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Effect of prefiring temperature on the texture and optical property of $Bi_4Ti_3O_{12}$/MgO(100) prepared by using a metal naphthenate precursor

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The effect of prefiring temperature on the crystal structure and optical property of the $Bi_4Ti_3O_{12}$ films on MgO substrates by using a metal naphthenate precursor was investigated. As-deposited films were prefired at 300 °C, 400 °C and 500 °C for 10 min, followed by annealing at 750 °C for 30 min. According to the pole-figure analysis, texture of the annealed films was found to depend on prefiring temperature. Transmittance and the variation of band gap with prefiring temperature were studied.

Keywords: prefiring temperature, metal naphthenate, texture, optical property.

1. Introduction

$B_4Ti_3O_{12}$ (BIT) with excellent anisotropic properties is a typical ferroelectric material with a layered-perovskite structure. During epitaxial growth of BIT its lattice parameter with a = 5.448 Å and b = 5.410 Å (ICDD file 35-0795) provides a suitable lattice match with that of substrates such as $SrTiO_3$ and $LaAlO_3$ single crystal [1–4]. The refractive index of $SrTiO_3$ (n = 2.39) is comparable to that of BIT (n = 2.4 ~ 2.6), so it is difficult to use this film as 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 epitaxial BIT on MgO (a_0 = 4.213 Å, ICDD file 45-0949) because the lattice mismatch between BIT and MgO is rather large. Moreover, in comparison to perovskite-related materials such as $BaTiO_3$ and PZT with cube-on-cube structured films [5], the surface morphology of BIT films has generally less homogeneity because of orthorhombic

structure. Thus, it is difficult to prepare high-density devices. Epitaxially and homogeneously grown films are suitable for preparing high-quality devices.

In this paper, highly-textured BIT films were grown on MgO(100) substrates by using a metal naphthenate, and the effects of pyrolysis temperature on texture and optical properties were investigated.

2. Experiment

Commercially available constituent metal naphthenates of Bi and Ti (Nihon Kagaku Sangyo Co., Ltd. and Soekawa Rika Co., Ltd.) were mixed with a Bi : Ti molar ratio of 4 : 3 and diluted with toluene (concentration of the metals: 118.4 mg metal(Bi+Ti)/ml coating sol).

MgO(100) was selected as a substrate. A sol was spin-coated onto the MgO(100) at 4000 rpm for 10 sec.

As-deposited films were prefired at 300 °C, 400 °C and 500 °C for 10 min in air. This procedure was repeated two times before further annealing. Films were finally annealed at 750 °C for 30 min in air, followed by fast cooling to room temperature.

Produced films were characterized by high resolution X-ray diffractormeter (HRXRD, X'Pert PRO, Philips, Netherlands) $\theta - 2\theta$ scans and pole-figure analysis. Surface morphology and chemical composition of the films were investigated by FE-SEM (S-4700, Hitachi, Japan) with an energy-dispersive X-ray spectrometer (EDS) and scanning probe microscope (SPM, XE-200, PSIA, Korea). Thickness of finally annealed BIT film was approximately 0.1 μm, as determined by observations of fracture cross-sections with FE-SEM. Transmittance in the visible range was measured using UV – visible – NIR spectrophotometer (CARY 500 Scan, Varian, Australia). Absorption coefficient was obtained from the transmittance curve.

3. Results and discussion

Residual carbon content in the precursor films was investigated by EDS. Figure 1 shows EDS spectra of the films pyrolyzed at 300 °C (**a**), 400 °C (**b**), and 500 °C (**c**), for 10 min in air. Comparing these three spectra, an apparent large peak of C-Kα was recognized in Fig. 1**a**. Precursor films pyrolyzed at higher temperature contained smaller amount of carbon than those pyrolyzed at lower temperature. We can easily conclude that final annealing concurrently proceeded with vaporization of the carbon in precursor films for the films pyrolyzed at 300 °C and 400 °C.

Figure 2 shows the XRD $\theta - 2\theta$ scans of BIT films pyrolyzed at various temperatures, followed by final annealing at 750 °C. Obviously, [00*l*]-oriented single phase was formed and the reflections for other phases such as BIT(111), (220) and (117) were faint. This means that the films are highly oriented in all the samples, since the BIT(117) is the strongest peak of the powder diffraction pattern. With increasing pyrolysis temperature from 300 °C to 500 °C, relatively strong BIT peaks were seen.

