Dielectric properties of $\text{BaTiO}_3\text{--Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ films with preferential crystal orientation

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Thin films of the $\text{BaTiO}_3\text{--Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ (BT–BMT) solid-solution system with preferential crystal orientation of (100) and (111) plane were fabricated on (100) SrRuO_3 /(100) SrTiO_3 and (111) SrRuO_3 /(111) SrTiO_3 substrates by CSD technique. Enhanced dielectric permittivity (ϵ_r) of approximately 800 was confirmed for the (111)-oriented BT–BMT film at room temperature, which is significantly larger than those of (100)- or randomly-oriented films. The BT–BMT films exhibited relatively stable temperature coefficient of capacitance (TCC) independent of their crystal orientation, that allows enhanced ϵ_r up to 400°C without drastic change of the capacitance. These properties can be favorable for the application of dielectric capacitors in high-temperature electronics.

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1. Introduction

Dielectric materials with high permittivity and stable temperature coefficient of capacitance (TCC) are strongly required for the application of high-temperature electronics because they act as important components of integrated circuits which drive under a high-temperature environment, e.g., directly-mounted control circuits for automobile engines, motors, electric lighting, and fuel cells.^{1)–4)} Conventional high-temperature capacitors consisting of simple oxides such as Al_2O_3 , MgO , MgTiO_3 and Ta_2O_5 exhibit significantly stable TCC behavior with $|TCC|$ values below 200 ppm/K.^{5)–9)} However, these materials are still insufficient for the application in integrated electronic devices because of their lower relative dielectric constant (ϵ_r) of less than 100. In contrast, recent high-permittivity capacitors mainly consist of barium titanate [BaTiO_3 (BT)] which exhibit larger ϵ_r of above 1000 at room temperature, although it suffers from rapid dielectric variation above the Curie temperature ($T_c = 120^\circ\text{C}$) owing to its phase transition from tetragonal to cubic symmetry.^{10)–12)} Therefore BT capacitors hardly utilize for high-temperature application because of its unstable TCC behavior, regardless of high permittivity.

BT-based solid solution can be one prospective approach for stabilizing the TCC behavior of dielectric capacitors. Combination with other perovskite compounds, such as SrTiO_3 ,^{13)–15)} CaTiO_3 ,^{16)–18)} BaZrO_3 ,^{19)–21)} and BiFeO_3 ,^{22),23)} have been reported for controlling their ϵ_r –temperature (T) behavior in order to obtain stable TCC. Our group also has reported thin-film capacitors of BT– $\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ (BMT) solid solution system for high-temperature dielectric application.^{24),25)} The BMT component, which is metastable phase itself under ambient temperature and pressure,^{26),27)} is typically utilized for synthesizing some perovskite-based solid solutions as a structural analogue of the PbZrO_3 component.^{28)–34)} Preceding research on BT–BMT bulks

revealed the relaxor-type ϵ_r – T behavior with higher ϵ_r of up to 1500. Also in our research, thin-film capacitors of BT–BMT solid solution were fabricated by pulsed laser deposition (PLD)²⁴⁾ and chemical solution deposition (CSD),²⁵⁾ which exhibited suppressed TCC behavior together with $\epsilon_r = 400$ –1000. These properties will be more suitable for constructing high-permittivity dielectric capacitors with stable performance against temperature changes, compared with those of conventional materials.

In the present research, we mainly focus on crystal-orientation dependency of dielectric/ferroelectric properties for the BT–BMT materials. Our previous report investigated compositional dependency of the TCC behavior for sol–gel-derived polycrystalline BT–BMT films,²²⁾ which revealed that the films of $(1-x)$ BT– x BMT exhibit stable TCC behavior in the compositional range of $x = 0.20$ – 0.40 although moderate permittivity of $\epsilon_r = \sim 500$. However, this result was somewhat different from another report on the PLD-derived epitaxial film on (111) SrRuO_3 /(111) SrTiO_3 , with enhanced permittivity of $\epsilon_r = \sim 1000$.²⁴⁾ The difference can arise from their crystal orientation, which is closely related to crystallographic anisotropy of dielectric permittivity^{35)–37)} or clamping effects that induce (or release) in-plane residual stress,^{24),38),39)} as frequently discussed for epitaxial films of other perovskite-based materials. Therefore, we fabricated BT–BMT films with different crystal orientation, i.e., randomly-oriented and preferential (100)- and (111)-oriented films, for evaluating the orientation dependency of their dielectric and ferroelectric properties. Findings in the present work will be of help for achieving enhanced dielectric permittivity on the BT–BMT capacitors with stable TCC behavior.

