

## BARIUM TITANATE THIN FILMS PREPARED ON MgO (100) SUBSTRATES BY COATING-PYROLYSIS PROCESS

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**Abstract** – Barium titanate (BaTiO<sub>3</sub>) thin films were prepared on MgO (100) substrates using metal naphthenate solution by a coating-pyrolysis process. Amorphous films pyrolyzed at 470 °C were crystallized to BaTiO<sub>3</sub> phase by heat treatment at higher temperatures. The crystallinity and alignment of the films depended on temperature and on atmosphere during heat treatment. Epitaxial BaTiO<sub>3</sub> film having (100)-orientation was obtained by heat treatment at 900 °C under oxygen partial pressure of  $2 \times 10^{-4}$  atm. The epitaxial BaTiO<sub>3</sub> film had a lattice constant of 0.401<sub>6</sub> nm and displayed a smooth surface with some pores dispersed on the surface. By heat treatment in air, amorphous BaTiO<sub>3</sub> film was obtained at 900 °C or below, and textured film with less strong (100) orientation was obtained at 1,200 °C and consisted of grains with diameter about 0.3 μm.

**Key words:** Barium Titanate, Thin Film, Coating-Pyrolysis, Crystallinity, Epitaxy

### INTRODUCTION

Bulk semiconducting doped-BaTiO<sub>3</sub> possesses positive temperature coefficients of resistivity (PTCR) characteristics and is applied to electrical devices such as degaussers in color TV and self-regulated heaters and sensors [Moulson and Herbert, 1990]. BaTiO<sub>3</sub> thin films are promising materials for electronic device applications because of their useful ferroelectricity, high dielectric constant and large electro-optic coefficients [Glass, 1987]. Thin films such as BaTiO<sub>3</sub>, Pb(Zr, Ti)O<sub>3</sub> and TiO<sub>2</sub> were prepared by various processing techniques such as metal-organic chemical vapor deposition (MOCVD) [Chung et al., 1997; Lee et al., 1997; Kaiser et al., 1995; Willis et al., 1992], laser ablation [Nose et al., 1994], radio-frequency sputtering [Kim et al., 1995; Fujimoto et al., 1989], pulsed laser deposition [Kim and Kwok, 1995; Srikant et al., 1995; Norton et al., 1992] and reactive evaporation [Yano et al., 1994]. In particular, epitaxial BaTiO<sub>3</sub> thin films having a smooth surface are required for electro-optical applications because of their low propagation loss. Various substrates such as MgO (100), LaAlO<sub>3</sub> (100), SrTiO<sub>3</sub> (100), MgO/GaAs (100) and Pt/MgO (100) were used for preparation of the epitaxial BaTiO<sub>3</sub> thin films. Among these various substrates, MgO can facilitate a waveguiding in BaTiO<sub>3</sub> thin films because the refractive index of MgO ( $n=1.7$  at 0.6 μm) is lower than that of BaTiO<sub>3</sub> ( $n=2.4$  at 0.6 μm). The lattice constant of MgO (NaCl-type structure) is 0.4213 nm, while tetragonal BaTiO<sub>3</sub> (perovskite structure) has lattice constants of  $a=0.3994$  nm and  $c=0.4038$  nm. The lattice misfit between MgO and tetragonal BaTiO<sub>3</sub> is 5.2% and 4.3% along the  $a$ - and  $c$ -axes, respectively. These misfit values are larger than that between BaTiO<sub>3</sub> and SrTiO<sub>3</sub>: 2.3% and 3.4% along the  $a$ - and  $c$ -axes, respectively. So it is considered to be more difficult to

prepare epitaxial BaTiO<sub>3</sub> films on MgO than on SrTiO<sub>3</sub>.

Actually, so far as we know, there have been no reports about the preparation of epitaxial BaTiO<sub>3</sub> films on MgO substrates by a chemical solution process. A number of papers have been reported about polycrystalline BaTiO<sub>3</sub> thin films prepared by sol-gel [Kamalasanan et al., 1993] and a chemical solution process [Benomar et al., 1994]. Chemical solution processes such as coating-pyrolysis (CP) or sol-gel process have the following advantages: they are simple and low-cost chemical processes that are easily applicable to the substrates of any shape and size.