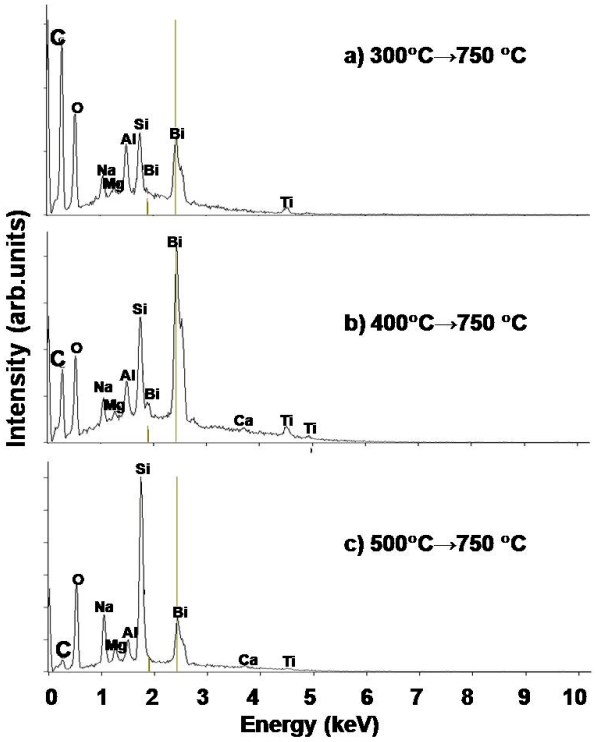

Fig. 1. EDS spectra of BIT on MgO(100) substrates pyrolyzed at various temperatures.

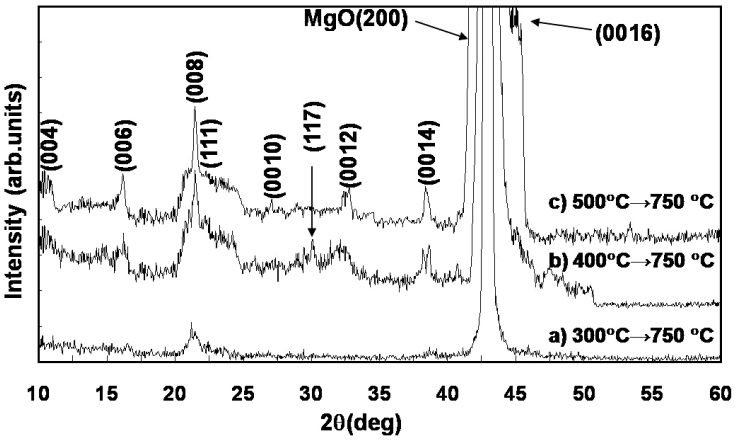

Fig. 2. XRD θ-2θ scans of the BIT films pyrolyzed at various temperatures, followed by final annealing at 750°C.

To further elucidate the orientation of the films, their in-plane alignment was investigated by X-ray pole-figure analysis. We chose the BIT(117) reflection for study because of its high intensity and separation from the MgO substrate reflection. Figure 3

shows the (117)-pole figures for BIT films on MgO substrates. After 2θ was set at 30.06°, which corresponds to the BIT(117) reflection, the BIT film was rotated from $\varphi = 0°$ to 360° at tilted angles between $\psi = 30°$ and 70°. As shown in Figure 3**c**, the four sharp spots due to the BIT(117) reflection at $\psi \approx 40°$ were observed at every 90° for the film pyrolyzed at 500 °C. The [117] direction of the BIT grains is aligned in the *ac*-plane of the MgO lattice with the polar angle of about 50° from the *c* axis of the substrate. This means that this film was grown texturally on the substrate surface. However, highly oriented films pyrolyzed at 300 °C and 400 °C that confirmed no pyrochlore phases by XRD $\theta - 2\theta$ scans showed no distinct spots or rings.

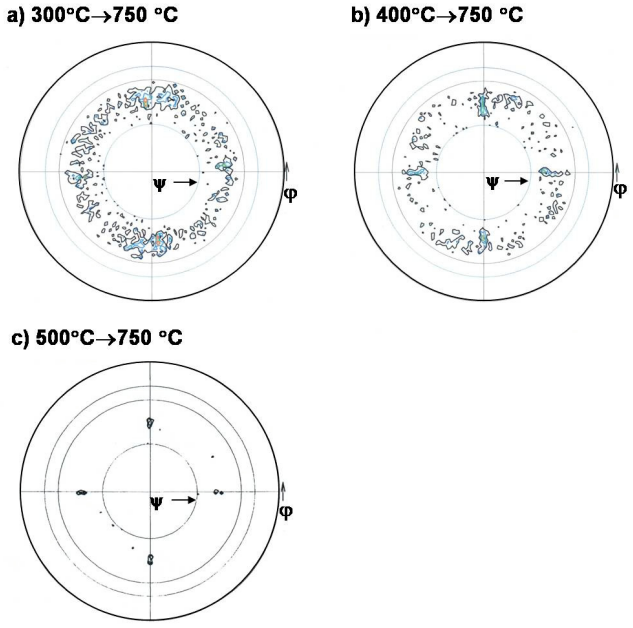

Fig. 3. X-ray pole-figures of BIT films pyrolyzed at various temperatures, followed by final annealing at 750 °C.

