Available online at www.sciencedirect.com
SCIENCE DIRECT

Journal of the European Ceramic Society 24 (2004) 1621–1624
www.elsevier.com/locate/jeurceramsoc

Effects of Bi_2O_3 seeding layer on crystallinity and electrical properties of CSD-derived $Bi_{4-x}La_xTi_3O_{12}$ ferroelectric thin films

Takashi Hayashi[a], Daichi Togawa[a,*], Wataru Sakamoto[b], Shin-ichi Hirano[c]

[a]Department of Materials Science and Engineering, Shonan Institute of Technology, 1-1-25 Tsujido-Nishikaigan, Fujisawa, Kanagawa 251-8511, Japan
[b]Center for Integrated Research in Science and Engineering, Nagoya University, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan
[c]Department of Applied Chemistry, Graduate School of Engineering, Nagoya University Furo-cho, Chikusa-ku, Nagoya, 464-8603, Japan

Abstract

The effects of Bi_2O_3 seeding layer on crystallization temperature, crystallinity and ferroelectric properties of $Bi_{3.35}La_{0.75}Ti_3O_{12}$ (BLT) thin films prepared by chemical solution deposition (CSD) method were investigated. BLT thin films were prepared on $Pt/TiO_x/SiO_2/Si$ substrates with Bi_2O_3 seeding layer by a spin-coating technique from metal alkoxide solutions of BLT precursors. BLT gel thin films were calcined at 500 °C for 10 min using rapid thermal annealing (RTA), and then heated at 600–700 °C for 30 min in an O_2 atmosphere. Bi_2O_3 seeding layer was found to be effective to achieve the low-temperature crystallization up to 600 °C and improve the crystallinity and electrical properties of BLT thin films. 650 °C-annealed BLT thin films with the seeding layer showed a high crystallinity with a strong (117) preferred orientation and a dense microstructure with grain sizes of 200–300 nm. They showed a well-saturated P–E hysteresis loop with a P_r of 5.0 μC/cm² and E_c of 78.8 kV/cm.

Keywords: BLT thin film; Chemical solution deposition; Ferroelectric properties; Seeding layer

1. Introduction

Recently, a significant amount of research and development has focused on $Bi_{4-x}La_xTi_3O_{12}$ (BLT)[1] thin films for nonvolatile memory application because of its fatigue-free property and low-voltage operation, compared with those of $Pb(Zr, Ti)O_3$ (PZT). Furthermore, in general, BLT has been more attractive for their larger ferroelectricity than $SrBi_2Ta_2O_9$ (SBT).[1] BLT thin films are typically deposited by spin-coating technique using a chemical solution process and fabricated at 650–750 °C by furnace annealing or rapid thermal annealing (RTA). However, the high-temperature annealing process is not suitable for high-density memory devices because BLT contains unstable Bi ion which are easily diffused into Pt bottom electrode, resulting in the formation of the secondary phase such as Bi_2Pt[2] and $Bi_4Ti_3O_{12}$ (BIT).[3] Moreover, this volatility of Bi ions accompanied with oxygen vacancies which acts as a space charge does affect the ferroelectric and fatigue characteristics.

For the preparation of BLT thin films by a CSD method, it has been reported[4–6] that processing factors such as the control of Bi-excess composition as well as annealing temperature and time strongly affected the crystallinity, the crystal orientation, the microstructure and ferroelectric properties of BLT films.

In this work, we focused on low-temperature preparation of BLT thin films by a CSD method using Bi_2O_3 seeding layer, and investigated their crystallinity, microstructure and ferroelectric properties.

