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Effect of pyrolysis temperature on $Bi_4Ti_3O_{12}$/MgO(100) structures prepared by chemical solution deposition

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Epitaxially grown $Bi_4Ti_3O_{12}$ thin films on MgO(100) substrates were prepared by a chemical solution deposition process using metal naphthenates as the starting materials. A homogeneous Bi-Ti solution with toluene was spin-coated onto the substrates and pyrolyzed at 300 °C, 400 °C and 500 °C for 10 minutes in air. Final annealing was performed at 750 °C for 30 minutes in air. The effects of pyrolysis temperature on the crystallinity, epitaxy and surface morphology of the films were investigated. Highly *c*-axis oriented $Bi_4Ti_3O_{12}$ thin films were confirmed by X-ray diffraction θ-2θ scans. According to the pole-figure analysis, epitaxy of the annealed films was found to depend on the pyrolysis temperature.

Key words: $Bi_4Ti_3O_{12}$ thin film, MgO(100), Pyrolysis, Epitaxy.

Introduction

$Bi_4Ti_3O_{12}$ (BIT) is one of the potential candidate materials to process into ferroelectric thin films. It has lattice parameters of 5.448 Å and 5.410 Å along the *a*- and *b*-axis [1], respectively, which provide a suitable lattice match for epitaxial growth onto substrates such as $SrTiO_3$ and $LaAlO_3$ single crystals [2, 3]. The refractive index of $SrTiO_3$ (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 (a_0=4.213 Å) [4] because the lattice mismatch between BIT and MgO is rather large, *i.e.*, approximately 22%. Moreover, in comparison to perovskite-related materials such as $BaTiO_3$ and $Pb(Zr,Ti)O_3$ with cube-on-cube structured films [5, 6], the surface morphology of BIT films has generally less homogeneity because of its orthorhombic structure. Thus, it is very difficult to prepare high-density devices. Random orientation and the nonuniform surface of the film result in nonuniform device functions. Only epitaxial and homogeneously-grown films are suitable for preparing high-quality devices.

A chemical solution deposition (CSD) process consists of the following two heating stages; pyrolysis at 200 °C~500 °C and final annealing at 500 °C~1000 °C. Pyrolysis is the process for pyrolytic conversion of metal organic acid salts into metal oxides, while the final annealing is the process of a solid-state reaction among the constituent oxides. In previous studies [2, 6] on the CSD process, pyrolysis has mostly been carried out at 500 °C, however, the present authors have suspected that the film might be excessively or locally heated up to a higher temperature, such as 700 °C~800 °C since the decomposition rate of the organic component during the pyrolysis should be different at 200 °C~500 °C. Thus, a comparison between the pyrolysis temperatures was considered to be important in order to achieve homogeneous nucleation and obtain a high level of epitaxy.

In this study, epitaxial BIT thin films were grown on polished MgO(100) substrates by the CSD process, and the effects of pyrolysis temperature on crystallinity, epitaxy and surface morphology of the films were investigated. We placed a particular emphasis on examining the effect of temperature during the pyrolysis on the epitaxy of the film.

Experimental

A coating solution was prepared by mixing Bi- and Ti-naphthenates with a Bi:Ti molar ratio of 4:3 and diluting the solution with toluene (concentration: 118.4 mg metal/ml of coating sol). Double-sided polished and cleaned MgO(100) substrates were spin-coated

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with the precursor solution at 4000 rpm for 10 s and then directly pyrolyzed at 300 °C, 400 °C and 500 °C for 10 minutes in air to examine effect of pyrolysis temperature on the properties of the annealed films. The spin coating and pyrolysis were repeated two times. The films were subsequently heat-treated at a final temperature of 750 °C for 30 minutes in air by directly inserting the samples into a preheated furnace.

Thermogravimetric analysis (TGA, DTG-60, Shimadzu, Japan) was performed using an α-alumina reference and a heating rate of 3 K·minutes^{-1} from 28 °C to 550 °C. The thickness of the BIT thin films was estimated to be about 0.2 μm, which was confirmed by the observation of fracture cross sections with a field emission – scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). Crystallinity and in-plane alignment of the films were examined by high-resolution X-ray diffraction (HRXRD, X'Pert PRO, Philips, Netherlands) θ-2θ scans and X-ray pole-figure analysis. Surface morphology and surface roughness of the films were observed by FE-SEM and a scanning probe microscope (SPM, XE-200, PSIA, Korea).

