Journal of Electroceramics, 13, 339–343, 2004
© 2004 Kluwer Academic Publishers. Manufactured in The Netherlands.

Preparation and Properties of $Bi_{4-x}Nd_xTi_3O_{12}$ Thin Films by Chemical Solution Deposition

WATARU SAKAMOTO,[1] MIO YAMADA,[2] NAOYA IIZAWA,[3] YU-KI MIZUTANI, DAICHI TOGAWA,[3] KOICHI KIKUTA,[2] TOSHINOBU YOGO,[1] TAKASHI HAYASHI[3] & SHIN-ICHI HIRANO[2]

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

Submitted February 8, 2003; Revised December 8, 2003; Accepted January 6, 2004

Abstract. Neodymium-modified $Bi_4Ti_3O_{12}$, $(Bi,Nd)_4Ti_3O_{12}$ (BNT) ferroelectric thin films have been prepared on $Pt/TiO_x/SiO_2/Si$ substrates using metal-organic precursor solutions by the chemical solution deposition method. The BNT precursor films crystallized into the Bi layered perovskite $Bi_4Ti_3O_{12}$ (BIT) as a single-phase above 600°C. The synthesized BNT films revealed a random orientation having a strong 117 reflection, whereas non-substituted BIT thin films exhibited a random orientation with strong 00*l* diffractions. Among $Bi_{4-x}Nd_xTi_3O_{12}$ [$x = 0.0, 0.5, 0.75, 1.0$] thin films, $Bi_{3.25}Nd_{0.75}Ti_3O_{12}$ thin films showed a well-saturated P-E hysteresis loop with the highest P_r (22 $\mu C/cm^2$) and a low E_c (69 kV/cm) at an applied voltage of 5 V. The Nd-substitution with the optimum amount for the Bi site in the BIT structure was effective not only for promoting the 117 preferred orientation but also for improving the microstructure and ferroelectric properties of the resultant films.

Keywords: $Bi_4Ti_3O_{12}$, thin film, chemical solution deposition, Nd substitution, surface morphology, ferroelectric properties

1. Introduction

$Bi_4Ti_3O_{12}$ (BIT) is one of the most attractive ferroelectric materials for various thin film device applications such as nonvolatile memories because of its large remanent polarization (P_r), small coercive field (E_c) and high Curie temperature. Compared with $SrBi_2Ta_2O_9$ (SBT) and its related materials, BIT is known to be a compound of which processing temperatures can be lowered in the fabrication of thin films. In addition, Bi^{3+} ions in the BIT structure can be substituted by trivalent rare-earth ions, such as La^{3+}, Nd^{3+} and Sm^{3+}. Recently, the improvement of electrical properties of BIT thin films by rare-earth ion doping has been reported by several researchers [1–10]. Among them, $Bi_{4-x}Nd_xTi_3O_{12}$ (BNT) has been receiving much attention due to its larger ferroelectricity than that of the other rare-earth ion doped BIT [5–10]. Therefore, the optimization of the amount of neodymium (Nd) substitution into BIT films is strongly required for the fabrication of BNT films with excellent ferroelectricity.

The chemical solution deposition (CSD) method using metal-organic compounds is considered to be useful for the low-temperature fabrication and the precise control of the chemical composition of thin films. In this process, factors such as the selection of starting materials and the optimization of chemical compositions as well as the annealing conditions strongly affect the crystallographic phase, crystallinity, crystal orientation, microstructures and ferroelectric properties of resultant films.

This paper describes the processing of $Bi_{4-x}Nd_x$-Ti_3O_{12} (BNT) thin films by a CSD method using designed metal-organic precursor solutions. The crystallization behavior, crystal orientation and surface morphology of synthesized films were investigated. The ferroelectric properties were also evaluated.