2. Experimental

$Bi(O^tC_5H_{11})_3$, $La(O^iC_3H_7)_3$ and $Ti(O^iC_3H_7)_4$ were used as starting materials. All procedures were conducted in a dry N_2 atmosphere. The desired amounts of $Bi(O^tC_5H_{11})_3$, $La(O^iC_3H_7)_3$ and $Ti(O^iC_3H_7)_4$ corresponding to $Bi_{3.35}La_{0.75}Ti_3O_{12}$ compositions were dissolved in absolute 2-methoxyethanol, and then 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 of the coating solution was greatly improved by the addition of acetylacetone. BLT thin films were prepared on Pt(200 nm)/Ti (50 nm)/SiO_2/Si and Pt(200 nm)/TiO_x(50 nm)/SiO_2/Si substrates by a spin-coating

* Corresponding author. Tel.: +81-466-30-0224; fax: +81-466-30-0224.

0955-2219/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00395-9

technique from alkoxide precursor solutions of BLT. As-deposited precursor films were dried at 150 °C for 5 min, and then were calcined at 500 °C for 10 min in an O_2 flow, and then were annealed at 600–700 °C for 30 min in an O_2 flow by RTA. The film thickness of BLT was adjusted to approximately 200 nm by repeating the coating/calcining cycles by four times. In the preparation of some of BLT thin films, a bismuth oxide layer was used as a seed which was inserted between the BLT thin film and the substrate. The Bi_2O_3 seeding layer was spin-coated from 0.1 mol/l alkoxide precursor solution of Bi_2O_3 onto the substrates and annealed at 600 °C for 5 min by RTA.

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).

Prior to electrical measurements, circular Pt electrodes of 0.20 mm diameter were deposited by $_r$f sputtering onto the surface of the films, which was followed by annealing at crystallization temperatures for 30 min. The ferroelectric properties of the films were also evaluated with a ferroelectric test system (TFA-Analyzer 2000, AixACCT. Inc.) at 100 Hz. The applied voltage was 5 V.

3. Results and discussion

3.1. Effects of Bi_2O_3 seeding layer on the crystallization of BLT thin films

Fig. 1 shows XRD patterns of BLT thin films on Pt/TiO_x/SiO_2/Si substrates prepared at temperatures of 600–700 °C without and with Bi_2O_3 seeding layers. As-deposited BLT thin films without the seeding layer started to crystallize at 600 °C and exhibited a high crystallinity with random orientation at 650 °C annealing temperature, as shown in Fig. 1(a). On the other hand, BLT thin films using the seeding layer crystallized at a low temperature of 600 °C with a high crystallinity and a strong (117) preferred orientation, as shown in Fig. 1(b).

The insertion of Bi_2O_3 seeding layers between the BLT layer and the substrate was very effective for the decrease of crystallization temperature, the increase of the crystallinity and the promotion of (117) preferred orientation of BLT films.

3.2. Surface morphology of BLT thin films

Fig. 2 shows AFM images of the surfaces of BLT thin films on Pt/TiO_x/SiO_2/Si substrate prepared at 650 °C without and with Bi_2O_3 seeding layer. The BLT thin films prepared at 650 °C without the seeding layer showed a smooth surface microstructure consisting of fine grains of approximately 100–200 nm in size, while those prepared at 650 °C with the seeding layer showed a dense microstructure with larger grains of 200–300 nm. The use of Bi_2O_3 seeding layer was found to be useful to improve the surface morphology of BLT films.

3.3. Ferroelectric properties of BLT thin films

Fig. 3 shows *P–E* hysteresis loops of 700 °C-annealed BLT thin films on two kinds of Pt/Ti/SiO_2/Si and Pt/TiO_x/SiO_2/Si substrates without Bi_2O_3 seeding layer. BLT thin films prepared on Pt/TiO_x/SiO_2/Si substrate showed the improved ferroelectric properties with a

