# Preparation and Properties of $Bi_{4-x}La_xTi_3O_{12}$ Ferroelectric Thin Films Using Excimer UV Irradiation

Takashi HAYASHI, Daichi TOGAWA, Mio YAMADA<sup>1</sup>, Wataru SAKAMOTO<sup>1</sup> and Shin-ichi HIRANO<sup>1</sup>

Department of Materials Science, Shonan Institute of Technology, 1-1-25 Tsujido-Nishikaigan, Fujisawa, Kanagawa 251-8511, Japan

<sup>1</sup>Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

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Low-temperature processing of  $Bi_{4-x}La_xTi_3O_{12}$  (BLT) thin films was investigated by chemical solution deposition using an excimer UV irradiation, and their ferroelectric properties, crystallinity and microstructure were characterized. BLT thin films were prepared on Pt(200 nm)/TiO<sub>2</sub>(50 nm)/SiO<sub>2</sub>/Si substrates by a spin-coating technique from alkoxide precursor solutions. The excimer UV irradiation onto as-deposited BLT thin films was highly effective in removing organic species of the gel films, leading to the decrease of the crystallization temperature and an increase of the crystallinity. The UV-processed BLT films started to crystallize at 550°C and showed a high crystallinity and a high (117) preferred orientation for 600°C-annealed films. BLT thin films prepared at 600°C showed a homogeneous and dense microstructure with grain sizes of 200–300 nm. The excimer UV irradiation onto as-crystallized BLT thin films was also effective in improving the ferroelectric properties of the thin films. Bi<sub>3.35</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> thin films prepared at 600°C using excimer UV irradiation showed a well-saturated P-E hysteresis loop with a  $P_r$  of 9.8  $\mu$ C/cm<sup>2</sup> and  $E_c$  of 78 kV/cm. Moreover, the Bi<sub>3.35</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> thin films exhibited good fatigue endurance up to 10<sup>10</sup> switching cycles. [DOI: 10.1143/JJAP.41.6814]

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#### 1. Introduction

Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> (BIT) is an attractive ferroelectric material for several applications such as nonvolatile memories because of its large remanent polarization ( $P_r$ ), small coercive field ( $E_c$ ), and high Curie temperature. Compared with SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> and its related materials, BIT thin films are known to crystallize at lower temperatures with a high crystallinity. However, BIT contains unstable Bi ions which are easily evaporated during the heating process. This volatility of Bi ions affects the ferroelectric and fatigue characteristics. Bi<sup>3+</sup> ions in the BIT structure can be substituted by ions such as La<sup>3+</sup>, Nd<sup>3+</sup> and V<sup>5+</sup> for the improvement of its properties.<sup>1-3)</sup> Among them, Bi<sub>4-x</sub>La<sub>x</sub>Ti<sub>3</sub>O<sub>12</sub> (BLT) has been intensively investigated as a promising ferroelectric material for nonvolatile randomaccess memory because of its fatigue-free property and lowvoltage operation, compared to those of Pb(Zr, Ti)O<sub>3</sub> (PZT).

BLT thin films are typically deposited by a spin-coating technique using a chemical solution process and crystallized by furnace annealing or rapid thermal annealing (RTA) at  $650-750^{\circ}$ C.

Regarding the preparation of BLT thin films by the sol-gel method, it has been reported<sup>4,5)</sup> that processing factors such as the control of Bi-excess composition as well as annealing temperature and time strongly affect the crystallinity, the orientation, the crystalline structure and ferroelectric properties of BLT films. Moreover, the high-temperature annealing process is not suitable for high-density memory devices, because the silicon semiconductor is often seriously damaged during the annealing process. Recently, in order to lower the processing temperature, a new process for film preparation using an excimer laser or Hg UV lamp accompanying a photolysis reaction of organic species and crystallization has been actively investigated.<sup>6–8)</sup>

In this work, we focused on the low-temperature processing of BLT thin films by chemical solution deposition using an excimer UV irradiation, and investigated their ferroelectric properties, crystallinity and microstructures.