2. Experimental Procedures

$Bi(OC_5H_{11})_3$, $Ti(O^iC_3H_7)_4$ [Kojundo Chemical, Japan], and $Nd(CH_3COO)_3{\cdot}H_2O$ [Mitsuwa Chemical, Japan] were used as starting materials. Anhydrous $Nd(CH_3COO)_3$ was prepared from Nd $(CH_3COO)_3{\cdot}H_2O$ by removing the hydrated water. $Nd(CH_3COO)_3{\cdot}H_2O$ was heated at 110°C under vacuum for 4 h yielding $Nd(CH_3COO)_3$. 2-Methoxyethanol as a solvent was dried over a molecular sieve and distilled prior to use. Since the starting materials are extremely sensitive to moisture, the entire procedure was carried out in a dry N_2 atmosphere. The required amounts of $Bi(OC_5H_{11})_3$, $Nd(CH_3COO)_3$, and $Ti(O^iC_3H_7)_4$ corresponding to $Bi_{4-x}Nd_xTi_3O_{12}$ [$x = 0.0$, 0.5, 0.75, 1.0] compositions (with 3% of excess Bi) were dissolved in absolute 2-methoxyethanol. Then, acetylacetone was added to the solution as a stabilizing agent. The molar ratio of acetylacetone to BNT precursor was set at 6. The solution was refluxed for 18 h yielding a homogeneous solution. The precursor solution was concentrated to approximately 0.1 M by removal of the solvent by vacuum evaporation.

BNT precursor films were prepared using the BNT precursor solutions by a spin-coating on $Pt/TiO_x/SiO_2/Si$ substrates. As-deposited precursor films were dried at 150°C for 5 min, calcined at 500°C for 10 min in an O_2 flow, and were annealed at 600–700°C for 30 min at a rate of 150°C/min by rapid thermal annealing (RTA) in an O_2 flow. The film thickness of BNT was adjusted to approximately 200 nm by repeating the coating/calcining cycle.

The crystallinity and the crystal orientation of the films were identified by X-ray diffraction (XRD) analysis using CuKα radiation with a monochromator. The surface morphology of the thin films was observed using an atomic force microscope (AFM).

After the film deposition, platinum top electrodes with a diameter of 0.2 mm 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 (TFA-ANALYZER 2000, AixACCT Inc.) at 100 Hz and room temperature. The applied voltage was from 1 to 10 V.

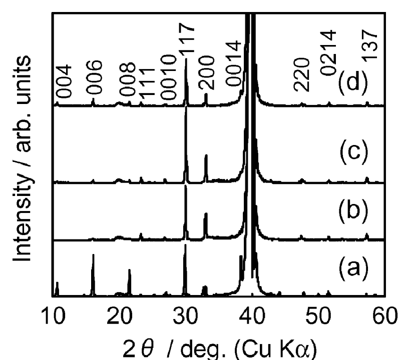

Fig. 1. XRD patterns of $Bi_{4-x}Nd_xTi_3O_{12}$ [(a) $x = 0.0$, (b) $x = 0.5$, (c) $x = 0.75$ and (d) $x = 1.0$] thin films on $Pt/TiO_x/SiO_2/Si$ substrates prepared at 700°C.

3. Results and Discussion

3.1. Synthesis of BNT Thin Films

Figure 1 shows the XRD profiles of $Bi_{4-x}Nd_xTi_3O_{12}$ (BNT) [$x = 0.0$, 0.5, 0.75, 1.0] thin films prepared at 700°C on $Pt/TiO_x/SiO_2/Si$ substrates. $Bi_{4-x}Nd_xTi_3O_{12}$ thin films crystallized in a single-phase of Bi layered perovskite $Bi_4Ti_3O_{12}$ (BIT) without any formation of the second phase. Non-substituted BIT thin films exhibited a random orientation with strong 00*l* diffractions as shown in Fig. 1(a). On the other hand, BNT [$x = 0.5$, 0.75, 1.0] thin films showed high crystallinity with a random orientation having a strong 117 reflection, as shown in Figs. 1(b)–1(d). The change in the crystal orientation due to the Nd-substitution was clearly observed.

Figure 2 illustrates the XRD profiles of BNT [$x = 0.5$] thin films prepared at temperatures between 600°C and 700°C for 30 min. BNT [$x = 0.5$] precursor films crystallized in the BIT single-phase at 600°C and revealed a random orientation with weak 00*l* diffraction peaks, as shown in Fig. 2(a). The 117 preferred orientation of the films became dominant with increasing annealing temperature. Figure 2 indicates that a heat treatment temperature above 600°C is required for the crystallization of BNT thin films on $Pt/TiO_x/SiO_2/Si$ substrates. In addition, the orientation of the films remarkably changed between BIT [$x = 0.0$] and BNT [$x = 0.5$]. The same crystallization behavior was observed for BNT [$x = 0.75$ [9] and 1.0] thin films.

