

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

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Abstract – Barium titanate (BaTiO_3) 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_3 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_3 film having (100)-orientation was obtained by heat treatment at 900 °C under oxygen partial pressure of 2×10^{-4} atm. The epitaxial BaTiO_3 film had a lattice constant of 0.401₆ nm and displayed a smooth surface with some pores dispersed on the surface. By heat treatment in air, amorphous BaTiO_3 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_3 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_3 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_3 , $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ and TiO_2 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_3 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_3 (100), SrTiO_3 (100), MgO/GaAs (100) and Pt/MgO (100) were used for preparation of the epitaxial BaTiO_3 thin films. Among these various substrates, MgO can facilitate a waveguiding in BaTiO_3 thin films because the refractive index of MgO ($n=1.7$ at 0.6 μm) is lower than that of BaTiO_3 ($n=2.4$ at 0.6 μm). The lattice constant of MgO (NaCl-type structure) is 0.4213 nm, while tetragonal BaTiO_3 (perovskite structure) has lattice constants of $a=0.3994$ nm and $c=0.4038$ nm. The lattice misfit between MgO and tetragonal BaTiO_3 is 5.2 % and 4.3 % along the a - and c -axes, respectively. These misfit values are larger than that between BaTiO_3 and SrTiO_3 : 2.3 % and 3.4 % along the a - and c -axes, respectively. So it is considered to be more difficult to

prepare epitaxial BaTiO_3 films on MgO than on SrTiO_3 .

Actually, so far as we know, there have been no reports about the preparation of epitaxial BaTiO_3 films on MgO substrates by a chemical solution process. A number of papers have been reported about polycrystalline BaTiO_3 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_3 thin films greatly depend on the preparation methods, preparation conditions and substrate materials. In case of the orientation of BaTiO_3 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_3 thin films on SrTiO_3 substrates by CP process [Kim et al., 1996, 1997]. The epitaxial BaTiO_3 thin films were pseudo-cubic with a tetragonality of 1.003.

In this paper, BaTiO_3 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_3 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 BaTiO₃ films on SrTiO₃ 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 2×10^{-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 LaCrO₃-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 α radiation with a graphite bent crystal monochromator. Surface morphologies of the BaTiO₃ 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 BaCO₃ and TiO₂, respectively, as confirmed by XRD $\theta/2\theta$ scans. The decomposition from barium naphthenate to BaCO₃ 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 BaCO₃ and TiO₂ 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 SrTiO₃ substrates. In the case of the BaTiO₃ films on SrTiO₃, the amorphous pyrolyzed films were crystallized show-

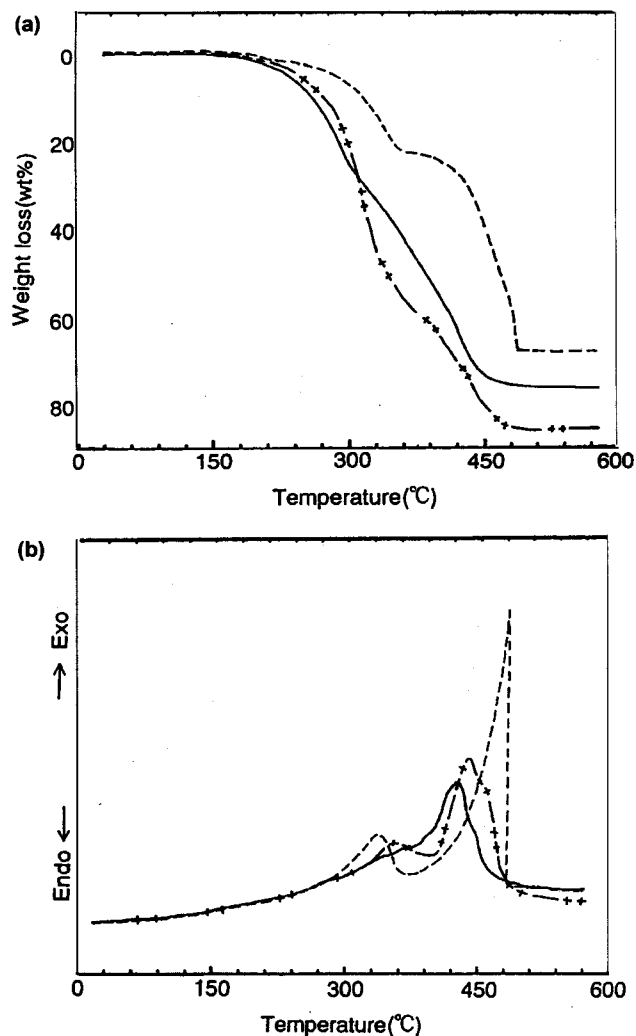


Fig. 1. TG/DTA plots of barium naphthenate (---), titanium naphthenate (-+--+), and mixed coating solution (—).

