The Korean Journal of Ceramics, **4** [1] 33 - 36 (1998)

Preparation of Epitaxial $Bi_4Ti_3O_{12}$ Thin Films on MgO(100) Substrates

Kyu-Seog Hwang and Byung-Hoon Kim

Department of Ceramic Engineering, Chonnam National University, 300 Yongbongdong, Bukku, Kwangju 500-757, Korea

(Received January 8, 1998)

Epitaxially grown $Bi_4Ti_3O_{12}$ thin films on the MgO(100) substrates was prepared by dipping-pyrolysis process using metal naphthenates as starting materials. The films annealed at various temperatures were characterized by X-ray diffraction θ-2θ scans and pole-figure analysis (β scanning). Highly *c*-axis oriented $Bi_4Ti_3O_{12}$ films were crystallized by heat-treatment at 700° and 750°C from precursor films pyrolyzed at 500°C. The X-ray pole-figure analysis indicated that the $Bi_4Ti_3O_{12}$ thin films have an epitaxial relationship with the MgO(100) substrates.

Key words : $Bi_4Ti_3O_{12}$ thin films, MgO(100), Dipping-pyrolysis process, Epitaxial relationship

I. Introduction

In recent years, many researchers have been performed to apply the ferroelectric thin films to dynamic random access memory (DRAM) and nonvolatile memory devices. The ferroelectric thin films in the memory applications must possess the following properties; large remanent polarization, low coercive field, low dielectric constant and low leakage current density.

Among the many ferroelectric materials, $Bi_4Ti_3O_{12}$ (BIT) is one of the potential candidate materials to process ferroelectric thin films. BIT has a Curie temperature (T_c) of 675°C and two polarization axes; the coercive field values of 3.5 and 50 kV/cm, and spontaneous polarization of 4.0 and 50 μC/cm^2 along the *c*- and *a*-axis, respectively.[1] BIT thin films with *c*-axis orientation are expected to be suitable for low power memory devices owing to the small coercive field along the *c*-axis. It's lattice parameters of 0.5448 nm and 0.5410 nm along *a*- and *b*-axis, respectively, provide a suitable lattice match for epitaxial growth onto substrates such as $SrTiO_3$ (STO), $LaAlO_3$ (LAO) and MgO single crystals. The refractive index of STO (n = 2.39) is comparable to that of BIT, so it is difficult to use this film for optical waveguide devices. A substrate with a lower refractive index is more desirable. MgO has a refractive index of 1.74. However, it is difficult to prepare highly oriented BIT on MgO because the lattice mismatch between BIT and MgO is rather large, i.e., about 9%.

Recently, a variety of processing techniques including metalorganic chemical vaper deposition (MOCVD),[2,3] pulsed laser deposition (PLD)[4,5] and molecular beam epitaxy (MBE)[6] have been attempted to fabricate the highly *c*-axis oriented BIT thin films.

A wet chemical processes such as sol-gel[7,8] and dipping-pyrolysis (DP) process[9,10] have been successfully used to prepared *c*-axis oriented BIT films. Until now, however, there has been little information such as in-plane alignment and determination of *d*-value ($d_{//}$) parallel to the substrate surface on the high quality epitaxial BIT thin films prepared by the chemical solution process.

In this paper, epitaxial BIT thin films were grown on MgO(100) substrates by DP process, and the effects of annealing temperature on crystallinity and epitaxy of the films were investigated.

II. Experimental

To prepare the homogeneous coating solution, the commercially available constituent metal naphthenates of Bi and Ti were mixed and diluted with toluene to adjust the concentration (118.4 mg metal/ml coating solution). The solution was spin-coated onto the cleaned MgO(100) substrates at 4000 rpm for 10 seconds. The coated films were directly pyrolyzed at 500°C for 10 minutes in air and subsequently annealed at 600°~800°C for 30 minutes in air by directly inserting the samples into a preheated furnace, followed by rapid cooling.