2. Experimental

Thin films of BT–BMT solid solution were fabricated by CSD technique. $(\text{CH}_3\text{COO})_2\text{Ba}$, $\text{Ti}(\text{O}-n\text{-C}_4\text{H}_9)_4$, $\text{Bi}(\text{O}-t\text{-C}_5\text{H}_{11})_3$, $\text{Mg}(\text{OC}_2\text{H}_5)_2$, and acetylacetone were used as starting materials. A precursor solution with nominal composition of $\text{Ba}:\text{Bi}:\text{Mg}:\text{Ti} = 0.60:0.46:0.20:0.80$ (with 15% Bi excess) was prepared by

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dissolving the starting materials in 2-methoxyethanol solvent to yield the resulting films with the composition of 0.60 BaTiO₃–0.40 Bi(Mg_{1/2}Ti_{1/2})O₃. The chemical composition was determined on the basis of our previous work,²⁵⁾ in order to obtain the stable TCC behavior. The final concentration of the solution was approximately 0.1 mol/dm³. (100)SrRuO₃/(100)SrTiO₃ and (111)SrRuO₃/(111)SrTiO₃ substrates were used for the film deposition with preferential crystal orientation, while an (111)Pt/TiO₂/(100)Si substrate for random crystal orientation.

The precursor solution was spin-coated on the substrates at a rate of 3000 rpm for 50 s, followed by a drying process at 150°C for 1 min in air and a pyrolysis process at 400°C for 1 min in air. These processes were repeated until precursor films with thicknesses of ~100 nm were deposited on the substrates. Then, the precursor films were heated at 800°C for 5 min in air by rapid thermal annealing (RTA) for crystallization. All of these processes, from spin-coating to crystallization, were repeated three times to deposit the crystallized films with thicknesses of approximately 300 nm. After the spin-coating of the film, circular platinum electrodes with a diameter of 0.2 mm were deposited on the surface of the resulting films by electron beam evaporation.

Crystalline phase and crystal orientation of the films were identified by X-ray diffraction (XRD) with a Rigaku RINT 2000 diffractometer. The thicknesses of the films were determined by scanning electron microscopy (SEM) with a Hitachi SU8000 electron microscope. The chemical compositions were confirmed by X-ray fluorescence spectrometry (XRF) with a RIGAKU ZSX-Primus II spectrometer. The surface microstructure was observed by atomic force microscopy (AFM) with a Veeco INNOVA atomic force microscope. The dielectric property was evaluated using a 4294A impedance analyzer with an oscillation voltage of 1 V in the frequency range of $1 \times 10^3 - 2 \times 10^6$ Hz, with a sample heating unit for TCC measurement. The ferroelectric property was evaluated using a Toyo FCE-3 ferroelectric test system with a frequency of 10 kHz.

3. Results and discussion

Figure 1 shows XRD patterns of the BT–BMT films fabricated on various substrates. Diffraction peaks derived from perovskite phase was obtained for these films, as well as those from substrates (Si or SrTiO₃) and electrodes (Pt or SrRuO₃). The films fabricated on (111)Pt/TiO₂/(100)Si substrates showed diffraction peaks of perovskite (100), (110), (111) and (112), which indicates that the film consisted of polycrystalline structure without preferential crystal orientation. On the other hand, the films on (100)SrRuO₃/(100)SrTiO₃ and (111)SrRuO₃/(111)SrTiO₃ substrates showed only the peaks of perovskite (*h*00) and (111), which indicates the preferential orientation of perovskite (100) and (111) planes, respectively, normal to the substrate surface. Peak intensities of the BT–BMT on (100)SrRuO₃/(100)SrTiO₃ and (111)SrRuO₃/(111)SrTiO₃ substrates were significantly larger than that on (111)Pt/TiO₂/(100)Si substrate. These results suggest that the BT–BMT films were growth epitaxially on the perovskite-type surface, i.e., surfaces of SrRuO₃ (100) and (111) plane, depending of its crystallographic configuration similarly to other thin films of perovskite-type oxides. The films on (111)Pt/TiO₂/(100)Si substrates exhibited random crystal orientation, owing to insufficient lattice matching between the film and substrate surface. Lattice parameter of the BT–BMT was almost the same as that of BaTiO₃ (*a*-axis), as confirmed in previous report.²⁵⁾

