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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 0.401_6 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 $BaTiO_3$, Pb(Zr, Ti)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 $BaTiO_3$ films on $SrTiO_3$ 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 ($p(O_2)$) of 2×10^{-4} atm, respectively. The flow rate of the gas mixture was set as 300 ml/min. The $p(O_2)$ 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 $LaCrO_3$-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) θ/2 θ scans and x-ray pole figures using Cu Kα radiation with a graphite bent crystal monochromator. Surface morphologies of the $BaTiO_3$ 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 $BaCO_3$ and TiO_2, respectively, as confirmed by XRD θ/2 θ scans. The decomposition from barium naphthenate to $BaCO_3$ 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 $BaCO_3$ and TiO_2 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 θ/2 θ scan results not shown here, similar to the pyrolyzed films prepared on $SrTiO_3$ substrates. In the case of the $BaTiO_3$ films on $SrTiO_3$, the amorphous pyrolyzed films were crystallized showing highly oriented peaks of $BaTiO_3$ after heat treatment at 800 °C and higher temperatures in air [Kim et al., 1996, 1997]. XRD θ/2 θ scans of the films heat-treated under low-$p(O_2)$ at 800 ° 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-$p(O_2)$ showed strong (h00) reflections together with much weaker (101) and (111) reflections. This suggests that the film consisted of mainly (h00) oriented $BaTiO_3$ 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 $BaTiO_3$ appeared at 1,000 °C and increased with the temperature. However, the film heat treated at 1,200 °C showed strong $BaTiO_3$ (101) and (111) reflections together with $BaTiO_3$ (h00) reflections, suggesting that the film was mostly polycrystalline with less strong (100)-preferred orientation.

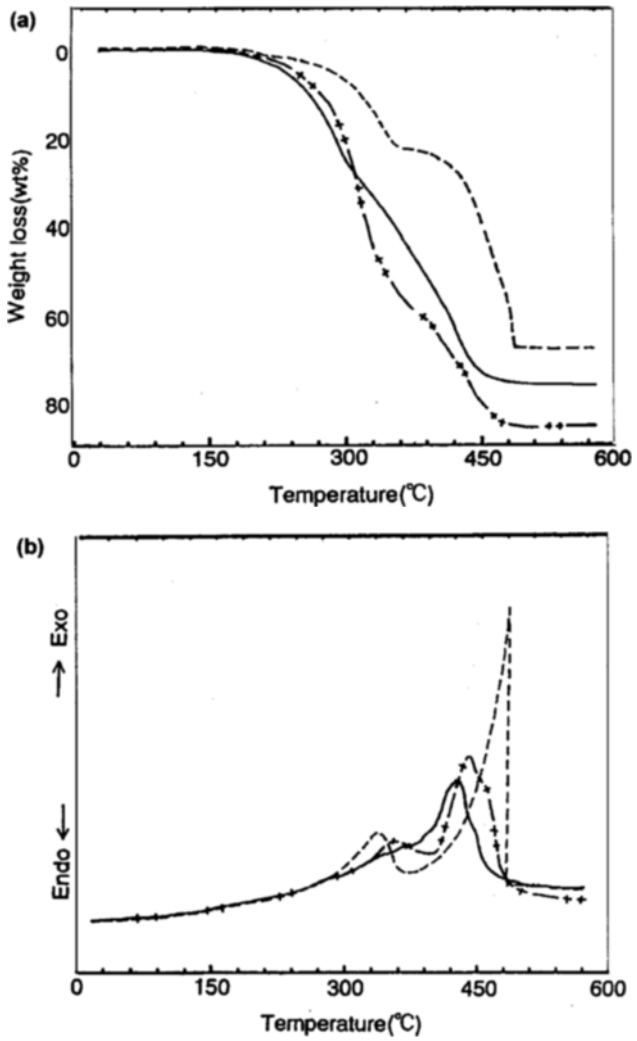

Fig. 1. TG/DTA plots of barium naphthenate (- - - -), titanium naphthenate (--++--) and mixed coating solution (------).

Using substrate MgO (200) peak as an internal calibration standard, we estimated the lattice constants for the films heat-treated under low-$p(O_2)$ at 900 °C and in air at 1,200 °C to be 0.401_6, 0.402_7 nm, respectively. These values are between *a*-

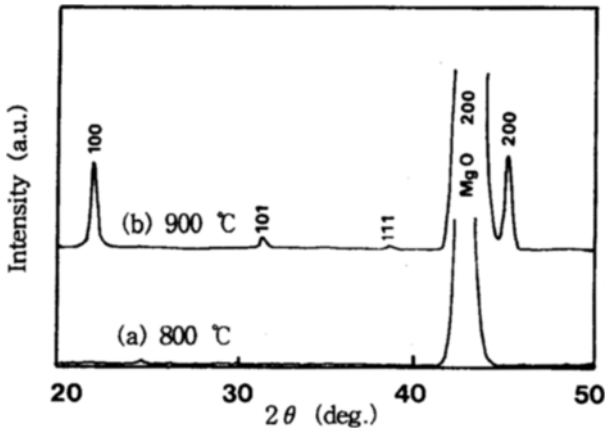

Fig. 2. XRD θ/2 θ scans of $BaTiO_3$ films heat treated under low-$p(O_2)$ at (a) 800 °C and (b) 900 °C.