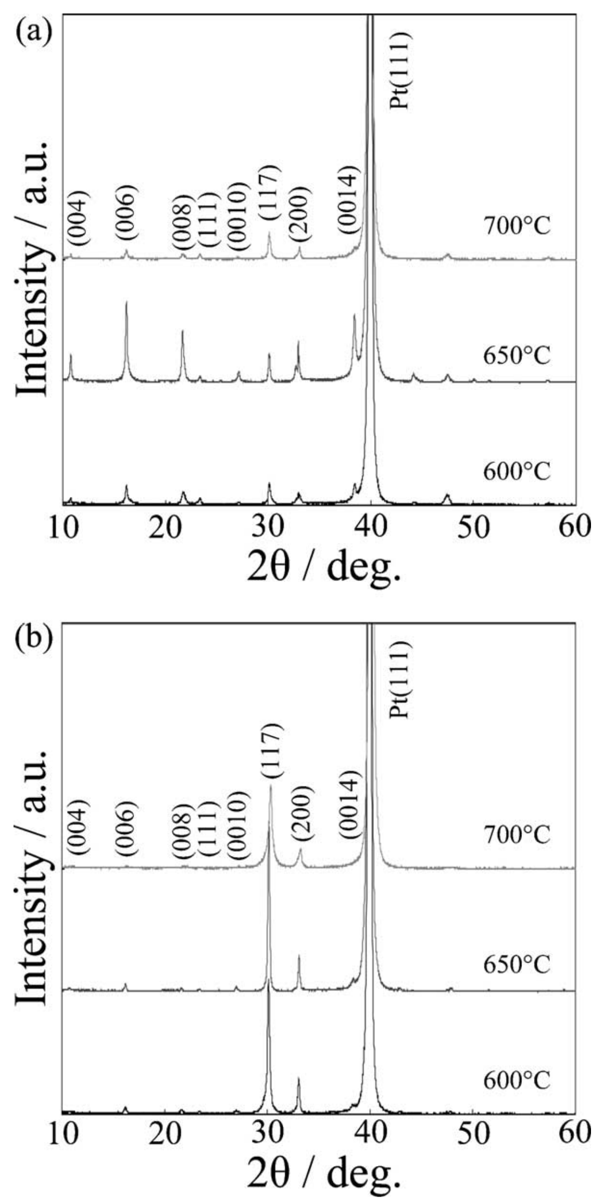

Fig. 1. XRD patterns of BLT thin films prepared at temperatures of 600–700 °C without (a) and with (b) Bi_2O_3 seeding layer.

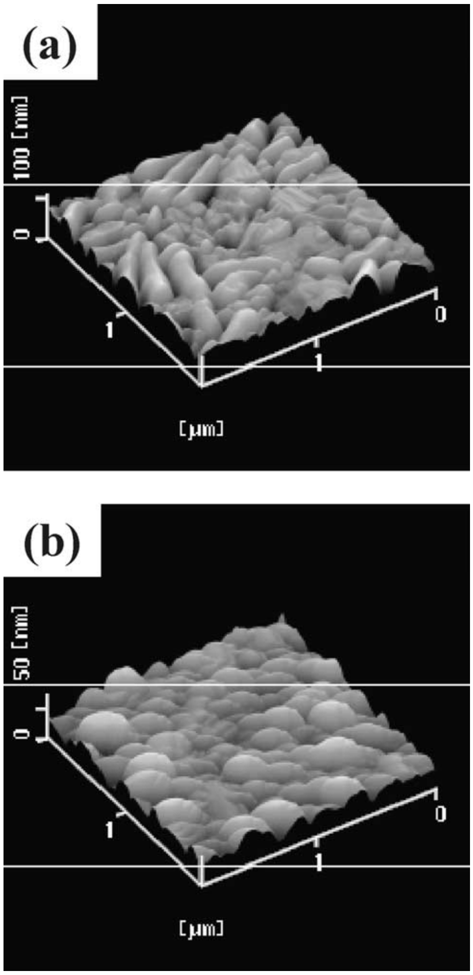

Fig. 2. AFM images of the surface of BLT thin films prepared at 650 °C without (a) and with (b) Bi_2O_3 seeding layer.