ing highly oriented peaks of BaTiO₃ 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 BaTiO₃ 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 BaTiO₃ appeared at 1,000°C and increased with the temperature. However, the film heat treated at 1,200°C showed strong BaTiO₃ (101) and (111) reflections together with BaTiO₃ (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 0.401₆, 0.402₇ nm, respectively. These values are between a -

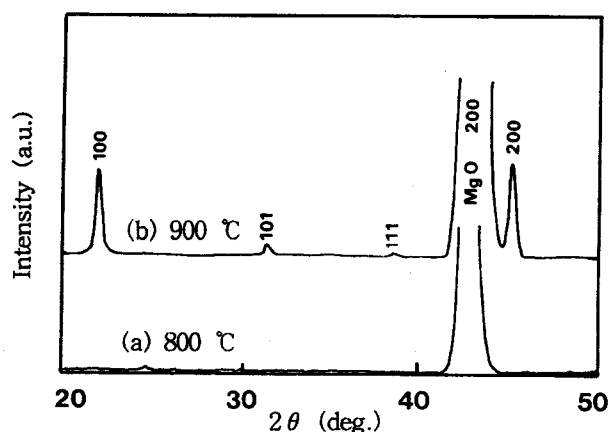


Fig. 2. XRD $\theta/2\theta$ scans of BaTiO_3 films heat treated under low- $p(\text{O}_2)$ at (a) 800 $^\circ\text{C}$ and (b) 900 $^\circ\text{C}$.

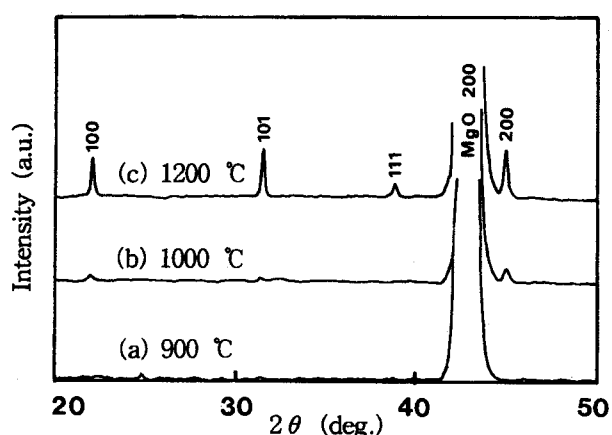


Fig. 3. XRD $\theta/2\theta$ scans of BaTiO_3 films heat treated in air at (a) 900 $^\circ\text{C}$, (b) 1,000 $^\circ\text{C}$ and (c) 1,200 $^\circ\text{C}$.

and c -axis values of the bulk tetragonal BaTiO_3 and closer to the a -axis value of the bulk cubic BaTiO_3 . These values are larger than that (0.399, nm) of the BaTiO_3 films on SrTiO_3 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_3 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_3 . Full width at half maximum (FWHM) values of BaTiO_3 (200) reflection in the XRD $\theta/2\theta$ scans were measured to evaluate the crystallinity of BaTiO_3 phase in the films. FWHMs for the films heat treated under low- $p(\text{O}_2)$ at 900 $^\circ\text{C}$ and in air at 1,200 $^\circ\text{C}$ were estimated to be 0.80 and 0.63 $^\circ$, respectively. This suggests that crystallinity of BaTiO_3 is improved by adopting higher annealing temperature.

Next, texture coefficient (TC) values were calculated to evaluate the preferred orientation of these BaTiO_3 films according to the following equation [Yoon et al., 1987],

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

where, $\text{TC}(hkl)$ is the texture coefficient of the plane (hkl) ,

Table 1. Texture coefficient (TC) values

Heat-treatment conditions	(hkl)		
	(100)	(101)	(111)
900 $^\circ\text{C}$ under low- $p(\text{O}_2)$	2.8	0.1	0.1
1,200 $^\circ\text{C}$ 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 $\text{TC}(hkl)$ is more than 1, the (hkl) plane is said to be preferably oriented. $\text{TC}(hkl)$ values calculated from the films heat treated under low- $p(\text{O}_2)$ at 900 $^\circ\text{C}$ and in air 1,200 $^\circ\text{C}$ were given in Table 1. $\text{TC}(100)$ values of these films are larger than 1.0, suggesting that the films showed stronger $(h00)$ orientation than non-oriented BaTiO_3 .