Compared with non-substituted BIT films, BNT [$x = 0.5$–1.0] films revealed the decreased intensity

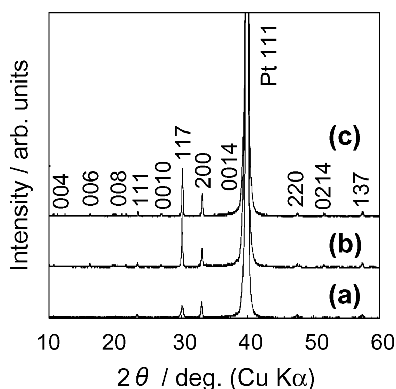

Fig. 2. XRD patterns of $Bi_{3.5}Nd_{0.5}Ti_3O_{12}$ thin films on $Pt/TiO_x/SiO_2/Si$ substrates prepared at (a) 600°C, (b) 650°C and (c) 700°C.

of 00*l* reflections, and had almost random orientation. BIT-based materials have a layered perovskite structure and exhibit strong anisotropic physical properties. The spontaneous polarization for BIT along a-axis is known to be much larger than that along c-axis [11]. From this point of view, randomly oriented films are considered to be more favorable than c-axis-oriented films. BNT films in this study, therefore, have a more suitable orientation in comparison with non-substituted BIT films for achieving the large ferroelectricity.

3.2. *Surface Morphology of BNT Thin Films*

Figure 3 shows AFM images of the surfaces of BNT [x = 0.0–1.0] thin films prepared at 700°C on $Pt/TiO_x/SiO_2/Si$ substrates. Non-substituted BIT thin films exhibited the inhomogeneous microstructures consisting of small grains and large grains with a statistical roughness, root mean square (RMS) of approximately 24.4 nm. Among these films, BNT [x = 0.75] thin films exhibited the most homogeneous microstructure with uniform grain size around 200 nm [RMS: 12.0 nm] as shown in Fig 3(c). The values of RMS decreased from 24.4 nm of BIT [x = 0.0] to

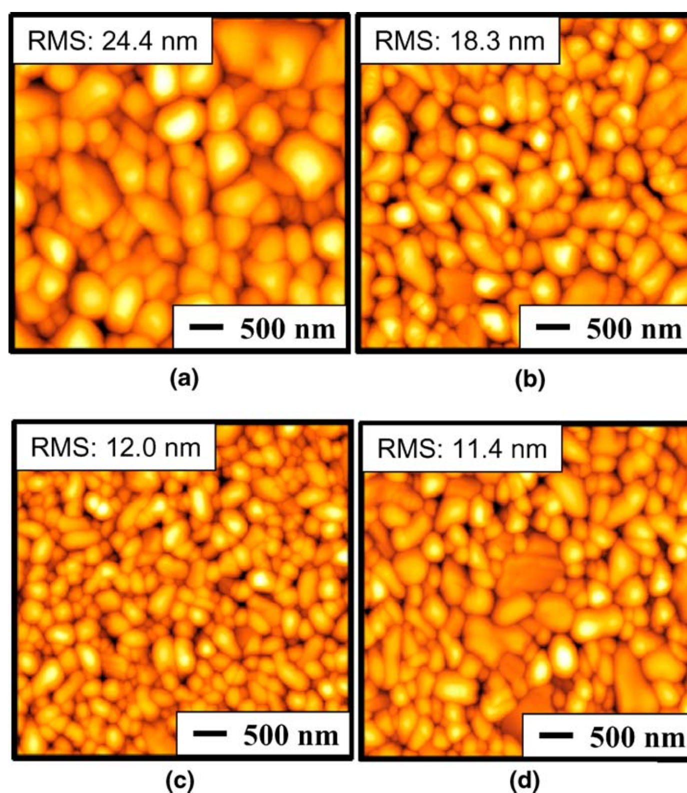

Fig. 3. AFM images of the surfaces of $Bi_{4-x}Nd_xTi_3O_{12}$ [(a) $x = 0.0$, (b) $x = 0.5$, (c) $x = 0.75$ and (d) $x = 1.0$] thin films on $Pt/TiO_x/SiO_2/Si$ substrates prepared at 700°C.

