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Crystal structure of the epitaxial $BaTiO_3$ thin film on the MgO (100) substrate prepared by the coating-pyrolysis process

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Abstract The epitaxial $BaTiO_3$ thin film was prepared on the MgO substrate by the coating-pyrolysis process using a mixed solution of Ba-naphthenate and Ti-naphthenate. The crystal structure of the epitaxial $BaTiO_3$ thin film was characterized by XRD $\theta/2\theta$ scan and asymmetric {303} rocking curve scan. The epitaxial $BaTiO_3$ thin film had the cubic phase with the lattice parameter of $a = c = 0.4018$ nm.

1. Introducton

Ferroelectric thin films having a perovskite structure such as $BaTiO_3$, $(BaSr)TiO_3$, $PbTiO_3$ and $Pb(Zr,Ti)O_3$ are of interest for electronic device applications. Because of their useful ferroelectricity, high dielectric constant and large electro-optic coefficient, they are used in non-volatile memory devices, electro-optic devices, thin film condensers and sensors [1, 2]. Especially, epitaxial $BaTiO_3$ thin films having a low propagation loss are applied to various nonlinear optical devices [3].

Various methods such as the metal-organic chemical vapor deposition [4, 5], radio frequency magnetron sputter deposition [6], reactive evaporation [7], laser molecular beam epitaxy [8] and coating- pyrolysis process [9, 10] were applied to the preparation of epitaxial $BaTiO_3$ thin films. The crystal structure and the lattice misfit between thin films and the substrate must be considered. MgO [4, 10], Pt/MgO [7], $SrTiO_3$ [8, 9] and $LaAlO_3$ [11] were used as substrates for the preparation of the epitaxial $BaTiO_3$ thin films. The crystal structure of the epitaxial $BaTiO_3$ thin films prepared on the various substrates depended on the preparation method and conditions. Although the same MgO substrates were used, the epitaxial $BaTiO_3$ thin films prepared by MOCVD have *a*-axis oriented structure [4], whereas those by radio frequency magnetron sputter deposition and pulsed laser deposition have *c*-axis oriented structure [6, 12].

The $BaTiO_3$ are two different crystal structures of the cubic and tetragonal phase above and below Curie temperature ($T_c = 120°C$), respectively. The lattice parameters of the bulk tetragonal $BaTiO_3$ were $a = 0.3994$ nm and $c = 0.4038$ nm, and that of cubic $BaTiO_3$ was $a = 0.4031$ nm. Since the c/a ratio ($= 1.010$) of the tetragonal $BaTiO_3$ is closer to 1, it is difficult to judge using an XRD $\theta/2\theta$ scan alone whether the epitaxial $BaTiO_3$ thin films have the tetragonal phase (*a*-or *c*-axis oriented) or cubic phase [6].

Recently, we have prepared the $BaTiO_3$ thin films on the MgO (100) substrates by coating-pyrolysis (CP) processing using metal-organic compounds [10]. The crystallinity and the in-plain alignment depended on the heat-treatment conditions. The polycrystalline film was prepared by the heat-treatment at 1200°C in air. On the other hands, the epitaxial $BaTiO_3$ thin film was prepared by the heat-treatment at 900°C under low oxygen partial pressure ($p(O_2)$) and low carbon dioxide partial pressure ($p(CO_2)$)[10]. It was, however, difficult to judge whether the epitaxial $BaTiO_3$ thin film prepared by the heat-treatment at 900°C under low $p(O_2)$ and low $p(CO_2)$ was in the tetragonal or cubic phase. In this paper, the crystal structure of the epitaxial $BaTiO_3$ thin film on the MgO (100) substrate prepared by the CP process was discussed in detail.

2. Experimental

The preparation method of the $BaTiO_3$ thin film on the MgO (100) substrate was reported in our previous result [10]. A mixed solution of Ba-naphthenate and Ti-naphthenate was spin-coated on the MgO substrate. The coated film was prefired at 470°C in air and then heat-treated under $p(O_2) = 2\times10^{-4}$ atm and $p(CO_2) < 10^{-5}$ atm at 900°C. The thickness of the final film

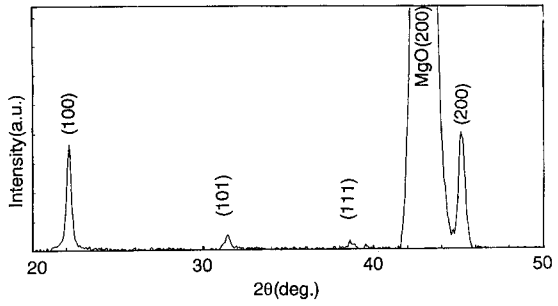

Fig. 1. XRD θ/2θ scan of the epitaxial $BaTiO_3$ thin film prepared on the MgO substrate by coating-pyrolysis process.

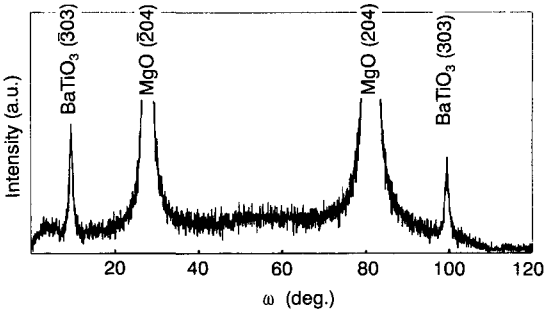

Fig. 2. Asymmetric {303} rocking curve scan of the epitaxial $BaTiO_3$ thin film on the MgO substrate.

was about 0.3 μm. The crystallographic properties were characterized by x-ray diffraction (XRD) θ/2θ scan and asymmetric {303} rocking curve scan.