Crystallinity and orientation of BaTiO<sub>3</sub> thin films greatly depend on the preparation methods, preparation conditions and substrate materials. In case of the orientation of BaTiO<sub>3</sub> thin films on MgO (100),  $a$ -axis-oriented thin films were prepared by MOCVD [Kaiser et al., 1995] and by pulsed laser deposition using ArF excimer laser [Kim and Kwok, 1995]. Whereas,  $c$ -axis-oriented thin films were prepared by RF-sputtering [Kim et al., 1995; Fujimoto et al., 1989] and by pulsed laser deposition using Nd:YAG laser [Srikant et al., 1995]. Recently, we succeeded in fabricating epitaxial BaTiO<sub>3</sub> thin films on SrTiO<sub>3</sub> substrates by CP process [Kim et al., 1996, 1997]. The epitaxial BaTiO<sub>3</sub> thin films were pseudo-cubic with a tetragonality of 1.003.

In this paper, BaTiO<sub>3</sub> thin films on MgO (100) substrates were prepared by CP process using mixed metal-naphthenate solution. By heat treatment under low oxygen partial pressure or in air, the crystallinity, in-plane alignment and surface morphology of BaTiO<sub>3</sub> thin films were investigated.

### EXPERIMENTAL

Commercial barium- and titanium-naphthenates were mixed for preparing a coating solution, in which the molar ratio of Ba/Ti was set as 1.0. This solution was diluted with to-

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luene to adjust a concentration and viscosity for spin coating. The metal concentration of the coating solution was about 0.2 mmol/g. The solution was spin-coated on cleaved MgO (100) substrates at 2,000 rpm for 5 sec. The coated films were pyrolyzed at 470°C for 10 min in air to eliminate organic components. The coating and pyrolysis condition was the same as that for the preparation of the epitaxial BaTiO<sub>3</sub> films on SrTiO<sub>3</sub> in our previous paper [Kim et al., 1996, 1997]. The pyrolyzed films were heat treated in a tube furnace at 800°C and 900°C for 2 h in air and under a gas mixture of argon and oxygen with oxygen partial pressure ( $p(\text{O}_2)$ ) of  $2 \times 10^{-4}$  atm, respectively. The flow rate of the gas mixture was set as 300 ml/min. The  $p(\text{O}_2)$  was checked by zirconia-type oxygen analyzer at an outlet of a tube furnace. In addition, some of the pyrolyzed films were heat treated at higher temperatures of 1,000°C and 1,200°C for 2 h in air using a LaCrO<sub>3</sub>-type high-temperature furnace.

Thermogravimetric and differential thermal analyses (TG/DTA) were carried out to determine the decomposition behaviors of barium naphthenate, titanium naphthenate and the mixed coating solution. The samples for TG/DTA were dried at 110°C for 12 h to remove the toluene. Thermal analyses were performed to a temperature up to 600°C with a heating rate of 10°C/min and a flow rate of air of 300 ml/min. The thickness of the final films was about 0.3 μm, confirmed by weight gain and by observation of a cross section of the films with a scanning electron microscope. Crystallinity and alignment of the films were examined by x-ray diffraction (XRD)  $\theta/2\theta$  scans and x-ray pole figures using Cu K $\alpha$  radiation with a graphite bent crystal monochromator. Surface morphologies of the BaTiO<sub>3</sub> thin films were observed by scanning electron microscope (SEM).

## RESULTS AND DISCUSSION

Fig. 1 shows TG/DTA plots of the barium and titanium naphthenates and the mixed coating solution. Weight losses corresponding to decompositions of barium and titanium naphthenates began around 200°C and completed at about 490°C, whereas that of the mixed coating solution completed at about 460°C, which was slightly lower than the decomposition temperatures for the metal naphthenates. The decomposition products of barium and titanium naphthenates were BaCO<sub>3</sub> and TiO<sub>2</sub>, respectively, as confirmed by XRD  $\theta/2\theta$  scans. The decomposition from barium naphthenate to BaCO<sub>3</sub> proceeded in two steps with a small exothermic peak at 350°C and a large exothermic peak at 480°C as shown in Fig. 1(b). For titanium naphthenate, two steps with exothermic peaks at 360°C and 440°C were observed. The decomposition from the coating solution to a mixture of BaCO<sub>3</sub> and TiO<sub>2</sub> was pseudo-one step having the exothermic peak at 440°C. These decomposition behaviors are thought to be related to the specific structure and a particular interaction of the organic metal components.

