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$BaTiO_3$ thin film prepared by coating-pyrolysis process on Nb-doped $SrTiO_3$ substrate

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Epitaxial $BaTiO_3$ thin film was prepared on Nb-doped $SrTiO_3$ substrate by coating-pyrolysis process using a mixed solution of barium and titanium naphthenates. The amorphous film pyrolyzed at 470 °C was crystallized with high orientation after heat-treatment at 850 °C under low oxygen partial pressure. X-ray diffraction $\theta/2\theta$ and β scans indicated that the $BaTiO_3$ film was epitaxial relationship with Nb-doped $SrTiO_3$ substrate. The dielectric constant was approximately 230 at 10^3 Hz and was monotonically decreased with increasing of frequency at room temperature. © *1999 Kluwer Academic Publishers*

1. Introduction

Perovskite $BaTiO_3$ thin films are of particular interest for electronic device applications due to their useful ferroelectric, dielectric and electro-optic properties [1]. These films are attractive for high capacitance integrated elements, dynamic random access memories (DRAM) and ferroelectric memories, etc. $BaTiO_3$ thin films were prepared by various fabricating methods such as metal-organic chemical vapor deposition (MOCVD) [2–4], radio-frequency sputtering [5-7], laser ablation [8], evaporation [9], laser deposition [10, 11], sol-gel [12, 13], metal-organic deposition (MOD) [14]. $LaAlO_3$ [2], MgO [3, 5, 10], Si wafer [4, 6, 13], $SrTiO_3$ [7], YBCO/$LaAlO_3$ [8], Pt/MgO [9], and MgO/GaAs [11] were used as substrates for $BaTiO_3$ thin films.

A chemical solution process such as coating-pyrolysis process and MOD using metal-organic compounds has the following distinct advantages. It is simple and inexpensive, and is easily applicable to substrate with any size and shape without requiring high vacuum. Recently, we have succeeded in preparing epitaxial $BaTiO_3$ thin films on $SrTiO_3$ and MgO substrates using metal-naphthenates [15, 16].

In this paper, we report on $BaTiO_3$ thin films prepared by coating-pyrolysis process. A mixed metal-naphthenate and Nb-doped $SrTiO_3$ were used as a precursor solution and a substrate, respectively. The orientation of film and epitaxy between $BaTiO_3$ film and Nb-doped $SrTiO_3$ substrate were examined by X-ray diffraction (XRD) $\theta/2\theta$ and β scans. The frequency and bias-voltage dependences of dielectric constant and dielectric loss were measured.

2. Experimental

$BaTiO_3$ thin film on Nb-doped $SrTiO_3$ substrate was prepared by similar methods reported in our previous paper [15, 16], which were described the preparation of the epitaxial $BaTiO_3$ thin films on $SrTiO_3$ and MgO substrates. In brief, the mixed solution of barium and titanium naphthenates was used as a precursor solution. The precursor solution was diluted in toluene to adjust the concentration (~0.2 mmol/g) and viscosity for spin coating. The precursor solution was spin-coated on Nb-doped $SrTiO_3$ substrate at 2000 rpm for 5 s. The Nb concentration and electric resistivity of Nb-doped $SrTiO_3$ substrate were 0.05 at % and 0.01 Ω·cm, respectively.

The thermogravimetric analysis of the precursor solution indicated that thermal decomposition of the mixed barium and titanium naphthenates to barium carbonate and titanium dioxide was completed at temperature range of 440 to 500 °C in air. Thus, the spin-coated film was pyrolyzed at 470 °C for 10 min in air to eliminate organic components. The pyrolyzed film was heat-treated at 850 °C for 1 h under oxygen partial pressure of 2×10^{-4} atm. The thickness of the prepared film was measured to be 0.33 μm by α-step method. The orientation of film and epitaxial relationship between $BaTiO_3$ thin film and Nb-doped $SrTiO_3$ substrate were examined by XRD $\theta/2\theta$ and β scans using CuK_α radiation with graphite bent optical monochromator. The surface morphology of thin film was observed by scanning electron microscope (SEM). A silver dot of 1.0 mm diameter was evaporated on the $BaTiO_3$ thin film as an upper electrode. Dielectric constant and dielectric loss tanδ were measured by using an impedance analyzer in the frequency range from 10^3 to 10^6 Hz at room temperature. The dependences of the bias-voltage on the dielectric constant and dielectric loss were also measured.