Results and Discussion

Figure 1 shows the XRD θ-2θ scans of BIT films pyrolyzed at various temperature, followed by final annealing at 750 °C. For the annealed film pyrolyzed at 300 °C, the BIT structure started to become visible with a peak corresponding to the (008) reflection. After annealing, the film pyrolyzed at 400 °C became more crystalline. This implies that the higher pyrolysis temperature is effective in transforming the amorphous phase to the BIT crystalline phase. Obviously, (00*l*)-oriented single phase was formed for the annealed film pyrolyzed at 500 °C and the reflections for other planes such as BIT(111), (220) and (117) were not recognized. By contrast, the film pyrolyzed at 400 °C showed misoriented peaks, as shown in Fig. 1(b). This means that the annealed film pyrolyzed at 500 °C is highly oriented, since the BIT(117) is the strongest peak of the powder diffraction pattern. Furthermore, the higher

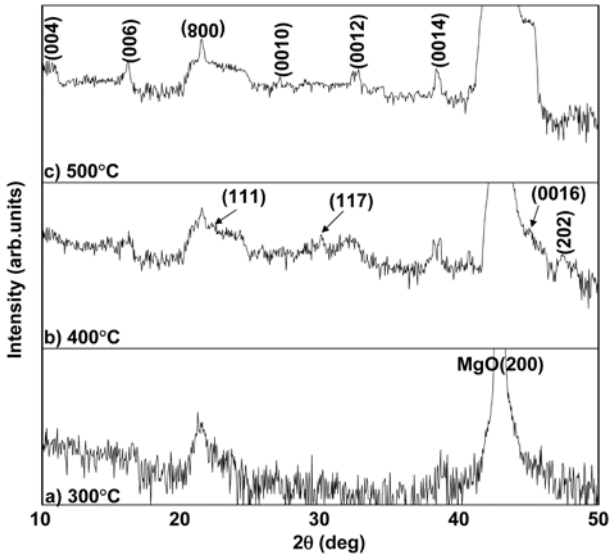

Fig. 1. XRD θ-2θ scans of BIT films on MgO(100) substrates pyrolyzed at various temperatures, followed by final annealing at 750 °C.

pyrolysis temperatures from 300 °C to 500 °C gave stronger BIT peaks.

The in-plane alignment of the BIT films was investigated by X-ray pole-figure analysis. Figure 2 shows the X-ray pole-figure of the BIT films pyrolyzed at 300 °C, 400 °C, and 500 °C, which was followed by a final annealing at 750 °C. After setting 2θ=30.06°, which corresponds to the BIT(117) reflection, each film was rotated from φ=0° to 360° at tilted angles between ψ= 30° and 70°. We chose the BIT(117) reflection for study because of its high intensity and separation from the MgO substrate reflections. As is clearly seen in Fig. 2, the films pyrolyzed at 500 °C showed four sharp spots, whereas no distinct spots or rings were observed in the films pyrolyzed at 300 °C and 400 °C. The BIT film with four sharp spots has grown epitaxilly with a *c*-axis orientation perpendicular to the substrate surface. Based on the relative positions of the spots in the pole-figure for the film pyrolyzed at 500 °C and the substrate orientation, the following crystallographic relationship was obtained: BIT(001)//MgO(100) and BIT[100],