BIT has an orthorhombic unit cell with an orthorhombic distortion, *b*/*a* (*a* = 5.410 Å and *b* = 5.448 Å) equal to 1.007 at room temperature. The unit cell parameter of BIT at room temperature is not close to the cubic cell of MgO. However, the tetragonal lattices constant *a* of BIT is 3.86 Å [6] when BIT transforms into a tetragonal unit cell at temperatures above T_c. Therefore, texturally grown BIT thin films pyrolyzed at 500 °C may be obtained by annealing above T_c, *i.e.*, 750 °C, due to more similarity between the lattice constants of BIT films and MgO substrates.

However, the films pyrolyzed at 300 °C and 400 °C had no epitaxial relationship with the substrates after the same heat treatment temperature. This growth behavior can be explained by the fact that precursor films pyrolyzed at lower temperatures are

assumed to contain some residual carbon or carbon hydroxides, as shown in Fig. 1. In this case, crystallization and textured-growth of the films may be suppressed by residual carbon during final heat treatment, since crystallization, textured-growth and decomposition of organic components concurrently proceeded.

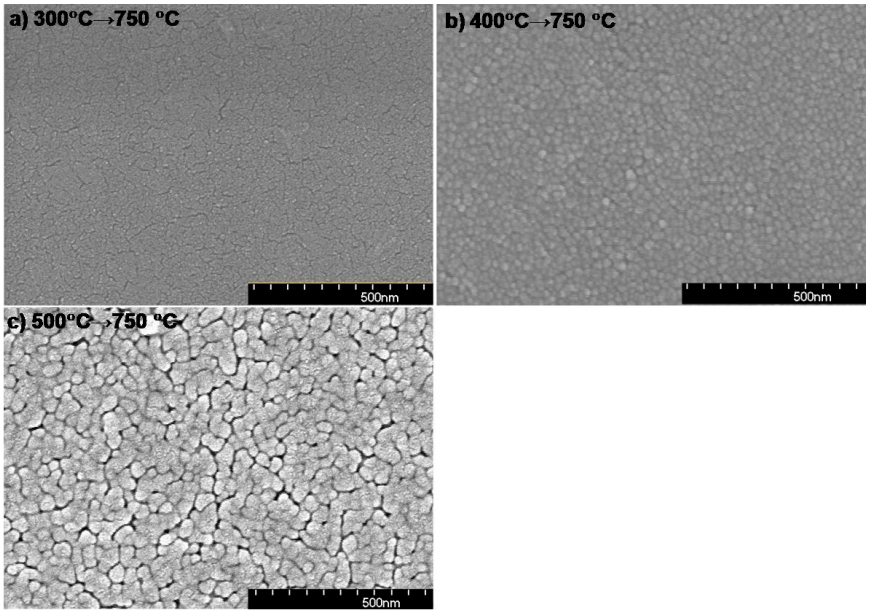

Fig. 4. FE-SEM images (×100,000) of BIT films pyrolyzed at various temperatures, followed by final annealing at 750 °C.

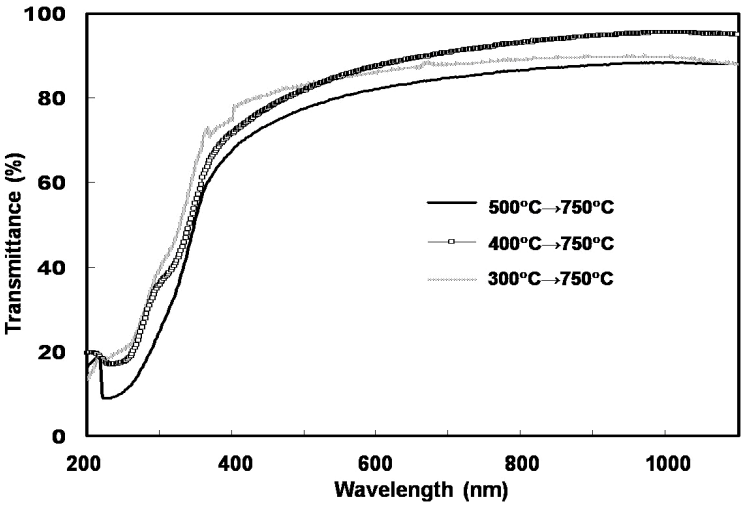

Fig. 5. Transmittance of BIT films pyrolyzed at various temperatures, followed by final annealing at 750 °C.

