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Preparation of Epitaxial $Bi_4Ti_3O_{12}$ Thin Films on $LaAlO_3(012)$ Substrates by a Spin Coating-Pyrolysis Process

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Abstract. Bismuth titanate $(Bi_4Ti_3O_{12})$ thin films were prepared on $LaAlO_3(012)$ substrates by a spin coating-pyrolysis process using metal naphthenates as starting materials. The *c*-axis oriented $Bi_4Ti_3O_{12}$ thin films, which contained no second phases as confirmed by X-ray diffraction θ–2θ scans, were obtained by heat-treatment in air at temperatures of 600°C and above. X-ray diffraction pole-figure analysis showed that the $Bi_4Ti_3O_{12}$ thin film has an epitaxial relationship with the $LaAlO_3$ substrate.

Keywords: $Bi_4Ti_3O_{12}$, $LaAlO_3(012)$, epitaxial relationship

1. Introduction

Recently, ferroelectric thin films have attracted much attention for application in non-volatile memories and capacitors for dynamic random access memories (DRAMs) due to their reversible spontaneous polarization and high dielectric constant, respectively. In particular, $Bi_4Ti_3O_{12}$ (BTO) is an interesting ferroelectric material with a layered-perovskite structure that shows excellent anisotropic properties. Single crystal BTO exhibits coercive field values (E_c) of 50 and 3.5 kV/cm, and spontaneous polarization values (P_s) of 50 and 4 μC/cm^2, along the *a*- and *c*-axis, respectively [1]. Although the P_s along the *c*-axis is smaller than that of $Pb(Zr, Ti)O_3$, BTO thin films with *c*-axis orientation are expected to be applied to electronic memory devices requiring a low drive power owing to the small E_c along the *c*-axis.

The preparation of BTO thin films with high *c*-axis orientation has been attempted using several techniques such as rf sputtering [2], sol-gel [3], metal organic chemical vapor deposition (MOCVD) [4,5] and pulsed laser deposition (PLD) [6].

Wet chemical solution-based processes such as sol-gel method and spin coating-pyrolysis [7–10] process have been noted as promising way for oxide thin film fabrication because of low cost and the fact that they allow precise control of the chemical composition of films and can be used for deposition over a large area. Metal naphthenates are more advantageous than metal alkoxides as starting materials, in terms of cost, stability in air and ease of handling. However, there is limited information available on the growth of high quality epitaxial BTO thin films prepared by chemical processes.

In the present work, preparation of epitaxial BTO thin films on $LaAlO_3(012)$ (LAO) (hexagonal index, h. i.) substrates has been carried out by a spin coating-pyrolysis process. The effect of annealing temperature on the crystallinity and epitaxy of the BTO thin films has been studied.

2. 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 coating solution) to achieve an appropriate viscosity for deposition of smooth films.

Single-crystal LAO(012) was selected as a substrate. This substrate was cleaned in neutral solution (Merck), immersed in H_2O_2 solution, and rinsed in

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toluene. The substrates were spin-coated with the dropping solution at 4000 rpm for 10 sec and preheated in air at 500°C for 10 min. These precursor films were subjected to heat treatments at 600°, 650°, 700° and 750°C for 30 min in air by directly inserting the samples into a preheated furnace. The samples were rapidly cooled (cooling rate: ~200°C/min at 675°C).

The thickness of the annealed BTO films was ~0.15 μm, as determined by observations of fracture cross sections with a scanning electron microscope (SEM) (JEOL JSH-5400). The crystallinity and in-plane crystallographic alignment of the annealed films were examined by X-ray diffraction (XRD) (MAC Science MXP^{3A}) θ–2θ scans and pole-figure analysis (β scans) by the Schulz reflection method.

3. Results

Figure 1 shows XRD patterns of BTO thin films on LAO(012) substrates heat-treated at various temperatures. As shown in Fig. 1, a single phase BTO film with *c*-axis orientation was observed in the XRD θ–2θ scans, thus, amorphous precursor films were crystallized after the final heat treatments at 600°–750°C. The reflections of other phases such as pyrochlore or misoriented BTO(117) were not observed in these BTO films, which indicates that the films are highly oriented. The highest heat-treatment temperature gave the strongest BTO peaks. The highest peak intensities were observed in the film annealed at 750°C.