The thickness of the annealed films was confirmed to be ~0.15 μm by scanning electron microscope (SEM). Crystallinity and in-plane alignment of the films were examined by X-ray diffraction (XRD) θ-2θ scans and X-ray pole-figure analysis (β scanning) using CuKα radiation with graphite bent-crystal monochrometor

III. Results and Discussion

Fig. 1 shows the XRD θ-2θ scans of the BIT thin films annealed at various temperatures. Crystallinity of the films strongly depends on the annealing temperature.

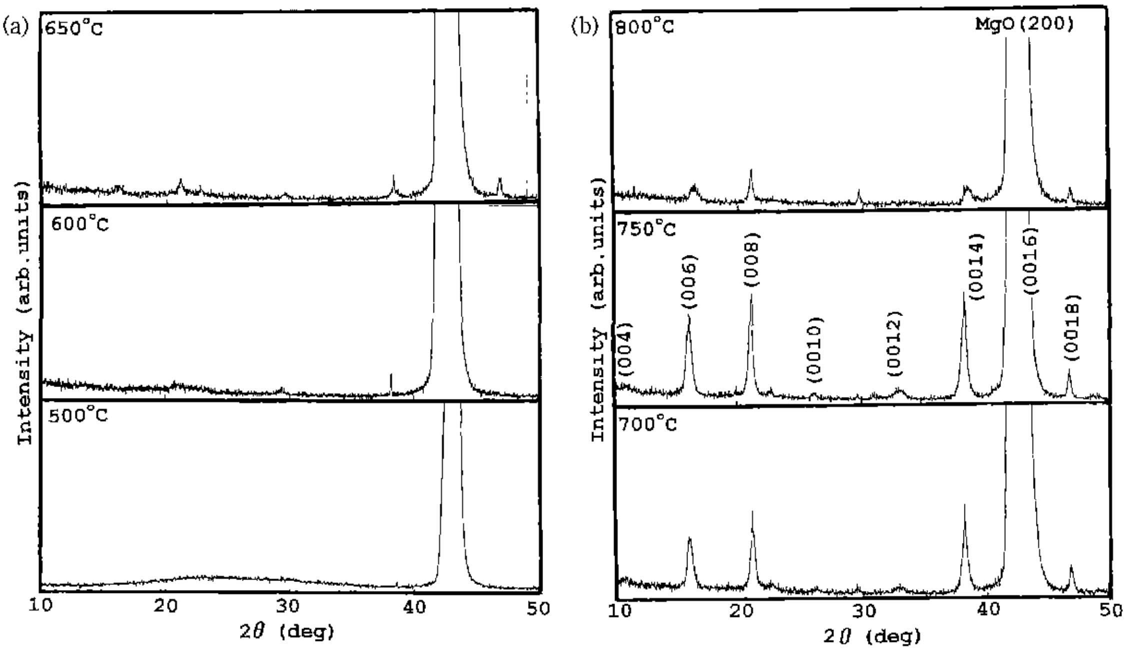

Fig. 1. XRD θ-2θ scans of BIT thin films grown on MgO(100) and annealed at various temperatures for 30 minutes.

The films started to crystallize by annealing at 600°C.

With increasing the annealing temperature, BIT peaks became stronger, and the film annealed at 750°C exhibited the highest X-ray peak intensities. On the contrary, peak intensities of the film annealed at 800°C was rather weaker than those of the films annealed at 700° and 750°C. Francombe[1] suggested that the titanium-rich leads to the formation of $Bi_2Ti_4O_{11}$ at higher temperatures Thus, we assume that epitaxial growth may be suppressed by titanium-rich phase owing to the Bi volatilization during annealing at 800°C, resulting in lower peak intensity of BIT. In all the films, only BIT(00*l*) peaks were observed. Peaks attributed to the impurity phases and those corresponding to other BIT(*hkl*) planes were hardly observed beyond the noise level. The result of XRD θ-2θ scans confirms that the BIT film is strongly *c*-axis oriented.