11.4 nm of BNT [$x = 1.0$]. This is due to the change of nucleation and growth process by Nd substitution into BIT structure. The homogeneous microstructure of the BNT [$x \geqq 0.75$] film might be attributable to the optimum amount of Nd-substitution. Nd-substitution was found to be effective in improving the surface morphology of synthesized BIT-based films, because the precursor film underwent the optimized nucleation and growth process producing films with a homogeneous and dense microstructure. Also, the homogeneous microstructure of BNT films may affect the ferroelectric properties, because the voltage can be applied uniformly onto the films.

3.3. Ferroelectric Properties of BNT Thin Films

Figure 4 shows the P-E hysteresis loops of BNT [$x = 0.0$–1.0] thin films prepared at 700°C. In order to clarify the effect of Nd-substitution in the BIT structure on the ferroelectric properties of resultant films, the full crystallization temperature was selected to be 700°C. From Fig. 4, the ferroelectric properties such as P_r, E_c and the degree of squareness of hysteresis loops for Nd-substituted BIT thin films were found to greatly improve in comparison with those of non-substituted BIT thin films. The well-saturated P-E hysteresis loops with a large P_r and a low E_c were observed for the BNT [$x = 0.75$, 1.0] films. Among these films, BNT [$x = 0.75$] thin films showed the highest remanent polarization (P_r) of 22 μC/cm^2 and a relatively low coercive electric field (E_c) of 69 kV/cm at an applied voltage of 5 V. This large ferroelectricity of current BNT films may be attributable to the change in crystal orientation from the random orientation having 00*l* diffractions with high intensities to the random orientation with a strong 117 reflection, and to the tilting of TiO_6^{8-} octahedra derived from the substitution of Nd^{3+} which has a smaller ionic radius than those of Bi^{3+} [7–10]. Uchida et al. achieved the P_r of 24 μC/cm^2 ($E_c > 100$ kV/cm) for 750°C annealed BNT films prepared by the CSD [6]. In this study, the comparable P_r with lower E_c is achieved at 50°C lower temperature (700°C) and at lower applied voltages. However, U. Chon et al. reported the larger ferroelectric properties (Pr: approximately 50 μC/cm^2) of BNT films by PLD[5]. Further investigation of the optimization of the processing conditions (amount of Nd substitution, etc.) is required to improve the ferroelectric properties of the present BNT films.

Figure 5 shows the saturation behaviors of P-E hysteresis curves at applied voltages from 1 to 10 V for BNT [$x = 0.0$-1.0] thin films prepared at 700°C. BNT [$x = 0.75$, 1.0] thin films exhibited P_r values of around 15 μC/cm^2, even when the applied voltage was as low as 3 V. Furthermore, the good saturation properties of P-E hysteresis loops were obtained for BNT [$x = 0.75$, 1.0] thin films, which had high P_r values as shown in Fig. 5. These behaviors are superior to those of the (104)-oriented epitaxial BNT films prepared by CVD process.[7, 8] The optimization of Nd content in BIT thin films was found to be a key for improving the ferroelectric properties of the resultant films. Since fatigue properties are also important for ferroelectric device applications, the

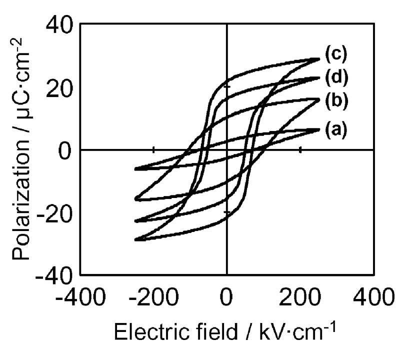

Fig. 4. P-E hysteresis loops of $Bi_{4-x}Nd_xTi_3O_{12}$ [(a) $x = 0.0$, (b) $x = 0.5$, (c) $x = 0.75$ and (d) $x = 1.0$] thin films on Pt/TiO_x/SiO_2/Si substrates prepared at 700°C. [Applied voltage: 5 V]