Using the LAO(012) peak as an internal calibration standard, the lattice constant perpendicular to the substrate surface ($d_\perp$) of the highly oriented BTO film heat-treated at 750°C was determined to be 3.281 nm. The $d_\perp$ value is close to the *c*-axis ($c_0 = 3.2815$ nm) of bulk BTO single crystals (ICDD File 35-079).

XRD rocking curves of the BTO(008) and LAO(012) reflections for the film heat-treated at 750°C are shown in Fig. 2. The full widths at half maximum (FWHM) of the rocking curves of the BTO(008) and LAO(012) reflections were 0.75° and 0.66°, respectively. Such a narrow FWHM of the film indicates that the BTO film was highly oriented and the deviation in tilt of the films (00*l*) lattice planes with respect to the substrate surface was very small.

To investigate the in-plane alignment of BTO films, we performed XRD pole-figure analysis using the Schulz reflection method. We chose the BTO(117) reflection for study because of it's high intensity and separation from the LAO substrate reflection. Figure 3

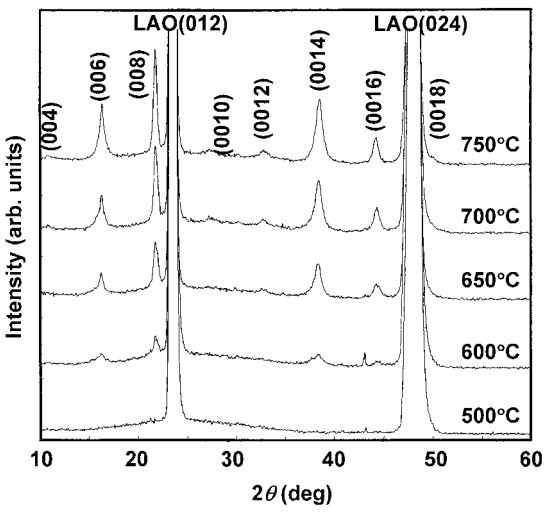

Fig. 1. XRD θ–2θ scans of the BTO films on LAO(012) substrates heat-treated at various temperatures.

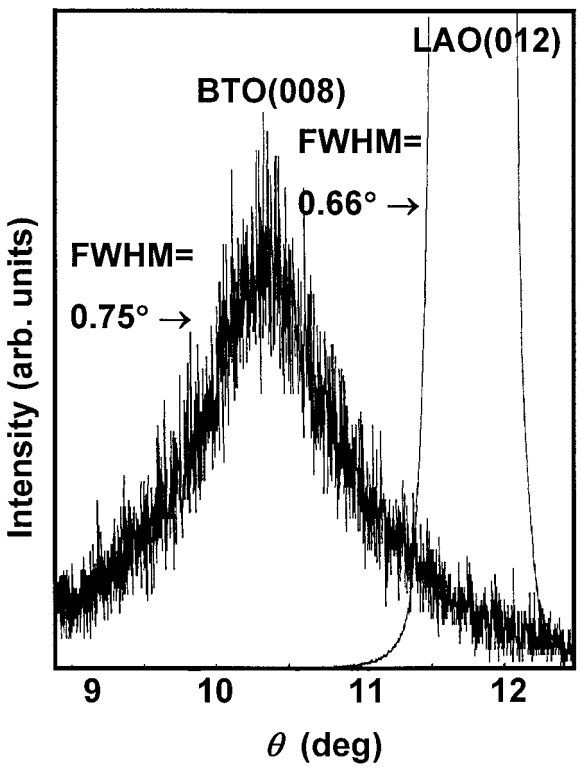

Fig. 2. XRD rocking curves of the BTO(008) and the LAO(012) reflections for the film heat-treated at 750°C.