#### 2. Experimental Procedures

Figure 1 shows the procedure for the preparation of a BLT precursor solution by chemical solution deposition. Bi(O<sup>t</sup>C<sub>5</sub>H<sub>11</sub>)<sub>3</sub>, La(O<sup>i</sup>C<sub>3</sub>H<sub>7</sub>)<sub>3</sub> and Ti(O<sup>i</sup>C<sub>3</sub>H<sub>7</sub>)<sub>4</sub> were used as starting materials. All procedures were conducted in a dry N<sub>2</sub> atmosphere. The desired amounts of Bi(O<sup>t</sup>C<sub>5</sub>H<sub>11</sub>)<sub>3</sub>, La(O<sup>i</sup>C<sub>3</sub>H<sub>7</sub>)<sub>3</sub> and Ti(O<sup>i</sup>C<sub>3</sub>H<sub>7</sub>)<sub>4</sub> corresponding to Bi<sub>3.25</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> and Bi<sub>3.35</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> compositions were dissolved in absolute 2-methoxyethanol, and subsequently acetylacetone was added to the solution as a stabilizing agent. The solution was refluxed for 18 h and condensed to approximately 0.1 mol/l. The homogeneity and stability



Fig. 1. Procedure for preparation of BLT coating solution by chemical solution deposition.

of the coating solution was significantly improved by the addition of acetylacetone. BLT thin films were prepared on Pt(200 nm)/TiO<sub>2</sub>(50 nm)/SiO<sub>2</sub>/Si substrates by a spin-coating technique from alkoxide precursor solutions of BLT. Asdeposited precursor films were dried at 150°C for 5 min, and then were irradiated using an Xe excimer UV lamp (172 nm) at 300°C for 30 min in O<sub>2</sub> atmosphere. The excimer UV-processed films were calcined at 500°C for 10 min in an O<sub>2</sub> atmosphere, and then were annealed at 550–700°C for 30 min in an O<sub>2</sub> atmosphere by RTA. The film thickness of BLT was adjusted to approximately 200 nm by repeating the coating/calcining cycles four times.

Optical properties of BLT precursor solution irradiated using a UV lamp (Ushio Electrics, UXM-501MD: 210– 580 nm) were evaluated using a UV-V spectrometer. The crystallinity and crystalline phase of BLT thin films were examined by X-ray diffraction (XRD). The surface morphology of the thin films was observed using an atomic force microscope (AFM) and a field-emission scanning electron microscope (FE-SEM). The chemical species in the excimer UVprocessed thin films were analyzed by a Fourier transform infrared spectrometer (FT-IR).

Prior to electrical measurements, circular Pt electrodes of 0.20 mm diameter were deposited by rf sputtering onto the surface of the films, which was followed by annealing at crystallization temperatures for 5 min. The ferroelectric properties of the films were also evaluated by means of a ferroelectric test system (TFA-ANALYZER 2000, AixACCT. Inc.) at 100 Hz. The applied voltage was 1–15 V.

### 3. Results and Discussion

#### 3.1 Optical properties of BLT precursor solutions

In order to investigate the change of **BLT** precursor solution after UV irradiation, optical properties of the BLT precursor solution were evaluated using a UV-V spectrometer. Figure 2 shows the UV-V spectra of BLT precursor solutions irradiated using a UV lamp at room temperature for 30-60 min in N<sub>2</sub>. At the stage of UV-nonirradiation, the BLT precursor solution showed a high transmittance over a wide wavelength



Fig. 2. UV-V spectra of BLT precursor solutions with acacH (a) before UV irradiation and after irradiation for 15 min (b) and for 30 min (c).

region, as shown in Fig. 2(a). On the other hand, in the UVirradiation time of 30 to 60 min, the transmittance decreased from approximately 65 to 40% at 500 nm, as shown in Fig. 2(b) and (c). This may be due to the dissociation of organic species, followed by the generation of organic radical and reduced Ti ion in the BLT precursor solution by the photolysis reaction. Hunt and Winter<sup>9)</sup> have reported the photoinduced reduction of Ti(IV) to Ti(III) alkoxides by sunlight. Therefore, Ti(IV) in the BLT precursor is reduced to Ti(III) by UV light. Due to the change in optical property of the BLT precursor solutions, UV irradiation is found to influence the chemical bonding between metal ion and organic ligands. Hence, in this work, excimer UV light (172 nm) with a high energy was employed to remove the organic species smoothly from the precursor films during the fabrication process of BLT films.