The spin-coated films on MgO substrates were pyrolyzed at 470°C based on the results of TG/DTA. The pyrolyzed films were amorphous according to the XRD  $\theta/2\theta$  scan results not shown here, similar to the pyrolyzed films prepared on SrTiO<sub>3</sub> substrates. In the case of the BaTiO<sub>3</sub> films on SrTiO<sub>3</sub>, the amorphous pyrolyzed films were crystallized show-

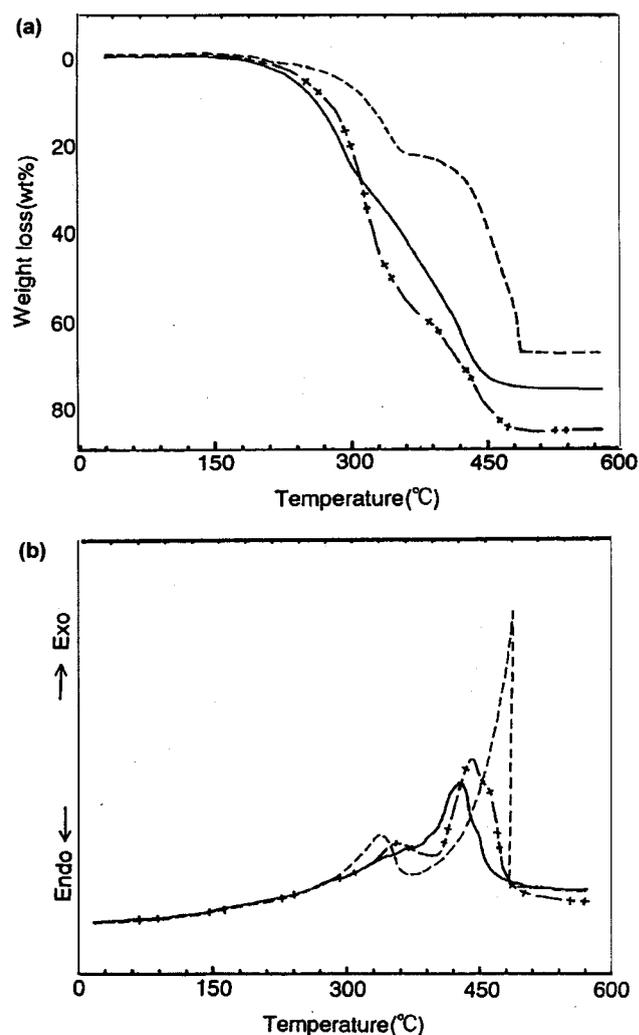


Fig. 1. TG/DTA plots of barium naphthenate (- - -), titanium naphthenate (-+--+), and mixed coating solution (—).

ing highly oriented peaks of BaTiO<sub>3</sub> after heat treatment at 800°C and higher temperatures in air [Kim et al., 1996, 1997]. XRD  $\theta/2\theta$  scans of the films heat-treated under low- $p(\text{O}_2)$  at 800°C and 900°C are shown in Fig. 2. The films heat-treated at 800°C were still amorphous as shown in Fig. 2 (a). The film heat-treated at 900°C under low- $p(\text{O}_2)$  showed strong (h00) reflections together with much weaker (101) and (111) reflections. This suggests that the film consisted of mainly (h00) oriented BaTiO<sub>3</sub> grains; while the film heat-treated in air at 900°C was still amorphous, which was similar to the film heat-treated at 800°C as shown in Fig. 3 (a). When the film was heat treated at higher than 1,000°C and 1,200°C, the peaks of BaTiO<sub>3</sub> appeared at 1,000°C and increased with the temperature. However, the film heat treated at 1,200°C showed strong BaTiO<sub>3</sub> (101) and (111) reflections together with BaTiO<sub>3</sub> (h00) reflections, suggesting that the film was mostly polycrystalline with less strong (100)-preferred orientation.