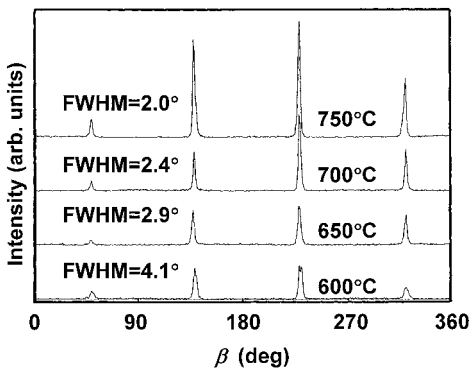

Fig. 3. Line profiles of β scans of the BTO(117) reflection for the films heat-treated at various temperatures.

shows the line profiles of β scans for which the α angle was fixed at 40°. The β scans of films heat-treated at 600°–750°C exhibit four sharp peaks. The intensity of the peaks increased and the FWHM of the peaks along the β direction decreased with increasing final heat-treatment temperature. A comparison of the peak intensities in Fig. 1 with those in Fig. 3, indicates a direct relationship between the final heat-treatment temperature and the crystallinity and epitaxy of BTO on LAO.

Figure 4 shows the (117)-pole-figures for films on LAO heat-treated at 600°C (a) and 750°C (b), respectively. After setting the 2θ at 30.057°, which corresponds to the BTO(117) reflection, the film was rotated from $\beta = 0°$ to $\beta = 360°$ at a tilt angle of $\alpha = 30°$ to $\alpha = 60°$. As shown in Fig. 4, the four sharp spots of the (117) reflection were observed every 90°. The [117] direction of the BTO grains is aligned in the *ac*-plane of LAO lattice with the polar angle of about 50° from the *c*-axis of the substrate. This means that these films were grown epitaxially on the substrate surface.

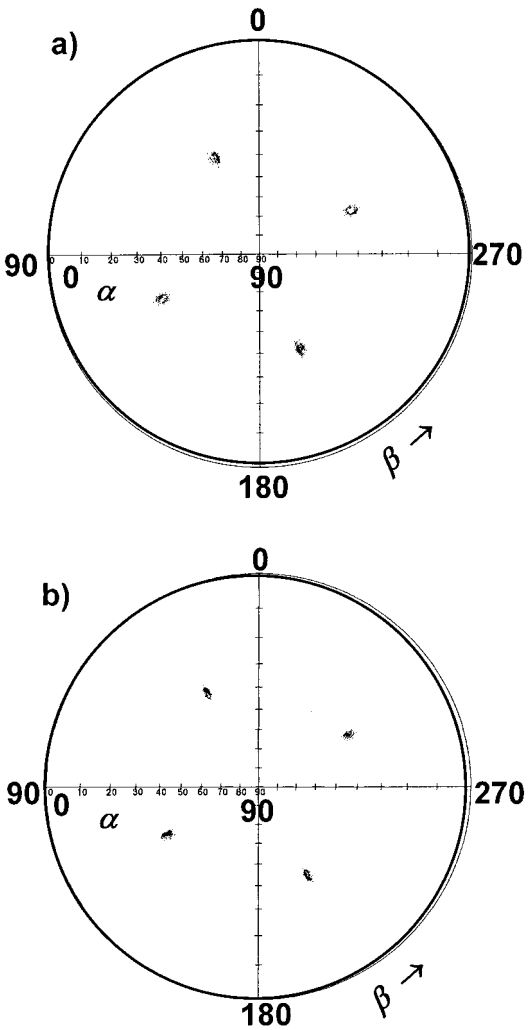

Fig. 4. Pole-figures of the BTO(117) reflection for the films heat-treated at 600°C (a) and 750°C (b).

4. Discussion

In this work, the epitaxial growth can be explained by the lattice-mismatch with LAO substrates at high temperature.

