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Effect of the thermal expansion matching on the dielectric tunability of (100)-one-axis-oriented $(Ba_{0.5}Sr_{0.5})TiO_3$ thin films

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The impact of the residual strain induced by the thermal strain on the dielectric tunability was systematically studied for rf sputtered (100)-one-axis-oriented polycrystalline $(Ba_{0.5}Sr_{0.5})TiO_3$ films. These films were grown on various substrates with different thermal expansion coefficients $[\alpha_{(sub)}]$ covered with a stack of $(100)_c SrRuO_3/(100)_c LaNiO_3/(111)Pt$ layers. The residual strain was ascertained to linearly increase with the increase in $\alpha_{(sub)}$ by enhancement of the surface-normal lattice spacing of $(Ba_{0.5}Sr_{0.5})TiO_3$ and Pt. Dielectric tunability of the films also linearly increased with the increase in $\alpha_{(sub)}$. These results clearly demonstrate that dielectric tunability tailoring of the $(Ba_{0.5}Sr_{0.5})TiO_3$ films can be achieved by using residual thermal strain. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2719621]

Thin films of (Ba, Sr)TiO_3 have been extensively studied for tunable capacitor applications employing their dielectric tuning—a change of a dielectric constant under applied electric field.[1,2] The origin of the dielectric tunability attributed is attributed to a polarizing of the crystal lattice.[3–5] *Sharma et al.* calculated the capacitance tunability change with the internal strain induced by the thermal mismatch for the (001)-oriented polycrystalline $(Ba_{0.5}Sr_{0.5})TiO_3$ films and indicated that a small residual strain in the films leads to the enhancement in the tunability of the films.[4] This suggests that if the films are prepared on substrates with various thermal expansion coefficients $[\alpha_{(sub)}]$ in regard to the $(Ba_{0.5}Sr_{0.5})TiO_3$ (BST) $[\alpha_{(film)}]$, the tunability of the films can be modulated.

An experimental trial was reported by *Taylor et al.*, in which the effect of the stress applied to the rf sputtered $(Ba_{0.24}Sr_{0.76})Ti_{0.96}O_3$ film on the tunability was investigated by changing $\alpha_{(sub)}$.[5] The obtained tunability dependence on the substrate, however, is different from the prediction of *Sharma et al.*[4] that the tunability increases monotonously with the increase in $\alpha_{(sub)}$ for all substrates, because of the development of compressive to tensile stress in the film. On the other hand, the report by *Taylor et al.* does not include any direct measurement of the residual strain in the film. Moreover, it is widely recognized that the predominant orientation of the BST films affects their tunability, but the films obtained by *Taylor et al.* did not have the same film orientation.[6,7] It must also be mentioned that the composition of the films produced by them is $(Ba_{0.24}Sr_{0.76})Ti_{0.96}O_3$, and with corresponding tunabilities somewhat different from the widely investigated $(Ba_{0.5}Sr_{0.5})TiO_3$ or $(Ba_{0.7}Sr_{0.3})TiO_3$. All of the above, in addition to the fact that a lower temperature of 100 K was used to record the tunability dependency on substrate, significantly influence the sensitivity of the tunability of the $(Ba_{0.24}Sr_{0.76})TiO_3$ films.[8] Therefore, the experimental evidence of the residual strain effect on the tunability of the film is still unclear, due to the lack of sufficient data based on strongly oriented polycrystalline films with the commonly investigated composition, as the ones analyzed by *Sharma et al.* $(Ba_{0.5}Sr_{0.5})TiO_3$.[4]

In the present study, the dielectric tunability was investigated using (100)-one-axis-oriented $(Ba_{0.5}Sr_{0.5})TiO_3$ thin films prepared on various kinds of substrates with wide range of $\alpha_{(sub)}$. One-axis-oriented films were selected, rather than the epitaxially grown ones, because of their suitability for real applications and the abundant choices of substrates with different $\alpha_{(sub)}$ that can be used.

BST films about 200 nm in thickness were deposited at 800 °C by rf magnetron sputter deposition method. The total gas pressure was 2.7×10 Pa with an Ar/O_2 gas ratio of 9/1. The deposition rate was as low as 67 nm/h to ensure a good quality of the films. The BST stacks were annealed at 500 °C for 30 min in atmospheric pressure O_2 flow condition after deposition and patterning of the top Pt electrode.