# 3.2 FT-IR spectra of excimer UV-irradiated BLT precursor thin films

Figure 3 shows FT-IR spectra of as-deposited BLT thin films irradiated using an excimer UV lamp at 300°C for 30 min in O<sub>2</sub> atmosphere. The absorbance peak assigned to stretching vibrations of C–H groups was observed at approximately 2900 cm<sup>-1</sup> for the samples calcined at 300°C without irradiation. However, at the excimer irradiation temperature of 300°C in O<sub>2</sub> atmosphere, the organic species in precursor gel films were completely removed during the irradiation time of 30 min. This may be attributable to the easier decomposition of organic groups by an oxidation reaction in O<sub>2</sub> atmosphere as well as the bond cleavage by the photolysis reaction.

# 3.3 Crystallization of BLT thin films

The crystallinity of BLT films was examined by changing the composition of the films. BLT thin films with Bi-excess,  $Bi_{3.35}La_{0.75}Ti_3O_{12}$ , exhibited a higher crystallinity than those with a stoichiometric composition of  $Bi_{3.25}La_{0.75}Ti_3O_{12}$ , as shown in Fig. 4.

Figure 5 shows XRD patterns of  $Bi_{3.35}La_{0.75}Ti_3O_{12}$  thin films without and with excimer UV irradiation at 300°C for 30 min in an O<sub>2</sub> atmosphere, followed by RTA at 550 and 600°C for 30 min. As-deposited thin films without excimer UV-irradiation crystallized at 550°C and exhibited random orientation with a weak (00*l*) diffraction peak, as shown in Fig. 5(a). On the other hand, excimer UV-processed thin films



Fig. 3. FT-IR spectra of as-deposited BLT gel thin films without and with excimer UV irradiation at 300°C for 30 min in O<sub>2</sub> atmosphere.



Fig. 4. XRD patterns of  $Bi_{3.25}La_{0.75}Ti_3O_{12}$  (a) and  $Bi_{3.35}La_{0.75}Ti_3O_{12}$  (b) thin films prepared at 700°C using excimer UV irradiation.

crystallized at 550°C, and the films crystallized at 600°C showed a high crystallinity and a high (117) preferred orientation, as shown in Fig. 5(b). The excimer UV-irradiation in O<sub>2</sub> atmosphere was very effective for the increase of the crystallinity and the promotion of (117) preferred orientation of BLT films. This may be attributable to the promotion of the decomposition of residual organic species with the formation of O<sub>3</sub> along with a photolysis reaction. Furthermore, the calcination at 500°C in an O<sub>2</sub> atmosphere was effective in increasing the crystallinity.

#### 3.4 Surface morphology of $Bi_{3.35}La_{0.75}Ti_3O_{12}$ thin films

Figure 6 shows AFM images of the surfaces of Bi<sub>3.35</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> thin films prepared at 550 and 600°C. The thin films prepared at 550°C using the excimer UV irradiation showed a smooth surface microstructure consisting of fine grains of approximately 100 nm in size, which grew to larger grains of 100-200 nm by annealing at 600°C, compared with those without the excimer UV irradiation. The excimer UV irradiation was found to be useful for improving the surface morphology of BLT films.

### 3.5 Ferroelectric properties of BLT thin films

Figure 7 shows P-E hysteresis loops of 700°Cannealed BLT thin films with an excess composition of Bi<sub>3.35</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> and with a stoichiometric composition of  $Bi_{3,25}La_{0,75}Ti_{3}O_{12}$ .  $Bi_{3,35}La_{0,75}Ti_{3}O_{12}$  thin films showed improved ferroelectric properties with a remanent polarization,  $P_{\rm r}$ , of 15.4  $\mu$ C/cm<sup>2</sup> and a coercive electric field,  $E_{\rm c}$ , of 64 kV/cm, compared with those of a stoichiometric composition of  $Bi_{3,25}La_{0,75}Ti_3O_{12}$ .

Figure 8 shows  $P_r$  and  $E_c$  as a function of applied voltage for Bi<sub>3.35</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> thin films prepared at 550°C using excimer UV irradiation. The thin films prepared at 550°C using excimer UV irradiation showed a saturation tendency over 5 V. A well-saturated P-E hysteresis loop was obtained at an applied voltage of 15 V for the thin film prepared at 550°C, which showed  $P_r$  of 4.4  $\mu$ C/cm<sup>2</sup> and  $E_c$  of 72 kV/cm.



 $2\theta / \text{deg.}$ 

40

600°C

550°C

60

50

Fig. 5. XRD patterns of Bi3.35La0.75Ti3O12 thin films using (a) excimer UV nonirradiation, and (b) irradiation at 300°C in O<sub>2</sub> atmosphere.