BTO has an orthorhombic unit cell with an orthorhombic distortion, b/a ($a_0 = 0.541$ nm and $b_0 = 0.545$ nm), of 1.007 at room temperature. On heating BTO, the lattice parameters expand at essentially linear rate at 675°C ($T_c =$ Curie temperature). The a parameter expands at a faster rate than b, so that the orthorhombic distortion decreases with increasing temperature. At T_c, a and c parameters undergo a sudden expansion and b contracts. Above T_c, the orthorhombic distortion disappears, and the unit cell seems to become tetragonal [11]. It may be noted that the tetragonal a of BTO is 0.386 nm, approximately the same as the lattice constants of perovskite-type compounds. LAO has a rhombohedral structure, however, its interaxial angle is so close to 60°, i.e., 60.1°, that LAO is often regarded as pseudocubic. $LAO(012)_{h.i.}$ approximately corresponds to LAO(001) (pseudocubic index, p.c.i.) and $LAO[421]_{h.i.}$ to $LAO[100]_{p.c.i.}$. The unit cell

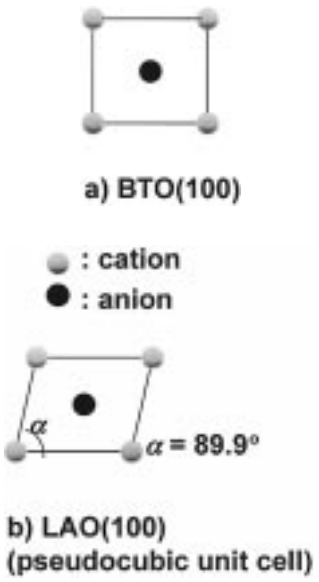

Fig. 5. Schematic drawing of arrangement of ions of the BTO(100) and the LAO(012).

parameter of the LAO pseudocubic cell is 0.379 nm [12]. The unit cell parameter (a or b) of BTO at room temperature is not close to pseudocubic cell of LAO. However, the tetragonal a of BTO is 0.386 nm [11], when BTO transforms to a tetragonal unit cell at temperatures above T_c, as shown in Figs. 5(a) and (b). Therefore, epitaxial BTO thin films may be obtained by the approach of the lattice constants of BTO thin films and LAO substrates by the annealing above T_c, i.e., 700° and 750°C. However, the films annealed at 600° and 650°C had an epitaxial relationship with the substrates, although they showed smaller crystallinity and larger FWHM value along the β direction in the pole-figure analysis than those for the films annealed above T_c. In order to explain the epitaxial growth in our films annealed below T_c, we illustrated atomic ion framework and lattice constants of LAO(012), as shown in Fig. 6. We assume that, in the films annealed below T_c, the small lattice-mismatch between the BTO along a-/b-axis ($a_0 = 0.541$ nm and $b_0 = 0.545$ nm) and LAO ($\sqrt{2}a = 0.5359$ nm) may favor the c-axis orientation.

We can conclude that high annealing temperatures above T_c improve the epitaxy and the crystallinity of BTO films.

It should be emphasized that several reports on the preparation of ''highly oriented'' BTO films by using

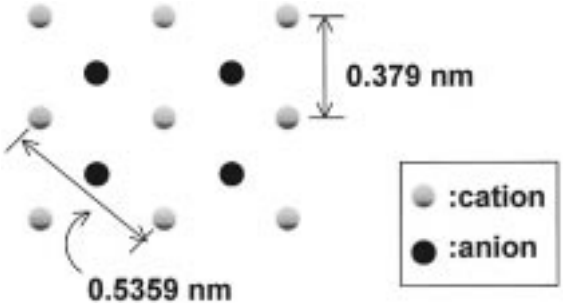

Fig. 6. Atomic ion framework and lattice constants of the LAO(012).

the chemical solution method have been published [13,14]. In these reports, however, the alignments of the films were discussed based only on the d-values determined from the XRD θ–2θ scans. In our results, the alignment of the film was clearly confirmed by XRD pole-figure analysis.

5. Summary

Highly c-axis oriented BTO thin films were prepared on LAO(012) substrates by a spin coating-pyrolysis process using metal naphthenates as starting materials. BTO thin films with no second phases and c-axis orientation, as confirmed by XRD θ–2θ scans, were obtained by heat-treatment at 600°C and above, in air. XRD pole-figure analysis showed that the thin films have an epitaxial relationship with the LAO substrate; the [117] direction of the BTO grains is aligned in the ac-plane of LAO lattice with the polar angle of about 50° from the c-axis of the substrate.

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