The in-plane alignment of the BIT films was investigated by X-ray pole-figure analysis. Fig. 2 illustrates the line profiles of β scans for which the α angles was fixed at 40°. As clearly seen in Fig. 2, the β scans of the films annealed at 700° and 750°C exhibited four sharp peaks. On the other hand, the intensity of the film annealed at 800°C was lower. These results of β scans agree with those of θ-2θ scans in Fig. 1. It is noted that the maximum annealing temperature of BIT films to obtain highly oriented BIT in our work is 750°C.

Fig. 3 shows the X-ray pole-figure of the BIT films annealed at 650°~800°C. After setting at 2θ=30.05$_7$° which corresponds to BIT(117) reflection, each film was rotated from β=0° to 360° at tilted angles between α=30° and 60°. As clearly seen in Fig. 3, the films annealed at 700° and 750°C showed four sharp spots, whereas no distinct spots

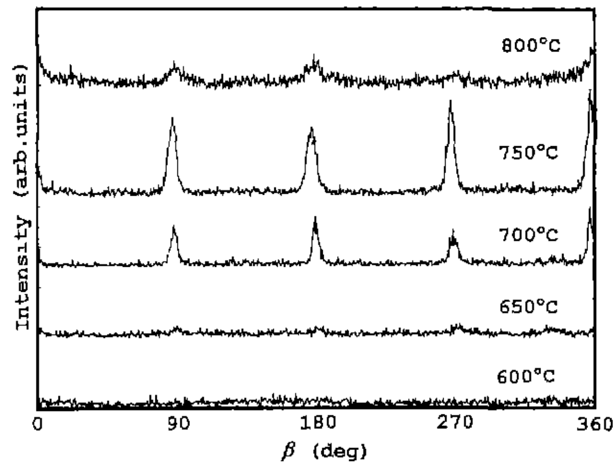

Fig. 2. Line profiles of β scans of BIT(117) reflection.

or rings were observed in the films annealed at 650° and 800°C. The BIT films with four sharp sopts have grown epitaxially with *c*-axis orientation perpendicular to the substrate surface.

Using the MgO(200) peak as an internal calibration standard, the lattice constant (*c*) perpendicular to the substrate surface was characterized as 3.291 nm, 3.293 nm, 3.298 nm and 3.285 nm for the films annealed at 650, 700, 750 and 800°C, respectively. The lattice constants of the epitaxial films annealed at 700° and 750°C are longer than the value of bulk crystal (3.281 nm), possibly due to the compressive stress effect in the *a*- and *b*-axis from the lattice misfit between the BIT film and MgO substrate (a_0=0.4213 nm, ICDD File 45-0946). On the contrary, *d*-value (d_l) of the polycrystalline BIT film annealed at 800°C is closer to *c* of bulk crystal than