In-plane alignment of the films was investigated by XRD pole-figure analysis using the Schulz reflection method of BaTiO_3 (101)/(110) reflections, having high intensity and separability from the MgO substrate reflections. The film was rotated from $\beta=0^\circ$ to 360° at a tilted angles between $\alpha=30^\circ$ and 60° . As shown in Fig. 4(a), the film heat treated under low- $p(\text{O}_2)$ at 900 $^\circ\text{C}$ exhibits four sharp spots at every 90° . The β angles of these spots were 45° -rotated to MgO (111) reflections. This result indicates that most of $(h00)$ -oriented BaTiO_3 grains in the film were epitaxially grown on MgO substrates and the relationship between BaTiO_3 and MgO was BaTiO_3 (100)// MgO (100) and BaTiO_3 [001]// MgO [001]. On the other hand, the film heat treated in air at 1,200 $^\circ\text{C}$ 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 $\text{TC}(100)$ values mentioned above indicate that the film heat-treated under low- $p(\text{O}_2)$ at 900 $^\circ\text{C}$ had larger $\text{TC}(100)$ value and showed a good in-plane alignment. On the other hand, the film heat treated in air at 1,200 $^\circ\text{C}$ showed much poorer in-plane alignment than the film heat treated under low- $p(\text{O}_2)$ at 900 $^\circ\text{C}$, although the film showed larger $\text{TC}(100)$ 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 $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ 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 $^\circ\text{C}$ 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 $^\circ\text{C}$ in air consisted of textured grains with diameter about 0.3 μm and gaps were recognized between each grain. This textured morphology of the film is similar to that of BaTiO_3 films prepared by MOCVD on LaAlO_3 substrates [Willis et al., 1992].

Compared to the preparation of the epitaxial BaTiO_3 films on SrTiO_3 substrates [Kim et al., 1996, 1997], higher annealing temperature and more precisely controlled atmosphere are required to obtain epitaxial BaTiO_3 films on MgO substrates. Higher annealing temperature and less strong orientation for the epitaxial BaTiO_3 films on MgO might be owing to larger lattice misfits between BaTiO_3 and MgO than those between BaTiO_3 and SrTiO_3 .

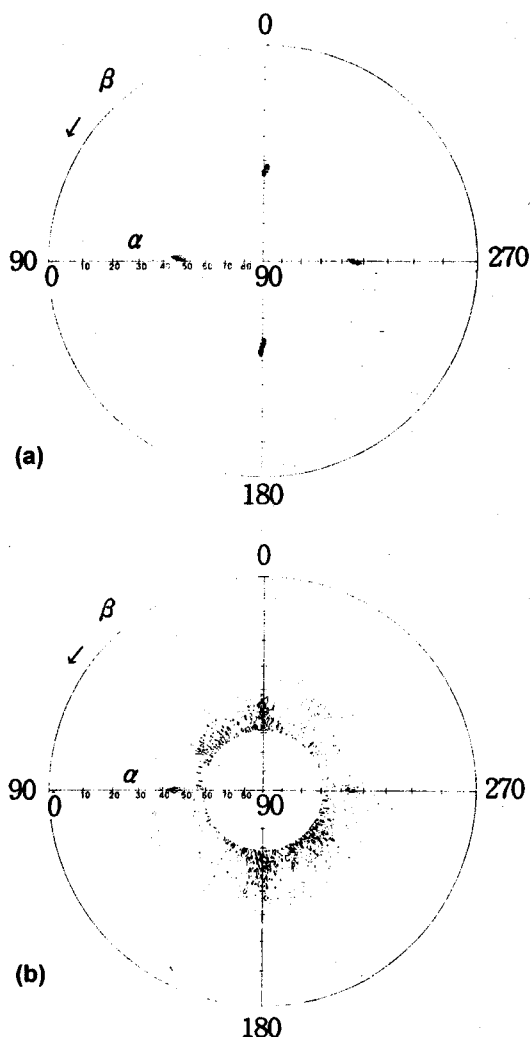


Fig. 4. Pole-figures of BaTiO₃ (101)/(110) reflections for the films heat treated (a) under low- $p(\text{O}_2)$ at 900°C and (b) in air at 1,200°C.

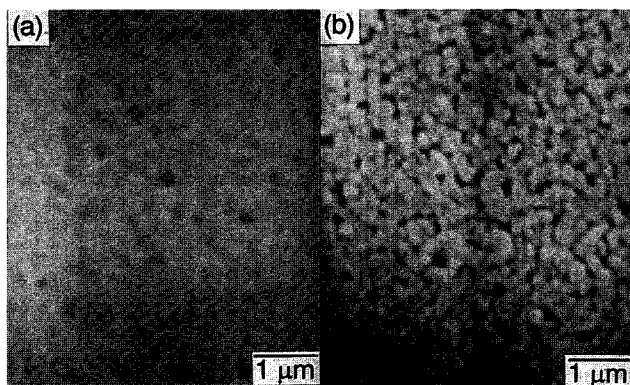


Fig. 5. Scanning electron micrographs of the free surfaces for the BaTiO₃ films heat treated (a) under low- $p(\text{O}_2)$ at 900°C and (b) in air at 1,200°C.

CONCLUSIONS

BaTiO₃ 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 BaTiO₃ 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 2×10^{-4} atm, (100)-oriented epitaxial BaTiO₃ film was obtained and the film displayed a smooth surface with some pores dispersed on the surface. On the other hand, amorphous BaTiO₃ film was obtained by heat treatment at 900°C in air, and textured BaTiO₃ 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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