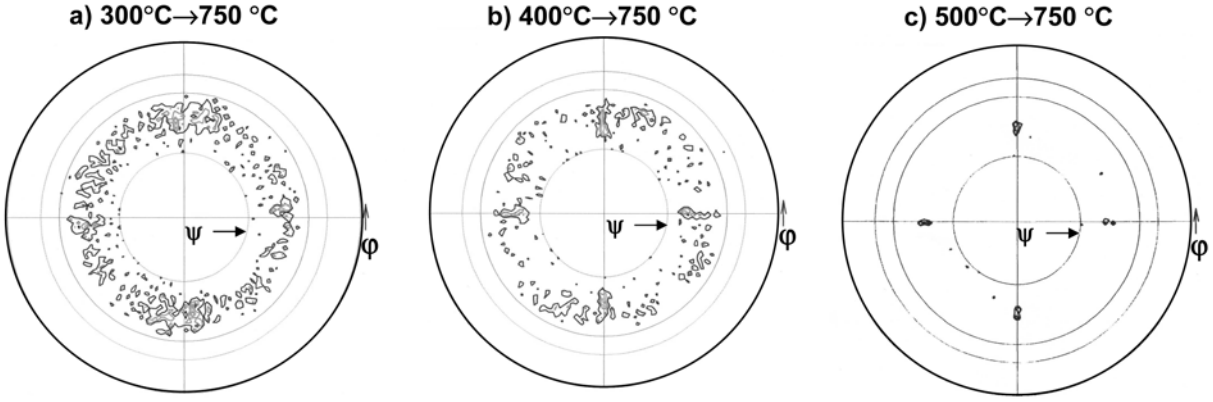

Fig. 2. X-ray pole-figures of BIT films pyrolyzed at various temperatures, followed by final annealing at 750 °C.

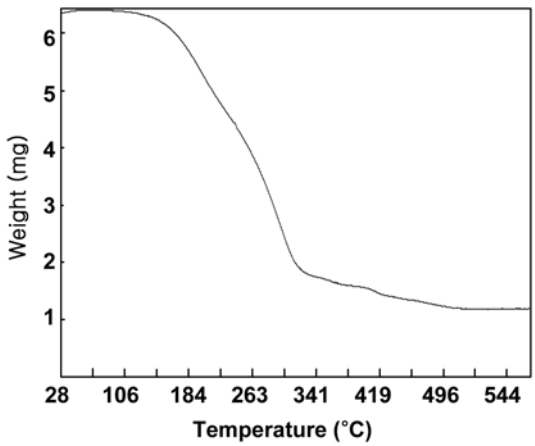

Fig. 3. TGA curve of the BIT solution used in this study.

[010]//MgO[001].

BIT has an orthorhombic unit cell with an orthorhombic distortion, b/a (a_0=5.448 Å and b_0=5.410 Å) of 1.007 at room temperature. The unit cell parameters of BIT at room temperature are not close to those of the cubic cell of MgO. However, the tetragonal a cell parameter of BIT is 3.86 Å [7] when BIT transforms to a tetragonal unit cell at temperatures above T_c. Therefore, epitaxial BIT thin films pyrolyzed at 500 °C may be obtained by annealing above T_c, *i.e.*, 750 °C, due to increase similarity of the lattice constants of BIT films and MgO substrates.

However, the films pyrolyzed at 300 °C and 400 °C did not have an epitaxial relationship with the substrates after being annealed at the same heat treatment temperature. This growth behavior can be explained by the fact that the precursor films pyrolyzed at lower temperatures are assumed to contain some residual carbon or carbon hydroxides, as shown in Fig. 3. In this case, crystallization and epitaxial growth of the films may be suppressed by the residual carbon during final heat treatment, since crystallization, epitaxial growth and decomposition of organic components proceeded concurrently.

Morphological characterization was carried out by FE-SEM and SPM. The surface morphology of the films pyrolyzed at various temperatures is shown in Fig. 4. For the epitaxial films pyrolyzed at 500 °C, an extremely fine grain structure is evident, with grain sizes of 20~30 nm. While the surface morphology of the films pyrolyzed at 300 °C and 400 °C exhibited some pores probably due to the volatilization of the residual organics during the final annealing, although the substrates used were flat and homogeneous.