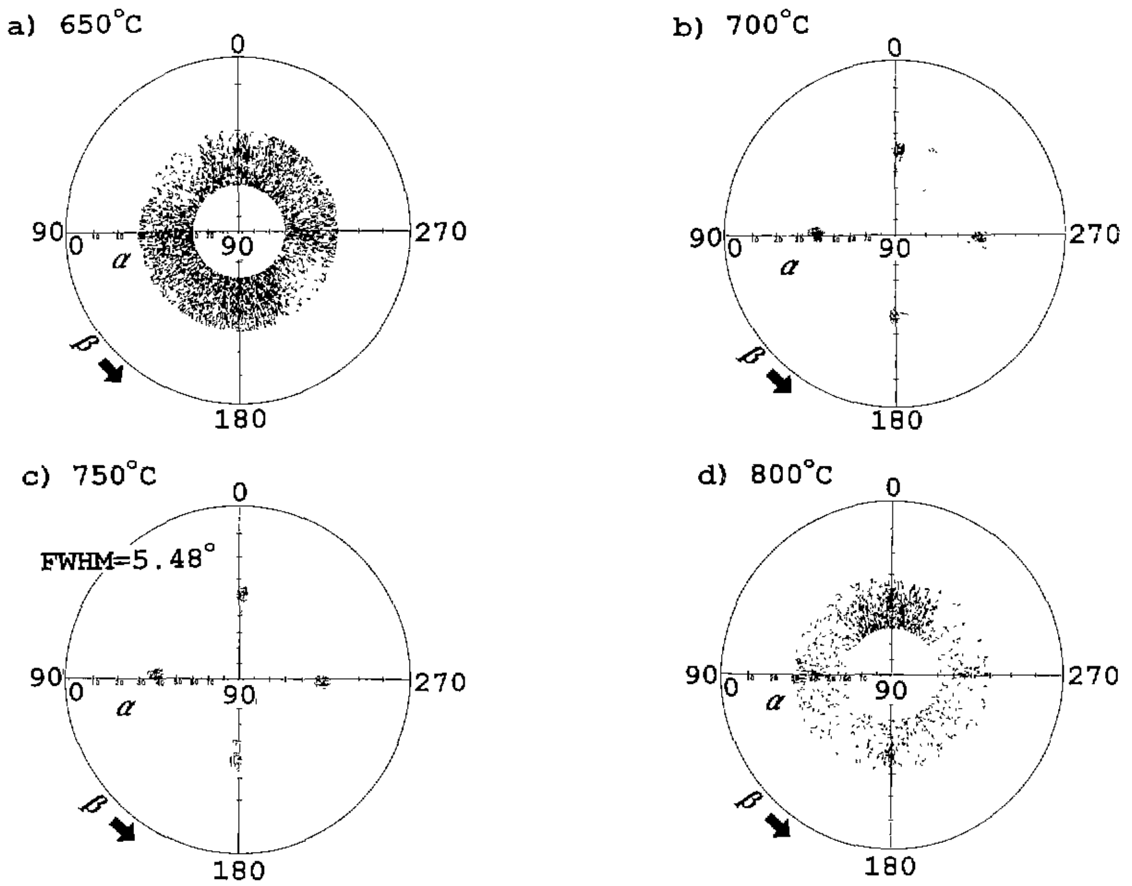

Fig. 3. X-ray pole-figures of BIT(117) reflection.

those of the epitaxial films. Since the film annealed at 800°C is polycrystalline, the $d_{\perp}$-value is assumed not to be affected by the MgO substrate.

Morphological characterization was carried out by SEM. Surface morphology of the epitaxial BIT film annealed at 750°C is shown in Fig. 4. Generally, the pores and cracks easily recognized in the films prepared by chemical solution methods such as sol-gel and DP process. However, the surface of the film annealed at 750°C was very flat and smooth; distinct grain boundaries, usually accompanying the typical polycrystalline texture, were not recognized. It was difficult to resolve any individual grains also in other films annealed at different temperature.

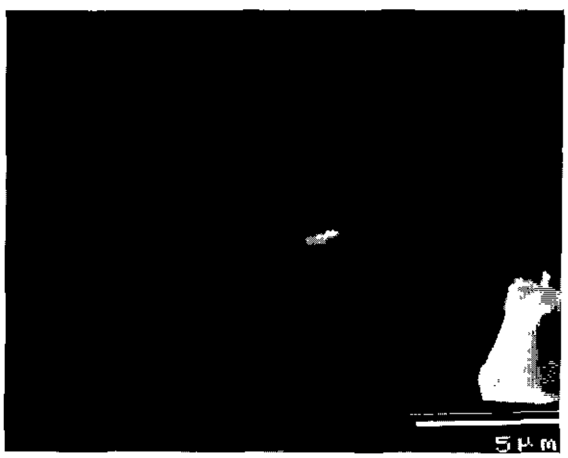

Fig. 4. SEM micrograph of the free surface of the epitaxial BIT thin film annealed at 750°C.

Consequently, in our work, the annealing temperature to obtain a high crystallinity and epitaxy of the BIT film with smooth surface was 750°C.

It should be noted that several reports on the preparation of "highly oriented" BIT thin films by chemical solution method such as sol-gel and DP process have been published.[7-10] On those reports, however, the alignment of the films was discussed only based on the d-values determined from XRD θ-2θ scans. In our results, the epitaxial relationship between the BIT film and MgO substrate was clearly confirmed by XRD pole-figure analysis

Further work is required to analyze the $d_{//}$ value of the films by reciprocal-space mapping.