Figure 4**a–c**, and **e** show the FE-SEM images of BIT films pyrolyzed at different temperatures. For the highly-textured films pyrolyzed at 500 °C, a fine grain structure is evident, with grains of 80~100 nm, while the surface morphology of the film pyrolyzed at 300 °C was smooth and there was no texture observed.

Figure 5 shows the optical transmission spectra for the annealed BIT film pyrolyzed at various temperatures. The films are colorless and transparent to light of wavelength longer than about 400 nm, and exhibit a sharp absorption edge. Maximum transmittance exceeds 80%, which indicates that the films do not have intrinsic absorption. However, the optical absorption edge of the annealed BIT pyrolyzed at 500 °C shifts toward longer wavelengths. The optical band gap E_g can be determined from absorption coefficient α, and has been investigated by plotting $(\alpha h\nu)^{1/2}$ *versus* $h\nu$ (for indirect allowed transition) and $(\alpha h\nu)^2$ *versus* $h\nu$ (for direct allowed transition) [7]. In this study, the best straight line plot extended over most data points is $(\alpha h\nu)^{1/2}$ *versus* $h\nu$, as shown in Figure 6. A linear behavior is presented in certain range, thus supporting the interpretation of indirect bandgap for BIT [7]. It is observed that the bandgap of the thin films increases from 3.53 eV to 3.67 eV with decreasing of prefiring temperature from 500 °C to 300 °C. Furthermore, the measured bandgap values for larger particle size of the film are found to be lower than those of smaller particle size of the films. The blue shift in the absorption band edge has been claimed as a consequence of quantum-size effect with a decrease of particle size. The peaks of XRD for the annealed BiT pyrolyzed at 300 °C are broadened, and there is no distinct grain structure in SEM. Therefore, there is a possibility of the presence of many small crystallites in the films which may behave like an amorphous phase and may contribute to blue shift.

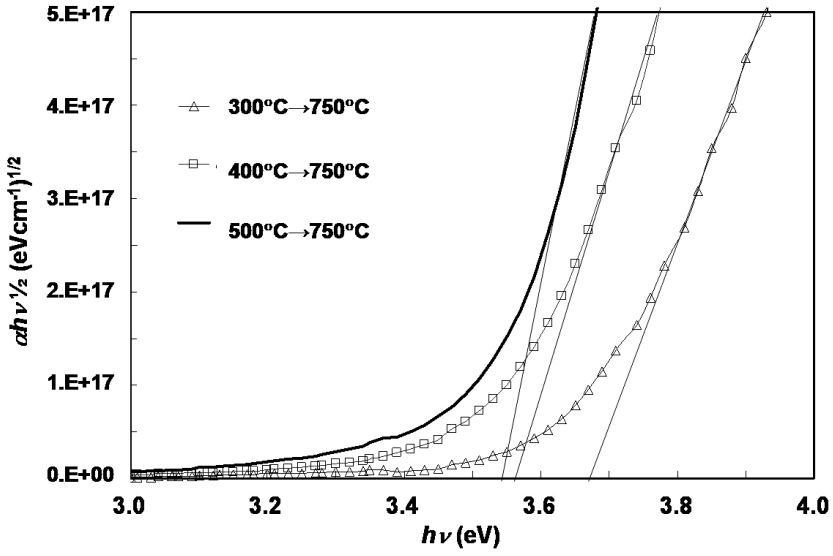

Fig. 6. Band gap of BIT films pyrolyzed at various temperatures, followed by final annealing at 750 °C.

To examine whether the crystal structure and optical property of BIT films on MgO substrates are affected by the mode of elimination of organic components, the prefiring temperature was varied. Here, we mainly present the effect of residual carbon in the precursor on the properties of the BIT films, particularly considering the effect of prefiring temperature on the textured-growth and optical properties. The results enabled us to develop guidelines for preparing high quality BIT films from a naphthenic acid.

4. Conclusions

BIT films were texturally grown on MgO(100) substrates by using a metal naphthenate precursor. After annealing at 750 °C, the X-ray pole-figure analysis indicated that the pyrolyzed BIT at 500 °C has an epitaxial relationship with the MgO(100) substrates. For the highly-textured film pyrolyzed at 500 °C, a distinct grain structure is evident, with grains of 80–100 nm. Band gap of the films increases from 3.53 eV to 3.67 eV with decreasing prefiring temperature from 500 °C to 300 °C and with decreasing particle size.

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