To more clearly elucidate the surface roughness of the film according to the pyrolysis temperature, SPM analysis was performed. Figure 5 shows the SPM top-view images and roughness profiles of BIT films on MgO(100) as a function of pyrolysis temperature. Epitaxial BIT films pyrolyzed at 500 °C showed surprisingly flat surfaces [Fig. 5(d)]. Although there is a larger lattice mismatch between the BIT along the a/b axes and the MgO than with other oxide substrates such as $SrTiO_3$ and $LaAlO_3$, the film shows coherent growth; *i.e.*, film growth is constrained by the substrate lattice. The film pyrolyzed at 300 °C showed the highest root mean square (RMS) roughness (=8.302 nm). However, by an increase of the pyrolysis temperature to 400 °C, the RMS roughness was decreased to 3.719

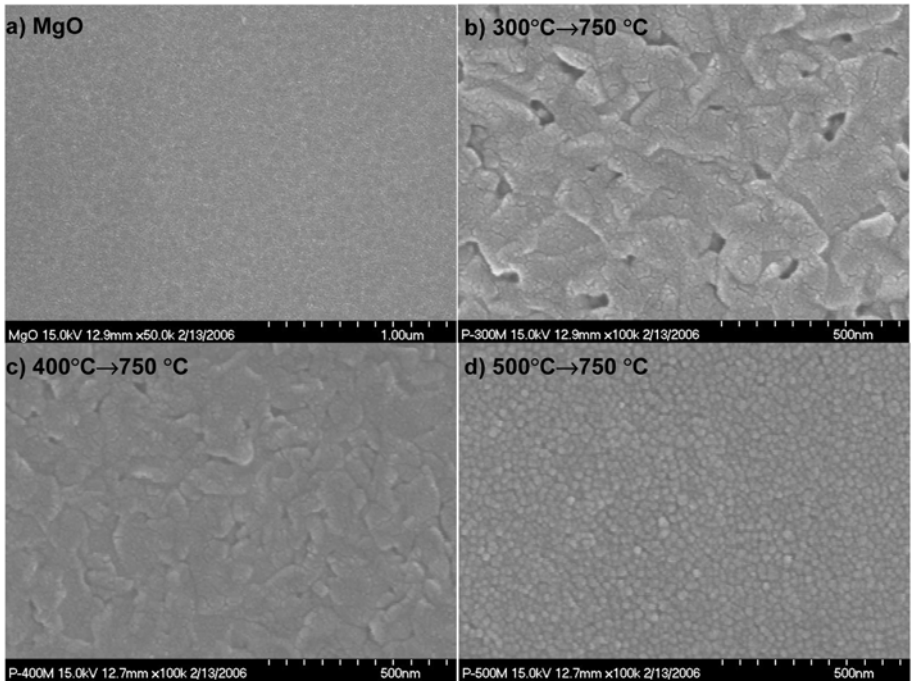

Fig. 4. FE-SEM images of BIT films pyrolyzed at various temperatures, followed by final annealing at 750 °C.

