Orientation Dependence of Epitaxial and One-Axis-Oriented (Ba$_{0.5}$Sr$_{0.5}$)TiO$_3$ Films Prepared by RF Magnetron Sputtering

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The dependences of electrical properties on (111) and (100) orientations were investigated for (Ba$_{0.5}$Sr$_{0.5}$)TiO$_3$ films with in-plane random (one-axis-oriented films) and aligned orientations (epitaxial films) prepared by RF magnetron sputtering. Epitaxial films with (100) and (111) orientations were grown on (100)SrRuO$_3$//(100)SrTiO$_3$ and (111)SrRuO$_3$//(111)SrTiO$_3$ substrates, while one-axis-oriented films were grown on (100),SrRuO$_3$//(100),LaNiO$_3$//(111)Pt/TiO$_2$/SiO$_2$/Al$_2$O$_3$ and (111),SrRuO$_3$//(111)Pt/TiO$_2$/SiO$_2$/Al$_2$O$_3$ substrates, respectively. Films with the (111) orientation had larger relative dielectric constants, $\varepsilon_r$, measured at an oscillation of 20 mV and 100 kHz under an applied dc bias electric field of 0 kV/cm and a larger tunability against the dc bias electric field than (100)-oriented films for both epitaxial and one-axis orientations. These data show the dependences of $\varepsilon_r$ and tunability on orientation were existed, irrespective of the in-plane orientation and the thermal strain caused in the film by the substrates. [DOI: 10.1143/JJAP.44.6881]

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1. Introductions

(Ba$_{0.5}$Sr$_{0.5}$)TiO$_3$ (BST) has been widely investigated in tunable microwave devices such as phase shifters, delay lines, resonators, tunable filters, and varactors due to its high relative dielectric constant ($\varepsilon_r$), tunability and low dielectric loss (tan $\delta$).$^1$ The BST ceramic system has a phase transition from a paraelectric cubic phase to a ferroelectric tetragonal phase and has a maximum in relative dielectric constant–temperature plots. In the case of thin film BST, the maximum in the $\varepsilon_r[\varepsilon_{\text{max}}(T)]$ has been suppressed and has shown a very broad temperature dependence accompanied with a temperature shift of $\varepsilon_{\text{max}}(T).$ $^2$

In capacitance–dc bias electric field (C–E) characteristics, a butterfly-shaped curve typically appearing in ferroelectric materials was frequently observed for paraelectric BST films.$^3$ This suggests the contribution of the ferroelectricity in the film. This also shows the possibility that $\varepsilon_r$ has an orientation dependence and that its tunability may be similar to that observed for ferroelectric BST thin films.$^3$ In fact, the orientation dependences of the dielectric property at zero dc bias electric field was reported for (100)-, (110)- and (111)-oriented BST films grown on (100), (110) and (111) MgO substrates, respectively.$^5$ However, the effect of an in-plane orientation in epitaxial BST films as reported by Moon et al.$^5$ was not made clear, even though for practical applications of BST films only non-epitaxial films, either randomly oriented or one-axis-oriented films, can be used. In addition, a dependence of $\varepsilon_r$ on orientation for films deposited on Si$^{2,6}$ or Al$_2$O$_3$$^7$ substrates has not been reported, in spite of the fact that the $\varepsilon_r$ and tunability of the BST film is known to be strongly affected by strain from the substrate.$^8,9$ Moreover, the thermal strain applied to the film, the dominant strain from the substrate, deposited on Si and Al$_2$O$_3$ substrates is opposite that of the BST films deposited on MgO substrates.

In this study, we first investigated the electrical properties of (100)- and (111)-oriented epitaxial BST films grown on SrRuO$_3$-coated SrTiO$_3$ substrates. In addition, we compare the results for the same out-of-plane-oriented films with those for in-plane randomly oriented (or one-axis-oriented) films deposited on Al$_2$O$_3$ ceramic substrates. On the basis of these results, we discuss the dielectric anisotropy of the films, taking into account the effect of in-plane orientation and the strain from the substrates on these properties.

2. Experimental

BST films 210 nm thick were deposited at 800°C by RF magnetron sputtering. Film thickness was ascertained using a field emission–scanning electron microscope (FE-SEM) with cross-sectional observation. The total gas pressure was 1.0 × 10 Pa under an Ar/O$_2$ gas ratio of 9/1. The films obtained were annealed at 500°C in atmospheric O$_2$ flow for 30 min. Epitaxial SrRuO$_3$ films 100 nm thick were deposited on (100) and (111) SrTiO$_3$ single crystals at 750°C by metal organic chemical vapor deposition (MOCVD), and (100),SrRuO$_3$//(100)SrTiO$_3$ and (111),SrRuO$_3$//(111)-SrTiO$_3$ shown in Figs. 1(a) and 1(b) were used as substrates for growing epitaxial BST film. A pseudo-cubic Miller index designated as $(hkl)$, was used for SrRuO$_3$,$^{10-12}$ as well as for LaNiO$_3$. On the other hand, the stacks of (100),SrRuO$_3$//(100),LaNiO$_3$//(111)Pt/TiO$_2$/SiO$_2$/Al$_2$O$_3$ and (111),SrRuO$_3$//(111)Pt/TiO$_2$/SiO$_2$/Al$_2$O$_3$ shown in Figs. 1(c) and 1(d) were used as substrates to prepare one-axis-oriented BST film. The details of the preparation of Pt/TiO$_2$/SiO$_2$/Al$_2$O$_3$ and the upper buffer layers have been reported elsewhere.$^{7,13}$