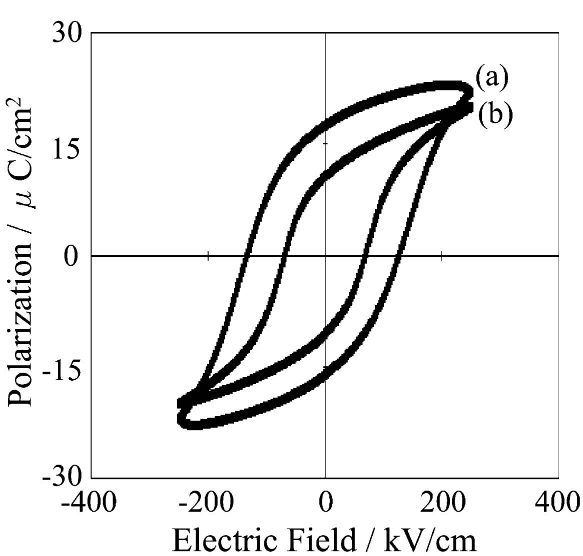

Fig. 3. *P–E* hysteresis loops of 700 °C-annealed BLT thin films on Pt/Ti/SiO_2/Si (a) and Pt/TiO_x/SiO_2/Si (b) substrates without Bi_2O_3 seeding layer.

remanent polarization, P_r, of 10.6 μC/cm^2 and a coercive field, E_c, of 69.1 kV/cm, compared with those of BLT thin films on Pt/Ti/SiO_2/Si. This may be attributable to the suppression of Bi diffusion to the substrate.

Fig. 4 shows *P–E* hysteresis loops at applied voltage of 5 V for BLT thin films prepared on Pt/TiO_x/SiO_2/Si substrates at 600–700 °C without and with Bi_2O_3 seeding layer. BLT thin films prepared at 600 and 650 °C without Bi_2O_3 seeding layer exhibited a *Pr* of 7.0 and 9.2 μC/cm^2, and a E_c of 75.2 and 77.5 kV/cm, respectively, as shown in Fig. 4(a). On the other hand, BLT thin films prepared at 600 °C with Bi_2O_3 seeding layer showed a P_r of 4.7 μC/cm^2 and a E_c of 75.0 kV/cm. Furthermore, the hysteresis loops are well-saturated, but the P_r value was not so high as we expected. They