Figure 2 shows surface AFM images of the BT–BMT films fabricated on various substrates. No crack or pore structure was

Fig. 1. XRD patterns of BT–BMT films fabricated on (a) (111)Pt/TiO₂/(100)Si, (b) (100)SrRuO₃/(100)SrTiO₃ and (c) (111)SrRuO₃/(111)SrTiO₃ substrates.

observed on the surface of these films. The surface roughness of the films fabricated on (100)SrRuO₃/(100)SrTiO₃ was relatively smaller than those on (111)Pt/TiO₂/(100)Si and (111)SrRuO₃/(111)SrTiO₃; the values of root-mean-square roughness (*RMS*) for these films were 5.4, 9.2 and 9.4 nm, respectively. Roughness of the oriented film is determined by the crystallographic feature:^{38),40)–42)} smooth surface of the film on (100)SrRuO₃/(100)SrTiO₃ reflects crystalline facet of perovskite (100) plane exposed on the film surface, while the (100) facet can enhance the roughness of (111) oriented films. The rough surface of the films on (111)Pt/TiO₂/(100)Si can arise from polycrystalline structure with random crystal orientation.

Figure 3 shows *P*–*E* hysteresis loops of the BT–BMT films on various substrates. Well-saturated *P*–*E* curves without distortion due to leakage current conduction were measured for these films. The films on (111)SrRuO₃/(111)SrTiO₃ substrates exhibited relatively higher remanent polarization (*P_r*) of 15 μC/cm² and coercive field (*E_c*) of 230 kV/cm, while lower *P_r* and *E_c* values were measured for the films on (111)Pt/TiO₂/(111)Si (*P_r* = 6 μC/cm², *E_c* = 170 kV/cm) and on (100)SrRuO₃/(111)SrTiO₃ (*P_r* = 7 μC/cm², *E_c* = 120 kV/cm). Ferroelectric property of the BT–BMT films varies depending on the crystal orientation. Higher *P_r* value was confirmed for (111)-oriented BT–BMT films on (111)SrRuO₃/(111)SrTiO₃, which suggests that the polar axis of BT–BMT lattice (with compositional ratio of BT:BMT = 0.60:0.40) can be along the [111]. The (111)-oriented films on (111)SrRuO₃/(111)SrTiO₃ also exhibited the breakdown field of 1870 kV/cm higher than those of the (100)-oriented films on

Fig. 2. Surface AFM images of BT-BMT films fabricated on (a) (111)Pt/TiO₂/(100)Si, (b) (100)SrRuO₃/(100)SrTiO₃ and (c) (111)SrRuO₃/(111)SrTiO₃ substrates.

(100)SrRuO₃/(100)SrTiO₃ and the randomly-oriented films on (111)Pt/TiO₂/(111)Si (1540 and 1310 kV/cm, respectively).

Figure 4 shows relative dielectric constant, ϵ_r , and dielectric loss, $\tan \delta$, as a function of the oscillation frequency of the BT-BMT films on various substrates, measured at room temperature. The ϵ_r value of these films all exhibited the frequency dependence, i.e. dielectric degradation, which is typically confirmed for the relaxor-type dielectric materials.^{32)–34)} Authors confirmed that the dielectric degradation arised from the addition of BMT components in their previous work. The $\tan \delta$ values were approximately 0.10 with a trace of frequency dependence, independent of the crystal orientation of the film or substrate species. The BT-BMT films on (111)SrRuO₃/(111)SrTiO₃ showed higher ϵ_r value compared with the films on (100)SrRuO₃/(100)SrTiO₃ and (111)Pt/TiO₂/(111)Si during the frequency range of 10³–10⁶ Hz; ϵ_r values at an oscillation frequency of 1 kHz were 800, 700 and 695, respectively. The difference in the dielectric permittivity can also arise from the crystal orientation of the BT-BMT lattice, as discussed previously for other materials.^{35)–37)} Preferential (111) orientation enhanced the ϵ_r value of the BT-BMT films successfully, however, although it is significantly lower than those reported for conventional bulk materials or films fabricated by vapor-phase deposition (above 1000),^{5)–7)} due to the size effect of the crystal grains. The bias-field dependency of the ϵ_r value for the BT-BMT films on various substrates, measured at room temperature, is also shown in **Fig. 5** All of the films exhibited relatively large capacitance tunability, $\Delta C = (C_{\max} - C_{\min})/C_{\max}$, above 50%, together with a small hysteresis loops, independent of the crystal orientation. These results mean the presence of ferroelectricity which is also confirmed in the experimental

Fig. 3. *P*-*E* hysteresis loops of BT-BMT films fabricated on (a) (111)Pt/TiO₂/(100)Si, (b) (100)SrRuO₃/(100)SrTiO₃ and (c) (111)SrRuO₃/(111)SrTiO₃ substrates measured at a frequency of 10 kHz.