30

10

20

Figure 9 shows P-E hysteresis loops at an applied voltage of 5V for Bi<sub>3,35</sub>La<sub>0,75</sub>Ti<sub>3</sub>O<sub>12</sub> thin films prepared at 550-700°C without and with excimer UV irradiation. Bi<sub>3.35</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> thin films prepared at 550 and 600°C without excimer UV irradiation exhibited  $P_r$  of 1.0 and 9.2  $\mu$ C/cm<sup>2</sup>, and E<sub>c</sub> of 38 and 75 kV/cm, respectively, as shown in Fig. 9(a). On the other hand, Bi<sub>3,35</sub>La<sub>0,75</sub>Ti<sub>3</sub>O<sub>12</sub> thin films prepared at 550°C using excimer UV irradiation showed  $P_r$  of 2.4  $\mu$ C/cm<sup>2</sup> and  $E_c$  of 44.4 kV/cm. Furthermore, well-saturated P-E hysteresis curves were obtained for Bi<sub>3.35</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> thin films prepared at 600°C using excimer UV irradiation. They showed  $P_r$  of 9.8  $\mu$ C/cm<sup>2</sup> and  $E_c$ of 78 kV/cm, as shown in Fig. 9(b), which are sufficient for ferroelectric memory device applications. The excimer UV irradiation onto as-crystallized BLT thin films was also found



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Fig. 6. AFM images of the surface of 500 and 600°C-annealed  $Bi_{3,35}La_{0.75}Ti_3O_{12}$  thin films: 550°C without excimer UV irradiation (a) and with excimer UV irradiation (b), 600°C without excimer UV irradiation (c) and with excimer UV irradiation (d).



Fig. 7. P-E hysteresis loops of Bi<sub>3.25</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> (a) and Bi<sub>3.35</sub>La<sub>0.75</sub>-Ti<sub>3</sub>O<sub>12</sub> (b) thin films prepared at 700°C.

to be effective in improving the ferroelectric properties of the thin films.

Figure 10 shows the fatigue property of  $Bi_{3.35}La_{0.75}Ti_3O_{12}$  thin films prepared at 600°C using excimer UV irradiation before and after the switching of 10<sup>10</sup> cycles at a frequency of 1 MHz. Similar hysteresis loops were observed before and after the switching, indicating good fatigue endurance.

## 4. Conclusions

BLT thin films were synthesized by chemical solution deposition using excimer UV irradiation, and their microstructure, crystal phase and ferroelectric properties were investigated. Our results are summarized as follows:

1. Ferroelectric BLT thin films were successfully synthesized on  $Pt/TiO_2/SiO_2/Si$  substrates using metal-organic precursor solutions. Homogeneous and stable BLT precursor solutions were prepared by controlling the reaction of starting metal alkoxides in 2-methoxyethanol with a key additive of acetylacetone. 6818 Jpn. J. Appl. Phys. Vol. 41 (2002) Pt. 1, No. 11B



Fig. 8.  $P_{\rm r}$  and  $E_{\rm c}$  as a function of applied voltage for Bi<sub>3.35</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> thin films prepared at 550°C using excimer UV irradiation: (a) Saturation property, (b) P-E hysteresis loop at applied voltage of 15 V.



Switching Cycles

Fig. 10. Fatigue property of Bi<sub>3.35</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> thin films prepared at 600°C using excimer UV irradiation before and after 10<sup>10</sup> switching cycles.

2. The excimer UV irradiation onto as-deposited films at  $300^{\circ}$ C in O<sub>2</sub> atmosphere was very effective in removing the residual organic groups in the gel films and in lowering the crystallization temperature of BLT to 550°C.

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Fig. 9. P-E hysteresis loops of Bi<sub>3.35</sub>La<sub>0.75</sub>Ti<sub>3</sub>O<sub>12</sub> thin films prepared at the temperature of 550-700°C by RTA without (a) and with (b) excimer UV irradiation.

- 3. The use of an excimer UV lamp further resulted in the easy formation of single-phase BLT thin films with a high (117) preferred orientation and with a homogeneous microstructure consisting of fine grains.
- 4. The 600°C-annealed BLT thin films subjected to excimer UV irradiation showed  $P_r$  of 9.8  $\mu$ C/cm<sup>2</sup> and  $E_c$  of 78 kV/cm. Synthesized BLT films with appropriate ferroelectric properties are expected for use in the ferroelectric layers of FeRAM devices.

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