Using substrate MgO (200) peak as an internal calibration standard, we estimated the lattice constants for the films heat-treated under low- $p(\text{O}_2)$  at 900°C and in air at 1,200°C to be 0.401<sub>6</sub>, 0.402<sub>7</sub> nm, respectively. These values are between *a*-

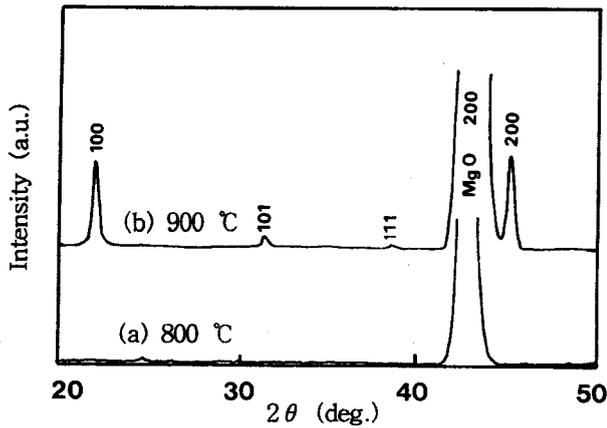


Fig. 2. XRD  $\theta/2\theta$  scans of BaTiO<sub>3</sub> films heat treated under low- $p(\text{O}_2)$  at (a) 800 °C and (b) 900 °C.

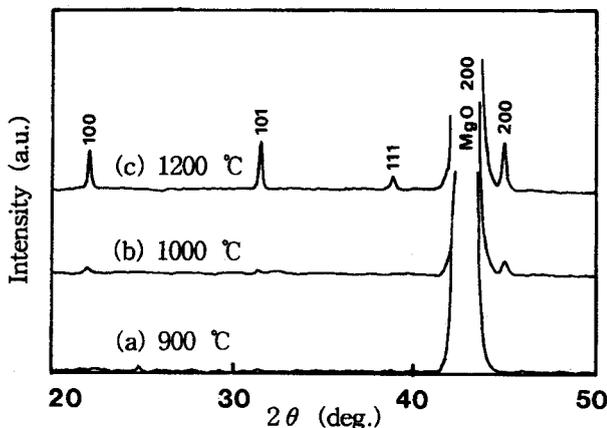


Fig. 3. XRD  $\theta/2\theta$  scans of BaTiO<sub>3</sub> films heat treated in air at (a) 900 °C, (b) 1,000 °C and (c) 1,200 °C.

and  $c$ -axis values of the bulk tetragonal BaTiO<sub>3</sub> and closer to the  $a$ -axis value of the bulk cubic BaTiO<sub>3</sub>. These values are larger than that (0.399, nm) of the BaTiO<sub>3</sub> films on SrTiO<sub>3</sub> substrates [Kim et al., 1997]. It is difficult to judge using the lattice constant alone whether the films prepared have a tetragonal phase or cubic. In this paper, BaTiO<sub>3</sub> is regarded as a cubic phase because of no peak splitting to 200 and 002, or 101 and 110 reflections [Shintani et al., 1970; Iijima et al., 1990], and reflective indexes in the XRD  $\theta/2\theta$  scans were denoted according to cubic BaTiO<sub>3</sub>. Full width at half maximum (FWHM) values of BaTiO<sub>3</sub> (200) reflection in the XRD  $\theta/2\theta$  scans were measured to evaluate the crystallinity of BaTiO<sub>3</sub> phase in the films. FWHMs for the films heat treated under low- $p(\text{O}_2)$  at 900 °C and in air at 1,200 °C were estimated to be 0.80 and 0.63°, respectively. This suggests that crystallinity of BaTiO<sub>3</sub> is improved by adopting higher annealing temperature.