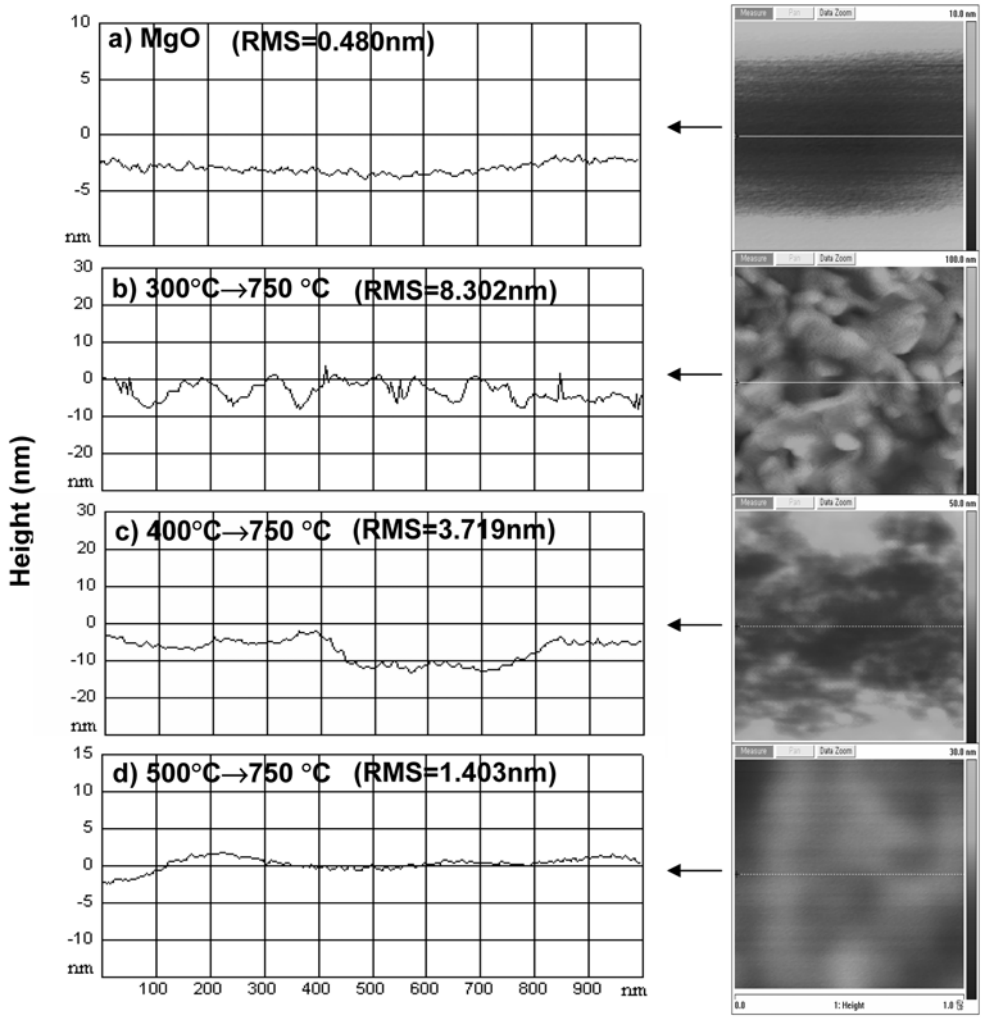

Fig. 5. SPM top-view images (1 μm × 1 μm) and surface roughness profiles of BIT films pyrolyzed at various temperatures, followed by final annealing at 750 °C.

nm. For the films pyrolyzed at lower temperatures, volatilization of residual organics and crystallization proceeded concurrently during final annealing at 750 °C. We consider volatilization of organics caused the defects in films, as shown in Fig. 4, resulting in a high RMS roughness.

Until now, few films were obtained on non-polished MgO substrates with flat and smooth surfaces by the CSD process. In this study, to exhibit ideal properties for device applications, we prepared smooth and flat epitaxial BIT films on MgO with atomically smooth surfaces by pyrolysis at 500 °C.

Conclusions

BIT thin films were epitaxially grown on MgO(100) substrates by a CSD process using metal naphthenates as starting materials. From XRD θ-2θ scans, highly *c*-axis-oriented BIT thin films were crystallized from pyrolyzed films at 500 °C by annealing at 750 °C. The X-ray pole-figure analysis indicates that the annealed BIT film pyrolyzed at 500 °C has an epitaxial relationship with its MgO(100) substrate. The surface morphology of the annealed film pyrolyzed at the higher temperature, i.e., 500 °C, exhibited a flat and smooth surface, while films pyrolyzed at lower temperatures, i.e., 300 °C and 400 °C, exhibited rough surface structures.

References

1. ICDD file 35-0795.
2. K. S. Hwang, Y. H. Yun, Y. H. Kim, H. W. Ryu, and B. A. Kang, Jpn. J. Appl. Phys. 41 (2002) 795-799.
3. K. S. Hwang, and Y. J. Park, J. Mater. Res. 16 (2001) 2519-2525.
4. ICDD file 45-0949.
5. Y. S. Kim, D. H. Kim, J. D. Kim, T. W. Noh, J. H. Kong, Y. D. Park, S. D. Bu, and J. G. Yoon, J. Korean Phys. Soc. 46 (2005) 55-58.
6. K. S. Hwang, C. K. Kim, S. B. Kim, J. T. Kwon, J. S. Lee, Y. H. Yun, Y. H. Kim, and B. H. Kim, Surf. & Coat. Tech. 150 (2002) 177-181.
7. E. C. Subbarao, Phys. Rev. 122 (1961) 804-807.