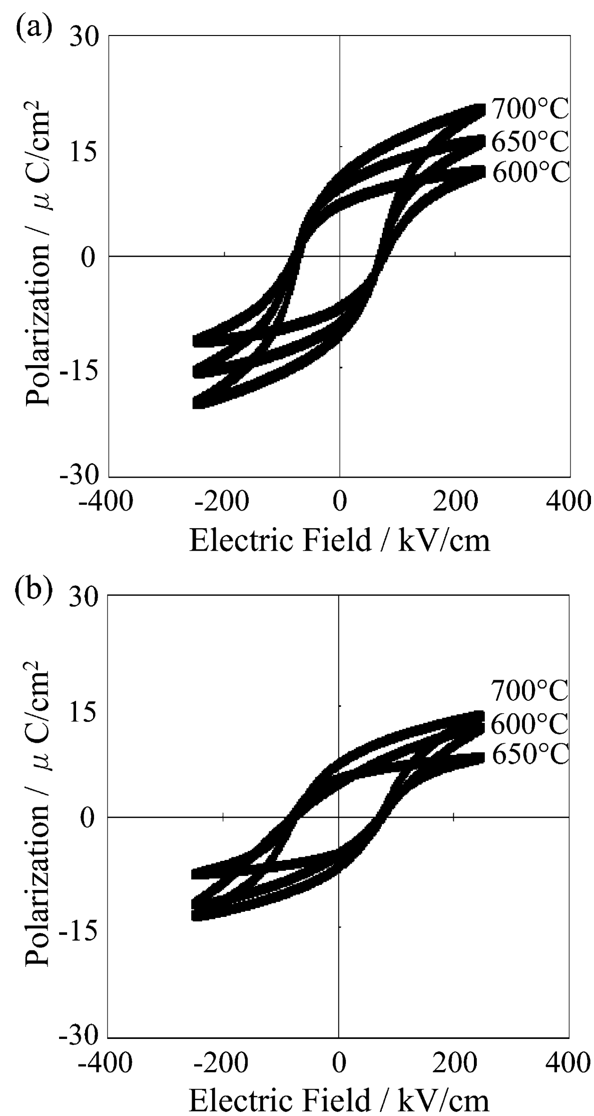

Fig. 4. *P–E* hysteresis loops of BLT thin films prepared on Pt/TiO_x/SiO_2/Si substrate at the temperatures of 600–700 °C without (a) and with (b) Bi_2O_3 seeding layer.

showed a P_r of 5.0 μC/cm^2 and a E_c of 78.8 kV/cm, as shown in Fig. 4(b), which are enough for ferroelectric memory device applications.

4. Conclusions

BLT thin films were prepared by a CSD method using Bi_2O_3 seeding layer, and their microstructure, crystal phase and ferroelectric property were investigated. Our results are summarized as follows:

1. Ferroelectric BLT thin films were successfully synthesized at 650 °C on Pt/TiO_x/SiO_2/Si substrates by a CSD method.
2. The use of Bi_2O_3 seeding layer led to the decrease of crystallization temperature up to 600 °C and the easy formation of single-phase BLT thin films with a high (117) preferred orientation.
3. BLT films on Pt/TiO_x/SiO_2/Si exhibited an excellent ferroelectric property, compared with BLT films on Pt/Ti/SiO_2/Si.
4. The 650 °C-annealed BLT thin films on Pt/TiO_x/SiO_2/Si using Bi_2O_3 seeding layer showed a well-saturated hysteresis loop with a P_r of 5.0 μC/cm^2 and a E_c of 78.8 kV/cm.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research on Priority Area (B), No. 12134203 from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

References

1. Park, B. H., Kang, B. S., Bu, S. D., Noh, T. W., Lee, J. and Jo, W., Lanthanum-substituted bismuth titanate for use in non-volatile memories. *Nature*, 1999, **401**, 682.
2. Atsuki, T., Soyama, N., Yonezawa, T. and Ogi, K., Preparation of Bi-based ferroelectric thin films by sol-gel method. *Jpn. J. Appl. Phys.*, 1995, **34**, 5096.
3. Seong, N. J., Yang, C. H., Shin, W. C. and Yoon, S. G., Oxide interfacial phases and the electrical properties of $SrBi_2Ta_2O_9$ thin films prepared by plasma-enhanced metalorganic chemical vapor deposition. *Appl. Phys. Lett.*, 1998, **72**, 1374.
4. Uchida, H., Yoshikawa, H., Okada, I., Matsuda, H., Iijima, T., Watanabe, T. and Funakubo, H., Fabrication of V-substituted $(Bi,M)_4Ti_3O_{12}$ [M = Lanthanoids] thin films by chemical solution deposition method. *Mat. Res. Soc. Symp. Proc.*, 2002, **688**, CC2.3.1.
5. Tokumitsu, E., Isobe, T., Kijima, T. and Ishiwara, H., Preparation and characterization of $(Bi,La)_4Ti_3O_{12}$ films by the sol-gel technique. *Mat. Res. Soc. Symp. Proc.*, 2001, **655**, CC13.9.1.
6. Hayashi, T., Togawa, D., Yamada, M., Sakamoto, W. and Hirano, S., Preparation and properties of $Bi_{4-x}La_xTi_3O_{12}$ ferroelectric thin films using excimer UV irradiation. *Jpn. J. Appl. Phys.*, 2002, **41**, 6814.