The crystal structure of the films was characterized by X-ray diffraction (XRD). The composition of the films was ascertained using a wavelength dispersion X-ray fluorescence (XRF) spectrometer. The electrical properties of Pt/BST/SrRuO$_3$ capacitors were characterized after making Pt top electrodes by electron-beam evaporation on BST films through dots 100 μm in diameter using a shadow mask.
Capacitance–dc bias electric field (C–E) characteristics with an oscillation at 20 mV and 100 kHz were measured using an HP 4194A. Tunability was measured under an applied dc bias electric field (also known as change in relative dielectric constant, \( \varepsilon_r \)) and loss tangent (\( \tan \delta \)) as functions of applied dc bias electric field for the same films as shown in Fig. 2. The \( \varepsilon_r \) of the (111)-oriented BST film was larger than that of the (100)-oriented film, particularly in the low dc bias electric field region, but the \( \varepsilon_r \) at a high dc bias electric field was almost the same for both films. This suggests that the change in \( \varepsilon_r \) with dc bias electric field (also known as tunability) of the (111)-oriented BST film was larger than that of the (100)-oriented film. It must be mentioned that the tunability in tan\( \delta \) of the (111)-oriented film was also larger than that of the (100)-oriented film. The tunabilities for the dc bias electric fields up to an \( E_{\text{max}} \) of 250 kV/cm and 700 kV/cm were 61.3% and 81.8% for (100)-oriented film, respectively and 66.6% and 83.3% for (111)-oriented BST film, respectively.

3.2 One-axis-oriented BST films

To clarify the effect of the strain applied to the BST film from the substrate and the in-plane orientation, (100)- and (111)-oriented films with an in-plane random orientation were deposited on Al\(_2\)O\(_3\) substrates, the thermal expansion coefficient (\( \alpha_{\text{TEC}} \)) of which was smaller than that of the BST film, while that of the SrTiO\(_3\) substrate was larger than that of the BST film.

Figure 4 shows the XRD patterns and the X-ray pole-figure plots fixed at the 2\( \theta \) position corresponding to 220/BST for the films grown on (100),SrRuO\(_3\)/(100)SrTiO\(_3\) and (111),SrRuO\(_3\)/(111)SrTiO\(_3\) substrates. Only (100) and (200) diffraction peaks of BST films were verified on 0-2\( \theta \) XRD patterns for the films grown on (100),SrRuO\(_3\)/(100)SrTiO\(_3\) substrates and (111) peaks for those on (111),SrRuO\(_3\)/(111)SrTiO\(_3\) substrates. In addition, four and three concentrated poles located at psi = 45 and 35° were observed in pole-figure plots as shown in the insets of Figs. 2(a) and 2(b), respectively. These data show that (100)- and (111)-oriented BST films were ascertained to be epitaxially grown on (100),SrRuO\(_3\)/(100)SrTiO\(_3\) and (111),SrRuO\(_3\)/(111)SrTiO\(_3\) substrates, respectively.

Figure 3 shows the change in \( \varepsilon_r \) and tan\( \delta \) as functions of the dc bias electric field for the same BST films shown in Fig. 2. The \( \varepsilon_r \) of the (111)-oriented BST film was larger than that of the (100)-oriented film, particularly in the low dc bias electric field region, but the \( \varepsilon_r \) at a high dc bias electric field was almost the same for both films. This suggests that the change in \( \varepsilon_r \) with dc bias electric field (also known as tunability) of the (111)-oriented BST film was larger than that of the (100)-oriented film. It must be mentioned that the tunability in tan\( \delta \) of the (111)-oriented film was also larger than that of the (100)-oriented film. The tunabilities for the dc bias electric fields up to an \( E_{\text{max}} \) of 250 kV/cm and 700 kV/cm were 61.3% and 81.8% for (100)-oriented film, respectively and 66.6% and 83.3% for (111)-oriented BST film, respectively.
axis-oriented BST films have larger $d_{\text{111}}$ values than one-axis-oriented films shown in Figs. 2 and 4. Epitaxial BST films showed those reported for bulk BST with the same Ba/Sr ratio. However, ringed poles located at $\psi = 45$ and $35^\circ$ were observed on X-ray pole-figure plots as shown in the insets of Figs. 4(a) and 4(b), respectively. These data show that (100)- and (111)-oriented one-axis-oriented films were prepared on (100)-SrRuO$_3$/LaNiO$_3$/SrTiO$_3$ and (111)-SrRuO$_3$/SrTiO$_3$ substrates, respectively.