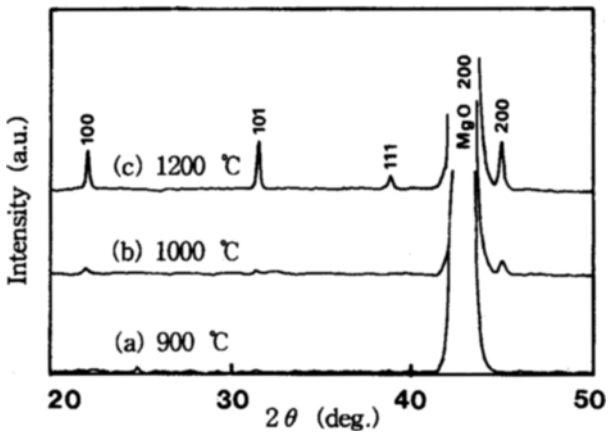

Fig. 3. XRD θ/2 θ scans of $BaTiO_3$ films heat treated in air at (a) 900 °C, (b) 1,000 °C and (c) 1,200 °C.

and *c*-axis values of the bulk tetragonal $BaTiO_3$ and closer to the *a*-axis value of the bulk cubic $BaTiO_3$. These values are larger than that (0.399_9 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 θ/2 θ scans were denoted according to cubic $BaTiO_3$. Full width at half maximum (FWHM) values of $BaTiO_3$ (200) reflection in the XRD θ/2 θ scans were measured to evaluate the crystallinity of $BaTiO_3$ phase in the films. FWHMs for the films heat treated under low-$p(O_2)$ 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 $BaTiO_3$ 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],

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

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-$p(O_2)$	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-$p(O_2)$ 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 $BaTiO_3$.

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 β=0° to 360° at a tilted angles between α=30° and 60°. As shown in Fig. 4(a), the film heat treated under low-$p(O_2)$ at 900 °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 °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-$p(O_2)$ 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-$p(O_2)$ 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-$p(O_2)$ is thought to originate from the enhanced oxygen vacancy concentration, which is similar to that obtained from the preparation of $YBa_2Cu_3O_{7-y}$ 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-$p(O_2)$ 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 (×15,000). The film heat treated at 1,200 °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 $SrTiO_3$.

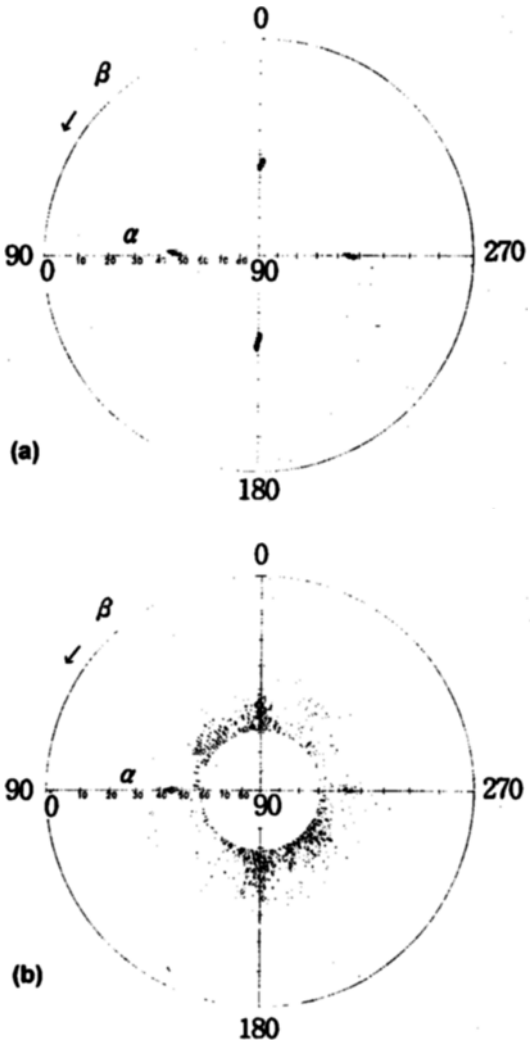

Fig. 4. Pole-figures of $BaTiO_3$ (101)/(110) reflections for the films heat treated (a) under low-$p(O_2)$ at 900 °C and (b) in air at 1,200 °C.

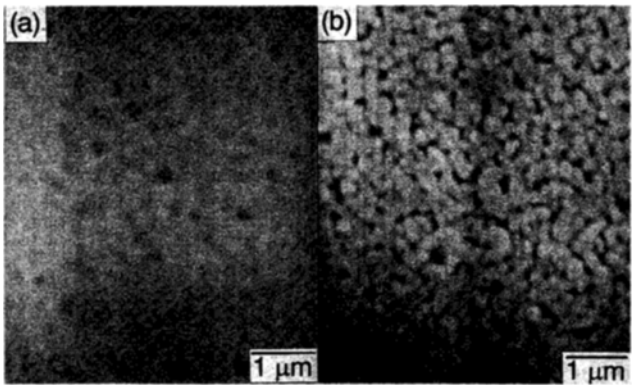

Fig. 5. Scanning electron micrographs of the free surfaces for the $BaTiO_3$ films heat treated (a) under low-$p(O_2)$ at 900 °C and (b) in air at 1,200 °C.

CONCLUSIONS

$BaTiO_3$ thin films were prepared on MgO (100) substrates by CP process using metal naphthenate solution. The amorphous films pyrolyzed at 470 °C were crystallized to $BaTiO_3$ 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 $BaTiO_3$ film was obtained and the film displayed a smooth surface with some pores dispersed on the surface. On the other hand, amorphous $BaTiO_3$ film was obtained by heat treatment at 900 °C in air, and textured $BaTiO_3$ 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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