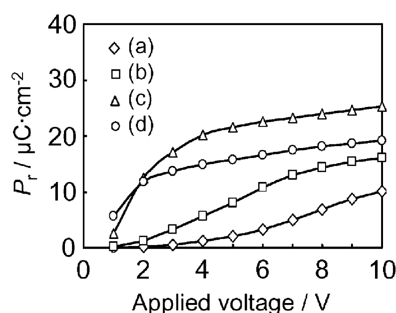

Fig. 5. Saturation property of remanent polarization (P_r) of P-E hysteresis loops for $Bi_{4-x}Nd_xTi_3O_{12}$ [(a) $x = 0.0$, (b) $x = 0.5$, (c) $x = 0.75$ and (d) $x = 1.0$] thin films on Pt/TiO_x/SiO_2/Si substrates prepared at 700°C. [Applied voltage: 1–10 V]

measurement of fatigue properties of the films is now in progress.

4. Conclusions

$Bi_{4-x}Nd_xTi_3O_{12}$ (BNT) thin films were synthesized by a chemical solution deposition, and their crystallographic phase, crystal orientation, microstructure and ferroelectric properties were examined. The results are summarized as follows:

1. Ferroelectric BNT thin films could successfully be synthesized on $Pt/TiO_x/SiO_2/Si$ substrates using metal-organic precursor solutions. The Nd-substitution for Bi site in $Bi_4Ti_3O_{12}$ led to the formation of single-phase BNT thin films with 117 preferred orientation on platinized silicon substrates at as low as 600°C.
2. By optimizing the amount of Nd-substitution into BIT, BNT thin films exhibited homogeneous grain microstructure and excellent ferroelectric properties, particularly at the composition of $Bi_{3.25}Nd_{0.75}Ti_3O_{12}$. $Bi_{3.25}Nd_{0.75}Ti_3O_{12}$ thin films showed a well-saturated P-E hysteresis loop with the highest P_r (22 μC/cm^2) and a low E_c (69 kV/cm) at an applied voltage of 5 V. The synthesized BNT films in this study are expected for application in several ferroelectric thin film devices such as non-volatile memories.

Acknowledgment

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

References

1. B.H. Park, B.S. Kang, S.D. Bu, T. W Noh, J. Lee, and W. Joe, *Nature*, **401**, 682 (1999).
2. D. Wu, A. Li, T. Zhu, Z. Li, Z. Liu, and N. Ming, *J. Mater. Res.*, **16**, 1325 (2001).
3. T. Hayashi, D. Togawa, M. Yamada, W. Sakamoto, and S. Hirano, *Jpn. J. Appl. Phys.*, **41**, 6814 (2002).
4. S.S. Kim, T.K. Song, J.K. Kim, and J. Kim, *J. Appl. Phys.*, **92**, 2213 (2002).
5. U. Chon, H.M. Jang, M.G. Kim, and C.H. Chang, *Phys. Rev. Lett.*, **89**, 87601 (2002).
6. H. Uchida, H. Yoshikawa, I. Okada, H. Matsuda, T. Iijima, T. Watanabe, and H. Funakubo, *Jpn. J. Appl. Phys.*, **41**, 6820 (2002).
7. T. Kojima, T. Sakai, T. Watanabe, H. Funakubo, K. Saito, and M. Osada, *Appl. Phys. Lett.*, **80**, 2746 (2002).
8. T. Kojima, T. Watanabe, H. Funakubo, K. Saito, M. Osada, and M. Kakihana, *J. Appl. Phys.*, **93**, 1707 (2003).
9. T. Hayashi, N. Iizawa, D. Togawa, M. Yamada, W. Sakamoto, and S. Hirano, *Jpn. J. Appl. Phys.*, **42**, 1660 (2003).
10. M. Yamada, N. Iizawa, T. Yamaguchi, W. Sakamoto, K. Kikuta, T. Yogo, T. Hayashi, and S. Hirano, *Jpn. J. Appl. Phys.*, **42**, 5222 (2003).
11. S.E. Cummins and L.E. Cross, *Appl. Phys. Lett.*, **10**, 14 (1967).