3. Results and Discussion

Figure 1 shows the XRD θ/2θ scan of the epitaxial $BaTiO_3$ thin film prepared. The epitaxial relationships between film and substrate were confirmed by XRD β scan and pole-figure analysis described in our previous paper [10]. Using the internal calibration standard of MgO (200) peak, the lattice parameter of the perpendicular axis (c) with the substrate was calculated to be 0.4018 nm. The epitaxial $BaTiO_3$ thin film was conducted to the cubic phase without confirming of the lattice parameter of the parallel axis(a) with the substrate, because no splitting peaks of $BaTiO_3$ (200) and (002) were observed as shown in Fig. 1 and lattice parameter was closer to the a-axis value of cubic $BaTiO_3$. But it could not strictly speaking that the epitaxial $BaTiO_3$ thin film was cubic phase.

Figure 2 is a {303} rocking curve scan of the epitaxial $BaTiO_3$ thin film on the MgO substrate, which was obtained as follows; the x-ray detector was fixed at the angle satisfying the Bragg condition of the $BaTiO_3$ {303} plane and then the $BaTiO_3$ thin film was rotated [6, 8]. The ($\bar{3}03$) and (303) peaks of the epitaxial $BaTiO_3$ thin film were displayed with the ($\bar{2}04$) and (204) peaks of the MgO substrate. The lattice parameter, a, was calculated by the following equation,

$$a = c \tan(\Delta\omega/2)$$

where $\Delta\omega$ is the difference between the ($\bar{3}03$) and (303) peaks in the asymmetric {303} rocking curve. The $\Delta\omega$ was measured to be 89.99°, therefore the lattice parameter of the parallel axis with the substrate, a, was calculated as 0.4018 nm. The results of the

Table 1
Comparison of the lattice parameter and crystal structure of the bulk $BaTiO_3$, substrates and $BaTiO_3$ thin films

Materials	Lattice parameter		Tetragonality	Crystal structure	Preparation method
	a (nm)	c (nm)			
Bulk $BaTiO_3$	0.3994	0.4038	1.010	Tetragonal	
	0.4031			Cubic	
Substrate					
$SrTiO_3$(100)	0.3905				
MgO (100)	0.4213				
Pt(100)	0.3992				
Film/substrate					
$BaTiO_3$/MgO	0.4018	0.4018	1.000	Cubic	CP [in this study]
$BaTiO_3$/$SrTiO_3$	0.3999	0.4011	1.003	Pseudocubic	CP [9]
$BaTiO_3$/MgO	0.4016	0.4067	1.013	Tetragonal	Sputter deposition [6]
$BaTiO_3$/Pt/MgO	0.4002	0.4044	1.010	Tetragonal	Reactive evaporation [7]

XRD θ/2θ scan and the asymmetric {303} rocking curve scan mean that the epitaxial $BaTiO_3$ thin film on the MgO substrate prepared by the CP process was of the cubic phase having lattice parameter of $a = c =$ 0.4018 nm.

The lattice parameter and crystal structure of the epitaxial $BaTiO_3$ thin films prepared by the different substrates and preparation methods were compared in Table 1. The lattice misfits between MgO and tetragonal $BaTiO_3$ are 5.2 % and 4.3 % in the a and c direction, respectively. These are larger than the misfit values between $BaTiO_3$ and $SrTiO_3$, which are 2.3 % and 3.4 % along the a and c direction, respectively. Thus, the preparation of the epitaxial $BaTiO_3$ thin film on the MgO substrates by the CP process using metal-naphthenates was required to high temperature and precisely heat-treatment conditions, compared with that of the epitaxial $BaTiO_3$ thin film on the $SrTiO_3$ substrates [9]. The lattice parameter ($a = 0.4018$ nm) of $BaTiO_3$ thin film on the MgO substrate was slightly larger than those ($a = 0.3999$, $c = 0.4011$ nm) on the $SrTiO_3$ substrate. This may be attributed to the larger lattice parameter of MgO ($a = 0.4213$ nm) than that of $SrTiO_3$ ($a = 0.3905$ nm).

Although the epitaxial $BaTiO_3$ thin films prepared on the various substrates had similar crystal structure, the lattice parameters of the thin films were dependent on the substrate used. The $BaTiO_3$ thin films having the tetragonal phase were prepared by the sputter deposition [6] and reactive evaporation [7]. The $BaTiO_3$ thin films having pseudo-cubic [9] and cubic phase (in this paper) were prepared by the CP process. It can be shown that the cubic $BaTiO_3$ at the high temperature of the heat-treatment was preserved at lower temperature to same crystal structure due to the fast cooling in the CP process. Thus, the various preparation conditions such as preparation method, substrates used and heat-treatment conditions must be considered to the preparation of the epitaxial $BaTiO_3$ thin films.

4. Conclusion

The crystal structure of the epitaxial $BaTiO_3$ thin film prepared on the MgO substrate by the CP process using metal-naphthenates was confirmed by XRD θ/2θ scan and asymmetric {303} rocking curve scan. The epitaxial $BaTiO_3$ thin film prepared on the MgO substrate had the cubic phase with the lattice parameter of $a = c = 0.4018$ nm.

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