3. Results and discussion

The film pyrolyzed at 470 °C in air was an amorphous by XRD $\theta/2\theta$ scan, similar to those on $SrTiO_3$ and MgO substrates [15, 16]. The amorphous pyrolyzed film was crystallized with high orientation after final heat-treatment at 850 °C for 1 h under oxygen partial pressure of 2×10^{-4} atm. Fig. 1 shows XRD $\theta/2\theta$ scan of $BaTiO_3$ film prepared on Nb-doped $SrTiO_3$ substrate. As it can be seen, only (h00) peaks of $BaTiO_3$ were revealed. Using the $SrTiO_3$ (200) peak as an internal

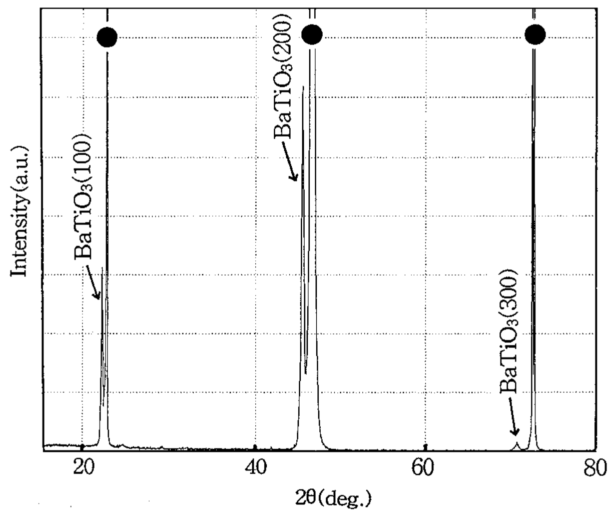

Figure 1 XRD pattern of $BaTiO_3$ thin film. (• indicates the XRD pattern of Nb-doped $SrTiO_3$ substrate.)

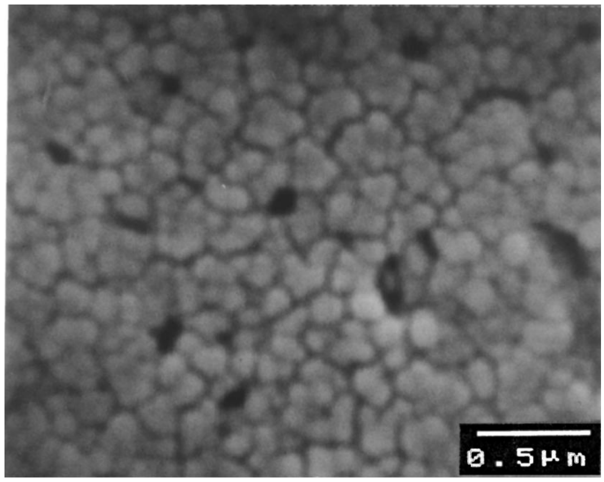

Figure 3 SEM morphology of $BaTiO_3$ thin film.

calibration standard, the lattice constant of $BaTiO_3$ film was determined to be 0.3998 nm, which is closer to a-axis lattice constant of bulk tetragonal $BaTiO_3$. This indicates that the $BaTiO_3$ film on Nb-doped $SrTiO_3$ substrate was oriented with a-axis orientation to substrate plane, which is consistent with the results of $BaTiO_3$ films on MgO substrates prepared by MOCVD [3] and pulse laser deposition [11]. The full width at half maximum (FWHM) of the rocking curve was measured to evaluate an in-plane alignment of $BaTiO_3$ film. The FWHMs of the rocking curves for $BaTiO_3$ (200) and $SrTiO_3$ (200) reflections were 0.32° and 0.12°, respectively. Such a narrow FWHM value of $BaTiO_3$ film indicates that the $BaTiO_3$ film was crystallized with high (100) orientation.

The epitaxial relationship between film and substrate was confirmed by XRD β scan of the $BaTiO_3$ (101) reflections as shown in Fig. 2. The four sharp peaks of $BaTiO_3$ (101) reflections were observed at every 90° and agreed with those of $SrTiO_3$ (101) reflections. The X-ray pole-figure measured at the tilted angle from 30 to 60°, not shown here, displayed the four sharp spots of $BaTiO_3$ (101) reflections at every 90°. The results of XRD β scan and pole-figure indicate that the $BaTiO_3$ film was a complete epitaxy with the Nb-doped $SrTiO_3$ substrate. The epitaxy is originated from the small lattice mismatch values between film and substrate. The substrate Nb-doped $SrTiO_3$ used in this study has a cubic perovskite structure with lattice constant of $a = 0.3905$ nm. The bulk $BaTiO_3$ with a same perovskite structure has a tetragonal phase having lattice constants of $a = 0.3994$ and $c = 0.4038$ nm at room temperature. Thus, the lattice mismatch values between tetragonal $BaTiO_3$ and cubic $SrTiO_3$ are −2.3 and −3.4% along a- and c-axis, respectively.

Fig. 3 shows the surface morphology of the $BaTiO_3$ thin film observed by SEM. The surface was consistent with round-shaped grains of diameters about 0.3 μm. Some voids formed during the pyrolysis of metal naphthenates were interspersed among grains. The morphology of film was similar to that of $BaTiO_3$ thin film prepared on $SrTiO_3$ substrate heat treated in air [15].