Fig. 4. Relative dielectric constant, ϵ_r , and dielectric loss, $\tan \delta$, of BT-BMT films fabricated on various substrates, as a function of oscillation frequency. The data were measured at room temperature.

results of Fig. 3. Note that large bias dependency of capacitance, i.e., tunable behavior, will not be favorable for the present application which aims for the high-temperature dielectrics: extra idea for material design shall be considered to combine the stable temperature- and bias dependencies.

Figure 6 shows the temperature dependence of the ϵ_r and $\tan \delta$ values of the BT-BMT films on various substrates measured at 10 kHz on heating from room temperature up to 400°C. The ϵ_r values of these films were maintained in the temperature range

Fig. 5. Relative dielectric constant, ϵ_r , of BT-BMT films fabricated on various substrates, as a function of bias field. The data were measured at room temperature and oscillation frequencies of (a) 10 kHz and (b) 1 MHz.

Fig. 6. Temperature dependence of relative dielectric constant, ϵ_r , and dielectric loss, $\tan \delta$, of BT-BMT films fabricated on various substrates. The data were measured at an oscillation frequency of 1 kHz.

from room temperature (R.T.) up to 400°C. No drastic variation of the ϵ_r and $\tan \delta$ values depending on the temperature was confirmed for these films, while the ϵ_r value of conventional BaTiO₃ film without BMT addition decreased drastically with increasing temperature above 100°C.^{24,25} Frequency dependence of the ϵ_r value indicated in Fig. 4 was confirmed during the temperature range of R.T. – 400°C, whereas it was also found for the bulk materials³¹ especially below the phase-transition temperature. Enhanced ϵ_r value of the (111)-oriented BT-BMT films on (111)SrRuO₃/(111)SrTiO₃ compared with those of other

films on different substrates was also confirmed at the elevated temperature as well as room temperature (in Fig. 4), which suggests that the anisotropy of dielectric permittivity depending on the crystal orientation still remained in the temperature range of R.T. – 400°C. The $|TCC|$ values of the films on (111)Pt/TiO₂/(111)Si (100)SrRuO₃/(100)SrTiO₃ and (111)SrRuO₃/(111)SrTiO₃ substrates were calculated to be 413, 134 and 460 ppm/K, respectively. These values are significantly smaller than that of BT film, meaning more stable TCC behavior, and then comparable with those of conventional high-temperature materials and advanced thin-film capacitors consisting of bismuth-layer-structured dielectrics (Ca,Sr)Bi₄Ti₄O₁₅ [$\epsilon_r \sim 200$, $|TCC| \sim 250$ ppm/K].^{43–46} The (111)-oriented BT-BMT film exhibited slightly higher $|TCC|$ value compared with that of the (100)-oriented film. The larger dependency of dielectric permittivity can arise from the crystal orientation along direction of polar axis, as confirmed in previous works of single crystal BaTiO₃ and bismuth-layer-structured dielectrics.^{35,43,44}

4. Conclusions

Crystal-orientation dependency of dielectric property for the BT-BMT film was evaluated for achieving enhanced dielectric permittivity with stable TCC behavior. The BT-BMT films with preferential orientation of (100) and (111) planes were fabricated on (100)SrRuO₃/(100)SrTiO₃ and (111)SrRuO₃/(111)SrTiO₃ substrates successfully by CSD technique. Dielectric and ferroelectric properties the BT-BMT films were varied depending on their crystal orientation; especially, enhanced ϵ_r value up to 800 was confirmed at room temperature for the (111)-oriented BT-BMT film on (111)SrRuO₃/(111)SrTiO₃ substrate, compared with (100)- or randomly-oriented films. The enhanced dielectric permittivity was not maintained only at room temperature but also at elevated temperature up to 400°C with keeping stable $|TCC|$ value. These properties will be favorable for the application of specialized dielectric capacitor of high-temperature electronics.

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