3$ revealed random orientation with a strong (117) reflection. The ferroelectricity of BLT films with (117) preferred orientation is expected to be larger than that of (00 l) oriented BLT, because the spontaneous

polarization for these materials along the a -axis is known to be much larger than that along the c -axis.

Bi-layered perovskite materials, such as BIT, thin films tend to show $00l$ preferred orientation on Pt(111). However, when the precursor in solution was molecular designed, the difference in the pyrolysis and crystallization behaviors resulted in the change in film orientation. La has an ionic radius (136 pm) which was close to that of Bi ion. Thus, BLT ($\text{La}(\text{O}^i\text{Pr})_3$) thin film showed $(00l)$ preferred orientation with anisotropic grain growth as described in the next section. Since the elimination of organic species in precursor films was accomplished at higher temperature region, the initiation of crystal nucleation may be preferred to occur gradually on the Pt(111) surface. On the other hand, in the case of BLT ($\text{La}(\text{OAc})_3$), the orientation of films changed because of the occurrence of random crystal nucleation in the film with decreasing the decomposition and combustion temperature of precursor. Thus, BLT thin films with relatively low temperature pyrolysis of precursor showed random orientation with enhanced (117) reflection.

3.3 Surface morphology of synthesized films

Fig. 3 shows AFM images of (a) BLT thin film prepared from the precursor solution using a La-alkoxide and (b) BLT thin films from a La-acetate synthesized at 700°C . BLT thin films (La-alkoxide) consisted of rod-like and large anisotropic grains [Fig. 3 (a)]. This microstructure of the films originates from the $(00l)$ preferred orientation. The microstructure of BLT films reflected the crystal orientation. BLT films (La-acetate) were comprised of

closely packed grains as shown in Fig. 3 (b), and these films showed random orientation with strong (117) reflection. In addition, the BLT thin film from the precursor solution using a La-acetate had a homogeneous and smooth surface. The microstructure of the films might be attributable to the kind of starting materials. The two types of $(\text{Bi,Lu})_4\text{Ti}_3\text{O}_{12}$ precursors showed different decomposition and burn-out behaviors of organics, which depended upon the starting La-sources as described in the previous section. Furthermore, the BLT precursor films (La-acetate) underwent the removal of organics at lower temperature resulting in films with dense microstructure.

3.4 Ferroelectric properties of synthesized films

P-E hysteresis measurement was also performed for the synthesized $(\text{Bi,Lu})_4\text{Ti}_3\text{O}_{12}$ thin films crystallized at 700°C on Pt/TiO₂/SiO₂/Si substrates. Fig. 4 shows P-E hysteresis loops of 200-nm-thick $(\text{Bi,Lu})_4\text{Ti}_3\text{O}_{12}$ thin films from the different precursor solutions measured at room temperature. These thin films showed typical ferroelectric P-E hysteresis loops at applied voltages of 5 V. The remanent polarization (P_r) of the films was different depending upon the using precursor solutions. Among them, BLT thin film from the precursor solution using a La-acetate revealed superior P_r and the degree of squareness of hysteresis loops to the BLT film from a La-alkoxide. The BLT thin film (Fig. 4 (b)) showed P_r of $15.6 \mu\text{C}/\text{cm}^2$, which was higher than that of BLT thin film (Fig. 4 (a)) of $9.1 \mu\text{C}/\text{cm}^2$ at the applied voltage of 5 V. This can be explained by the crystal orientation of the films. In this case, the orientation of films depended upon the using precursor solutions. Since the polar axis of

Fig. 3 AFM images of (a) BLT (La-alkoxide) and (b) BLT (La-acetate) thin films prepared at 700°C on Pt/TiO₂/SiO₂/Si substrates.

Fig. 4 P-E hysteresis loops of (a) BLT (La-alkoxide) and (b) BLT (La-acetate) thin films prepared at 700°C on Pt/TiO₂/SiO₂/Si substrates [Thickness: 200 nm, Applied voltage: 5 V].

these materials is almost along the *a*-axis, ferroelectricity of BLT film with random orientation with a strong (117) reflection was superior to BLT with (00*l*) preferred orientation. Furthermore, homogeneous and dense microstructure was also considered to be attributable to the superior ferroelectricity of the BLT films.

Ferroelectric fatigue behavior was also characterized for the (Bi,La)₄Ti₃O₁₂ thin films. Fig. 5 shows P-E hysteresis loops of the two types of BLT thin films prepared at 700 °C before and after 10¹⁰ switching cycles at a frequency of 1 MHz under an applied voltage of 5 V. The P_r values of the BLT thin film (La-acetate) decreased by about 15% after the fatigue measurement (Fig. 5 (b)). The fatigue of the BLT thin film was found to begin at around 10⁸ cycles. BLT thin films (La-alkoxide) prepared at 700 °C did not exhibit a fatigue phenomenon as shown in Fig. 5 (a). The fatigue phenomenon of the current film in Fig. 5 (b) 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)₄Ti₃O₁₂ thin films⁹.

4 Conclusions

Ferroelectric lanthanum-doped Bi₄Ti₃O₁₂ (BLT) thin films were successfully prepared by using metallo-organic precursor solutions. The pyrolysis behaviors of (Bi,La)₄Ti₃O₁₂ precursors depended upon the starting lanthanum sources, which strongly affected the crystal orientation and surface morphology of synthesized films. Single-phase (Bi,La)₄Ti₃O₁₂ films of Bi-layered perovskite were crystallized on Pt/TiO₂/SiO₂/Si substrates. BLT thin films prepared from the precursor solution using a La(OⁱPr)₃ exhibited strong (00*l*) peaks, while BLT thin films from a La(OAc)₃ had (117) preferred orientation. BLT thin film (La-acetate) showed the homogeneous microstructure and the better ferroelectric properties with large P_r. Fatigue properties of the BLT films also depend upon the starting La-sources. The process of the formation of precursor in solution is found to be one of the most important keys for controlling the properties of resultant (Bi,La)₄Ti₃O₁₂ thin films.

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Fig.5 P-E hysteresis loops of (a) BLT (La-alkoxide) and (b) BLT (La-acetate) thin films prepared at 700 °C on Pt/TiO₂/SiO₂/Si substrates before and after 10¹⁰ switching cycles at 1 MHz [Thickness: 200 nm, Applied voltage: 5 V].

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