Next, texture coefficient (TC) values were calculated to evaluate the preferred orientation of these BaTiO<sub>3</sub> films according to the following equation [Yoon et al., 1987],

$$TC(hkl) = \frac{I(hkl)/I_0(hkl)}{(1/N)\sum(I(hkl)/I_0(hkl))} \quad (1)$$

where, TC ( $hkl$ ) is the texture coefficient of the plane ( $hkl$ ),

Table 1. Texture coefficient (TC) values

Heat-treatment conditions	$(hkl)$		
	(100)	(101)	(111)
900 °C under low- $p(\text{O}_2)$	2.8	0.1	0.1
1,200 °C in air	2.3	0.4	0.4

and  $I(hkl)$  and  $I_0(hkl)$  are measured and standard [JCPDS cards No. 31-174] X-ray intensity of the plane ( $hkl$ ), respectively.  $N$  is the number of reflections. When TC ( $hkl$ ) is more than 1, the ( $hkl$ ) plane is said to be preferably oriented. TC ( $hkl$ ) values calculated from the films heat treated under low- $p(\text{O}_2)$  at 900 °C and in air 1,200 °C were given in Table 1. TC (100) values of these films are larger than 1.0, suggesting that the films showed stronger ( $h00$ ) orientation than non-oriented BaTiO<sub>3</sub>.

In-plane alignment of the films was investigated by XRD pole-figure analysis using the Schulz reflection method of BaTiO<sub>3</sub> (101)/(110) reflections, having high intensity and separability from the MgO substrate reflections. The film was rotated from  $\beta=0^\circ$  to  $360^\circ$  at a tilted angles between  $\alpha=30^\circ$  and  $60^\circ$ . As shown in Fig. 4(a), the film heat treated under low- $p(\text{O}_2)$  at 900 °C exhibits four sharp spots at every  $90^\circ$ . The  $\beta$  angles of these spots were  $45^\circ$ -rotated to MgO (111) reflections. This result indicates that most of ( $h00$ )-oriented BaTiO<sub>3</sub> grains in the film were epitaxially grown on MgO substrates and the relationship between BaTiO<sub>3</sub> and MgO was BaTiO<sub>3</sub> (100)//MgO (100) and BaTiO<sub>3</sub> [001]//MgO [001]. On the other hand, the film heat treated in air at 1,200 °C showed only traces of distinct spots beyond noise level in the pole-figure as shown in Fig. 4(b). The results of pole-figure analysis with TC (100) values mentioned above indicate that the film heat-treated under low- $p(\text{O}_2)$  at 900 °C had larger TC (100) value and showed a good in-plane alignment. On the other hand, the film heat treated in air at 1,200 °C showed much poorer in-plane alignment than the film heat treated under low- $p(\text{O}_2)$  at 900 °C, although the film showed larger TC (100) value and higher crystallinity. The good epitaxial quality of the film heat treated under low- $p(\text{O}_2)$  is thought to originate from the enhanced oxygen vacancy concentration, which is similar to that obtained from the preparation of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  films [McIntyre et al., 1992; Hou et al., 1994].

Fig. 5 shows scanning electron micrographs of free surfaces for the films. The film heat treated under low- $p(\text{O}_2)$  at 900 °C displayed a smooth surface with some pores dispersed on the surface, and the contour of grains was not recognized clearly in this magnification ( $\times 15,000$ ). The film heat treated at 1,200 °C in air consisted of textured grains with diameter about 0.3  $\mu\text{m}$  and gaps were recognized between each grain. This textured morphology of the film is similar to that of BaTiO<sub>3</sub> films prepared by MOCVD on LaAlO<sub>3</sub> substrates [Willis et al., 1992].

Compared to the preparation of the epitaxial BaTiO<sub>3</sub> films on SrTiO<sub>3</sub> substrates [Kim et al., 1996, 1997], higher annealing temperature and more precisely controlled atmosphere are required to obtain epitaxial BaTiO<sub>3</sub> films on MgO substrates. Higher annealing temperature and less strong orientation for the epitaxial BaTiO<sub>3</sub> films on MgO might be owing to larger lattice misfits between BaTiO<sub>3</sub> and MgO than those between BaTiO<sub>3</sub> and SrTiO<sub>3</sub>.

