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

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Thin films of the BaTiO$_3$–Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$ (BT–BMT) solid-solution system with preferential crystal orientation of (100) and (111) plane were fabricated on (100)SrRuO$_3$/SrTiO$_3$ and (111)SrRuO$_3$/SrTiO$_3$ substrates by solid solution were fabricated by pulsed laser deposition (PLD) and chemical solution deposition (CSD), which exhibited suppressed TCC behavior together with $\varepsilon_r = 400$–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, 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 $\varepsilon_r = \sim 500$. However, this result was somewhat different from another report on the PLD-derived epitaxial film on (111)SrRuO$_3$/SrTiO$_3$, with enhanced permittivity of $\varepsilon_r = \sim 1000$. The difference can arise from their crystal orientation, which is closely related to crystallographic anisotropy of dielectric permittivity clamping effects that induce (or release) in-plane residual stress, 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. (CH$_3$COO)$_2$Ba, Ti(O$_2$C$_2$H$_5$)$_2$, Bi(O$_2$C$_2$H$_5$)$_3$, Mg(O$_2$C$_2$H$_5$)$_2$, and acetylacetone were used as starting materials. A precursor solution with nominal composition of Ba:Bi:Mg:Ti = 0.60:0.46:0.20:0.80 (with 15% Bi excess) was prepared by...
dissolving the starting materials in 2-methoxyethanol solvent to yield the resulting films with the composition of 0.60 BaTiO$_3$-0.40 Bi(Mg$_{1/3}$Ti$_{2/3}$)$_2$O$_5$. The chemical composition was determined on the basis of our previous work, in order to obtain the stable TCC behavior. The final concentration of the solution was approximately 0.1 mol/dm$^3$. (100)SrRuO$_3$//(100)SrTiO$_3$ and (111)SrRuO$_3$//(111)SrTiO$_3$ substrates were used for the film deposition with preferential crystal orientation, while an (111)Pt/TiO$_2$//(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 5 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 (XRD) 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 $1 \times 10^2 - 2 \times 10^9$ 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 were obtained for these films, as well as those from substrates (Si or SrTiO$_3$) and electrodes (Pt or SrRuO$_3$). The films fabricated on (111)Pt/TiO$_2$//(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)SrRuO$_3$//(100)SrTiO$_3$ and (111)SrRuO$_3$//(111)SrTiO$_3$ showed only the peaks of perovskite (600) and (111), which indicates the preferential crystal orientation of perovskite (100) and (111) planes, respectively, normal to the substrate surface. Peak intensities of the BT–BMT on (100)SrRuO$_3$//(100)SrTiO$_3$ and (111)SrRuO$_3$//(111)SrTiO$_3$ substrates were significantly larger than that on (111)Pt/TiO$_2$//(100)Si substrate. These results suggest that the BT–BMT films were grown epitaxially on the perovskite-type surface, i.e., surfaces of SrRuO$_3$ (100) and (111) plane, depending on its crystallographic configuration similarly to other thin films of perovskite-type oxides. The films on (111)Pt/TiO$_2$//(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 BaTiO$_3$ (a-axis), as confirmed in previous report.

Figure 2 shows surface AFM images of the BT–BMT films fabricated on various substrates. No crack or pore structure was observed on the surface of these films. The surface roughness of the films fabricated on (100)SrRuO$_3$//(100)SrTiO$_3$ was relatively smaller than those on (111)Pt/TiO$_2$//(100)Si and (111)SrRuO$_3$//(111)SrTiO$_3$; 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, smooth surface of the film on (100)SrRuO$_3$//(100)SrTiO$_3$ 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/TiO$_2$//(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)SrRuO$_3$//(111)SrTiO$_3$ substrates exhibited relatively higher remanent polarization ($P_r$) of 15 μC/cm$^2$ 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/TiO$_2$//(111)Si ($P_r = 6$ μC/cm$^2$, $E_c = 170$ kV/cm) and on (100)SrRuO$_3$//(111)SrTiO$_3$ ($P_r = 7$ μC/cm$^2$, $E_c = 120$ 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)SrRuO$_3$//(111)SrTiO$_3$, 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)SrRuO$_3$//(111)SrTiO$_3$ also exhibited the breakdown field of 1870 kV/cm higher than those of the (100)-oriented films on
Figure 4 shows relative dielectric constant, \( \varepsilon_r \), 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 \( \varepsilon_r \) 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 arose 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)SrRuO\(_3\)/(111)SrTiO\(_3\) showed higher \( \varepsilon_r \) value compared with the films on (100)SrRuO\(_3\)/(100)SrTiO\(_3\) and (111)Pt/TiO\(_2\)/(111)Si during the frequency range of \(10^3\)–\(10^6\) Hz; \( \varepsilon_r \) 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 \( \varepsilon_r \) 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 \( \varepsilon_r \) 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, \( \Delta C = (C_{\text{max}} - C_{\text{min}})/C_{\text{max}} \) 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 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 \( \varepsilon_r \) and tan\( \delta \) of the BT–BMT films on various substrates, as a function of oscillation frequency. The data were measured at room temperature.
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 \(|\text{TCC}|\) values of the films on (111)Pt/TiO\(_2\)/(111)SrTiO\(_3\) and (111)SrRuO\(_3\)//(111)SrTiO\(_3\) 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)Bi\(_4\)Ti\(_4\)O\(_{15}\) \(\varepsilon_r = \sim 200, |\text{TCC}| = \sim 250 \text{ppm/K}\).\(^{43,46}\) The (111)-oriented BT–BMT film exhibited slightly higher \(|\text{TCC}|\) 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 BaTiO\(_3\) 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)SrRuO\(_3\)//(100)SrTiO\(_3\) and (111)SrRuO\(_3\)//(111)SrTiO\(_3\) substrates successfully by CSD technique. Dielectric and ferroelectric properties the BT–BMT films were varied depending on their crystal orientation; especially, enhanced \(\varepsilon_r\) value up to 800 was confirmed at room temperature for the (111)-oriented BT–BMT film on (111)SrRuO\(_3\)//(111)SrTiO\(_3\) 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 \(|\text{TCC}|\) value. These properties will be favorable for the application of specialized dielectric capacitor of high-temperature electronics.

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