The frequency and bias-voltage dependences of the dielectric constant and dielectric loss tan δ were measured by using an impedance analyzer at room temperature. Fig. 4 shows the dielectric constant of the $BaTiO_3$ film measured in the frequency range of 10^3 to 10^6 Hz at applying voltage of 50 mV. The dielectric constant was monotonically decreased with the increasing of the

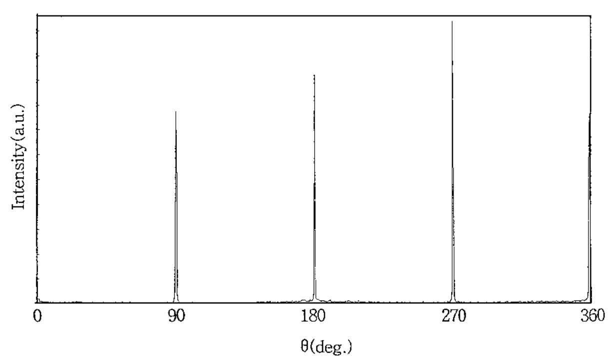

Figure 2 XRD β scan of $BaTiO_3$ (101) reflection.

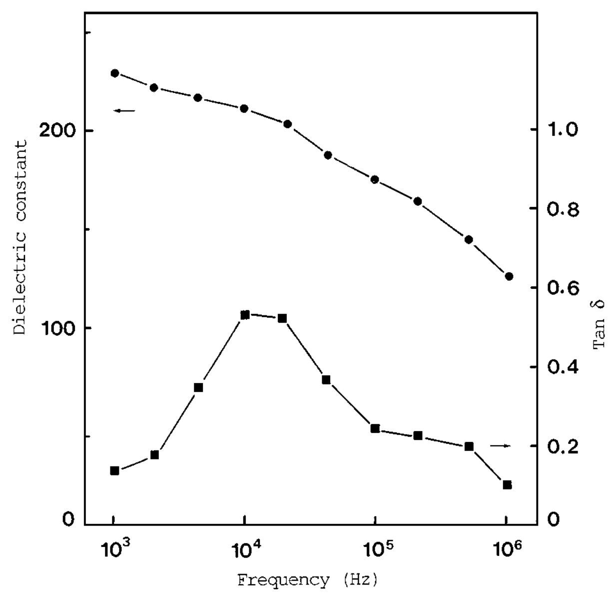

Figure 4 Frequency dependences of dielectric constant and dielectric loss.

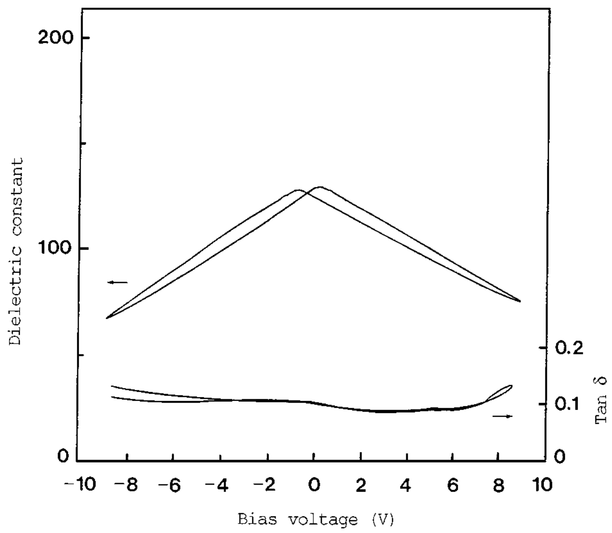

Figure 5 Bias-voltage dependences of dielectric constant and dielectric loss.

frequency. Dielectric constants were about 230 at the frequency of 10^3 Hz and 125 at 10^6 Hz. The dielectric behavior of this film is similar to those of $BaTiO_3$ films prepared by sol-gel process on $LaNiO_3$-coated $LaAlO_3$ substrate [17] and by hydrothermal-electrochemical method on Ti substrate [18]. The dielectric loss $\tan\delta$ showed a range of 0.1–0.5 and had a maximum value of 0.5 at a frequency around 10^4 Hz. The frequency dependence of the dielectric loss was also observed in $BaTiO_3$ thin film prepared on Pt/MgO (100) substrate [19], which is might be due to a contact resistance of the electrodes [20] and still needs further study. The bias-voltage dependences of the dielectric constant and dielectric loss for the $BaTiO_3$ film at the frequency of 10^6 Hz were measured from −9 to +9 V and back again as shown in Fig. 5. The bias-voltage dependence of the dielectric constant for the $BaTiO_3$ thin film with dielectric loss about 0.1 demonstrates the weak ferroelectric properties having small butterfly-type hysteresis.

4. Conclusion

Epitaxial $BaTiO_3$ thin film was prepared by coating-pyrolysis process on Nb-doped $SrTiO_3$ substrate. A mixed solution of barium and titanium naphthenates was used as a precursor solution. The amorphous film pyrolyzed at 470 °C was crystallized with high orientation after heat-treatment at 850 °C under low oxygen partial pressure. The results of X-ray diffraction indicated that the $BaTiO_3$ film had the lattice constant of 0.3998 nm and was epitaxial relationship with Nb-doped $SrTiO_3$ substrate. The dielectric constant was approximately 230 at 10^3 Hz and was monotonically decreased with increasing of frequency at room temperature.

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