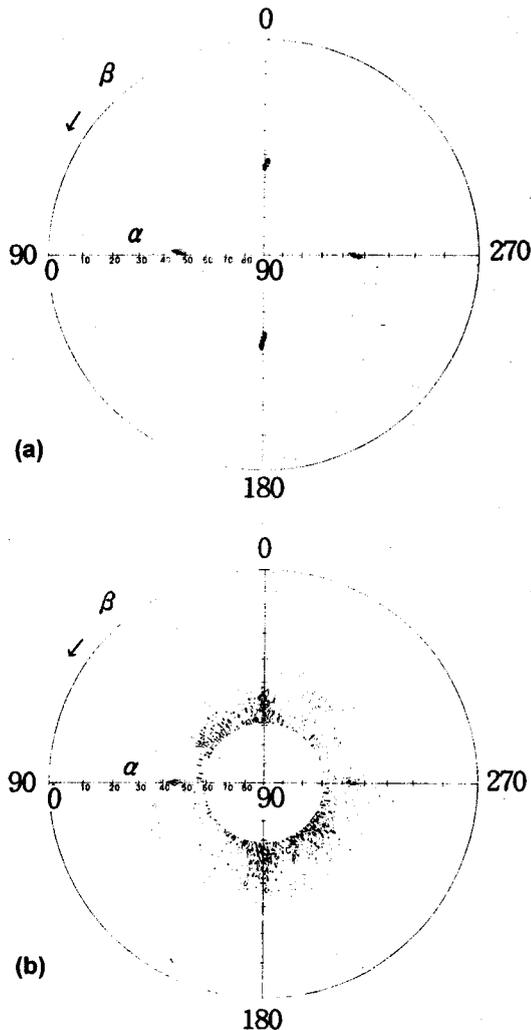


Fig. 4. Pole-figures of BaTiO<sub>3</sub> (101)/(110) reflections for the films heat treated (a) under low- $p(\text{O}_2)$  at 900°C and (b) in air at 1,200°C.

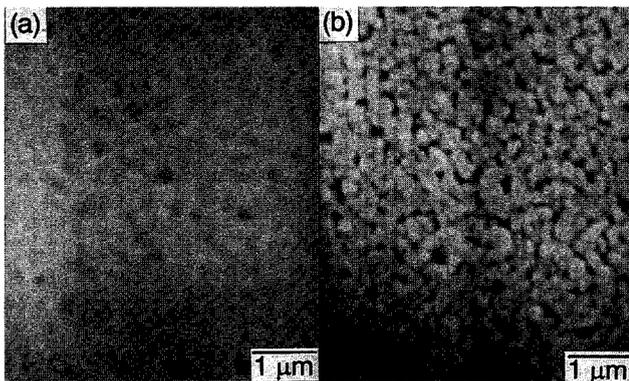


Fig. 5. Scanning electron micrographs of the free surfaces for the BaTiO<sub>3</sub> films heat treated (a) under low- $p(\text{O}_2)$  at 900°C and (b) in air at 1,200°C.

### CONCLUSIONS

BaTiO<sub>3</sub> thin films were prepared on MgO (100) substrates by CP process using metal naphthenate solution. The amor-

phous films pyrolyzed at 470°C were crystallized to BaTiO<sub>3</sub> phase by heat treatment at higher temperatures, and crystallinity and in-plane alignment of the films depended on temperature and on atmosphere during heat treatment. By heat treatment at 900°C under oxygen partial pressure of  $2 \times 10^{-4}$  atm, (100)-oriented epitaxial BaTiO<sub>3</sub> film was obtained and the film displayed a smooth surface with some pores dispersed on the surface. On the other hand, amorphous BaTiO<sub>3</sub> film was obtained by heat treatment at 900°C in air, and textured BaTiO<sub>3</sub> film with less strong (100) orientation was obtained at 1,200°C and consisted of grains with diameter about 0.3 μm.

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