Figure 5 summarizes the lattice spacing of $2\theta$ and $d_{200}$ and $d_{111}$ estimated from epitaxial and one-axis-oriented BST films shown in Figs. 2 and 4 for (100)- and (111)-oriented films, respectively. (a): BST/(100),SrRuO$_3$/SrTiO$_3$, (b): BST/(111),SrRuO$_3$/SrTiO$_3$, (c): BST/(100),SrRuO$_3$/LaNiO$_3$/SrTiO$_3$, (d): BST/(111),SrRuO$_3$/LaNiO$_3$/SrTiO$_3$. (e): reported data for bulk BST, (f): reported data for bulk (Ba,Sr)$_2$TiO$_5$.

as was the case for BST films grown on (100)-SrRuO$_3$/SrTiO$_3$ and (111)-SrRuO$_3$/SrTiO$_3$ substrates. However, ringed poles located at $\psi = 45$ and $35^\circ$ were observed on X-ray pole-figure plots as shown in the insets of Figs. 4(a) and 4(b), respectively. These data show that (100)- and (111)-oriented one-axis-oriented films with an in-plane random orientation were prepared on (100)-SrRuO$_3$/LaNiO$_3$/SrTiO$_3$ and (111)-SrRuO$_3$/SrTiO$_3$ substrates, respectively.

Figure 5 summarizes the lattice spacing of $2\theta$ and $d_{200}$ and $d_{111}$ estimated from epitaxial and one-axis-oriented BST films shown in Figs. 2 and 4 for (100)- and (111)-oriented films, respectively. These data show that (100)- and (111)-oriented films with an in-plane random orientation were prepared on (100)-SrRuO$_3$/LaNiO$_3$/SrTiO$_3$ and (111)-SrRuO$_3$/SrTiO$_3$ substrates, respectively.

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Figure 6 shows the change in $\varepsilon_r$ and tan$\delta$ as a function of the dc bias electric field for the same type of BST films as shown in Fig. 4. The $\varepsilon_r$ of (111)-oriented BST film was also larger than that of (100)-oriented film at the low dc bias electric field region, but those at the high dc bias electric field were comparable for both BST films and were very similar to the tunabilities of the epitaxial BST films shown in Fig. 3. The dependence of tan$\delta$ on the applied electric field demonstrated a similar behavior. These data allow us to conclude that the tunabilities in $\varepsilon_r$ and tan$\delta$ of (111)-oriented one-axis-oriented films were also larger than those of (100)-oriented films. The tunability for dc bias electric fields up to an $E_{\text{max}}$ of 250 kV/cm was 55.8 and 59.6% for (100)- and (111)-oriented films, respectively.

3.3 Comparison with dielectric properties of epitaxial and one-axis-oriented films

Figure 7 summarizes the tunability for the dc bias electric fields up to an $E_{\text{max}}$ of 250 kV/cm for the (100)- and (111)-oriented BST films. The tunability of the (111)-oriented one-axis film was larger than that of the (100)-oriented film for both films together with the same trend in tan$\delta$, suggesting crystal anisotropy in the $\varepsilon_r$ and tan$\delta$ of BST films. This anisotropy in the dielectric properties of BST films is very similar to the tendency reported at 9 GHz by Moon et al.\(^5\) They pointed out the following three possible reasons: polarization changes come from magnitude variations in the relative displacement of Ti ions with respect to O ions, the domain growth mechanism changes, and the strain and stress changes in perovskite BST films. In this study, a similar anisotropy was ascertained even at a low frequency of 100 kHz. These data suggest that the origin of the anisotropy can be applicable over a wider frequency range. One possibility, the strain and stress changes pointed out by Moon et al., is now under investigation by changing the substrate: Si, MgO, and SrTiO$_3$. In addition, the crystal anisotropy did not depend on the in-plane orientation and the thermal strain applied to the films from the substrates. These
data suggest that the crystal orientation of BST films engineered on templates used in this study produces a larger $\varepsilon_r$ near 0 kV/cm dc bias electric fields, and the tunability becomes as high as that for ferroelectric BST films.\(^4\)

4. Conclusions

(100)- and (111)-oriented one-axis and epitaxial BST films were prepared by RF magnetron sputtering. (100)- and (111)-oriented epitaxial films were grown on (100)$_c$SrRuO$_3$/(100)SrTiO$_3$ and (111)$_c$SrRuO$_3$/(111)SrTiO$_3$ substrates, while (100)- and (111)-oriented one-axis films were grown on (100)$_c$SrRuO$_3$/(100)$_c$LaNiO$_3$/(111)$_c$Pt/TiO$_2$/SiO$_2$/Al$_2$O$_3$ and (111)$_c$SrRuO$_3$/(111)$_c$Pt/TiO$_2$/SiO$_2$/Al$_2$O$_3$ substrates, respectively. A larger $\varepsilon_r$ near 0 kV/cm and tunability against the dc bias electric field were obtained for (111)-oriented BST films than for (100)-oriented films for both epitaxial and one-axis-oriented films. Crystal structure anisotropy, irrespective of the thermal strain applied to the film and the in-plane orientation, was confirmed for $\varepsilon_r$ near 0 kV/cm and for the tunability of BST films.

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