IV. Conclusion

Epitaxially grown BIT thin films on the MgO(100) substrates was prepared by DP process using metal naphthenates as starting materials. Highly c-axis oriented

BIT films were obtained by pyrolyzing the spin-coated films at 500°C and subsequently annealing at 700° or 750°C. The X-ray pole-figure analysis indicated that the BIT thin films annealed at 700° and 750°C have an epitaxial relationship with the MgO(100) substrates, while the polycrystalline character was observed in the film annealed at 800°C.

References

1. M. H. Francombe, "The Research Status and Device Potential of Ferroelectric Thin Films", *Ferroelectrics,* **3**, 199-211 (1972).
2. K Yoshimura, S Okamura and T Tsukamoto, "Preparation of $Bi_4Ti_3O_{12}$ Thin Films with *C*-Axis Orientation by MOCVD Using $Bi(O\text{-}C_7H_7)_3$ and $Ti(i\text{-}OC_3H_7)_2(DPM)_2$", *J. Ceram. Soc. of Jpn ,* **102** [5], 512-515 (1994).
3. T. Nakamura, R. Muhammet, M. Shimizu and T. Shiosaki, "Preparation of *C*-Axis-Oriented $Bi_4Ti_3O_{12}$ Thin Films by Metalorganic Chemical Vapor Deposition", *Jpn. J. Appl. Phys.,* **32**, Pt. 1, No. 9B, 4086-4088 (1993).
4. R Ramesh, K. Luther, B. Wilkens, D. L. Hart, E. Wang, J. M. Tarascon, A. Inam, X. D. Wu and T. Venkatesan, "Epitaxial Growth of Ferroelectric Bismuth Titanate Thin Films by Pulsed Laser Deposition", *Appl. Phys. Lett.,* **57** (15), 1505-1507 (1990).
5. H. Buhay, S Sinharoy, W. H. Kasner, M. H. Francombe, D. R. Lampe and E. Stepke, "Pulsed Laser Deposition and Ferroelectric Characterization of Bismuth Titanate Films", *Appl. Phys. Lett.,* **58** (14), 1470-1472 (1991).
6. S. Choopun, T. Matsumoto and T. Kawai, "Low-Temperature Growth of $Bi_4Ti_3O_{12}$ Epitaxial Films on $SrTiO_3$(001) and $Bi_2Sr_2CaCu_2O_8$(001) Single Crystals by Laser Molecular Beam Epitaxy", *Appl. Phys. Lett.,* **67** (8), 1072-1074 (1995).
7. H. Gu, D. Bao, S Wang, D. Gao, A. Kuang and X. Li, "Synthesis and Optical Properties of Highly *C*-Axis Oriented $Bi_4Ti_3O_{12}$ Thin Films by Sol-Gel Processing", *Thin Solid Films,* **283**, 81-83 (1996).
8. E. Kato, Y. Watanabe, T. Tsukamoto and T. Tsuchiya, "Preparation of Highly Oriented Bismuth Titanate Thin Films by Sol-Gel Process", *J. Ceram. Soc. of Jpn.,* **104** [11], 1015-1018 (1996).
9. A. Kakimi, S Okamura and T. Tsukamoto, "O_2 Gas Pressure Effects on Surface Morphology in Ferroelectric $Bi_4Ti_3O_{12}$ Thin Films Fabricated by Spin-Coating Pyrolysis", *Jpn. J. Appl. Phys.,* **33**, Pt 2, No. 12A, L1707-L1709 (1994).
10. A Kakimi, S. Okamura, S. Shizutoshi and T. Tsukamoto, "Effects of O_2 Gas Pressure in Heat Treatment on Surface Morphology and Electric Properties of Ferroelectric $Bi_4Ti_3O_{12}$ Thin Films with *C*-Axis Orientation", *Jpn. J. Appl. Phys.,* **34**, Pt. 1, No 9B, 5193-5197 (1995).