One-axis-oriented films were deposited on four kinds of substrates with different $\alpha_{(sub)}$: (100) Si, polycrystalline Al_2O_3, (100) $SrTiO_3$, and (100) MgO. Amorphous SiO_2 layer was firstly deposited to make a discontinuation layer and to eliminate the substrate crystal structure mismatch dependence. After that, $(100)_c SrRuO_3$(20 nm)/$(100)_c LaNiO_3$(100 nm)/(111)Pt (100 nm) layers [$SrRuO_3$ and $LaNiO_3$ labeled with pseudocubic Miller index designation $(hkl)_c$] were deposited on SiO_2,[7,9] where rf sputtered $LaNiO_3$ has self $(100)_c$-orientation characteristics on (111)Pt.[10] Finally, $(100)_c SrRuO_3$ was rf sputtered on $(100)_c LaNiO_3$ layer to promote the crystallinity enhancement of the BST films.[11] Common $(100)_c SrRuO_3$ layer was used as the top portion of the substrate irrespective to the kind of the substrate to keep the same lattice misfit stress and to ensure the high orientation control of (100)-one-axis-dominant BST films.

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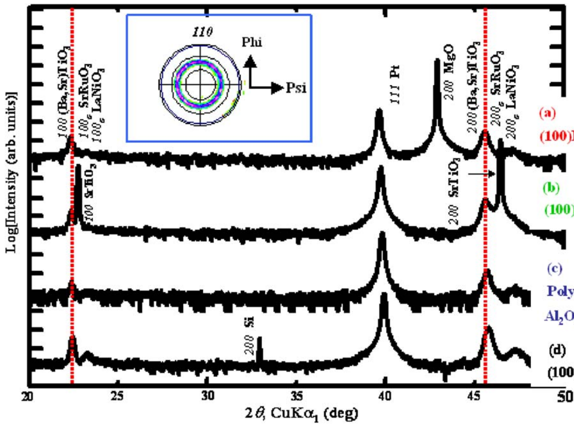

FIG. 1. (Color online) XRD patterns of the BST films deposited on (a) (100) MgO, (b) (100) SrTiO$_3$, (c) polycrystalline Al$_2$O$_3$, and (d) (100) Si substrates. The insert shows the x-ray pole figure data, measured at fixed 2θ angle, corresponding to BST110 for the film on (100) MgO substrate.

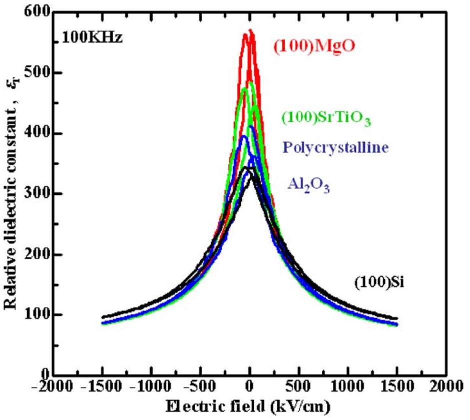

FIG. 3. (Color online) Change of the relative constant under the applied electric field for the BST films, shown in Figs. 1 and 2.

The crystal structure of the BST films was characterized by x-ray diffraction (XRD). By using wavelength dispersion x-ray fluorescence spectrometer, calibrated with standard samples, the compositions of the films were ascertained to be Ba/(Ba+Sr)=0.5 and (Ba+Sr)/Ti=1.0. The electrical properties of Pt/BST/SrRuO$_3$ capacitor were characterized after making $25\times25\ \mu\mathrm{m}^2$ Pt top electrodes that were rf magnetron sputtered on the BST films and patterned by standard lithography process. The relative dielectric constant under the applied electric field at a frequency of 100 kHz with a test signal level of 20 mV was measured at room temperature using an HP 4194A impedance analyzer.

Figure 1 shows the XRD patterns of the films deposited on four kinds of substrates. *h*00 diffraction peaks of BST were observed in all XRD patterns, suggesting that the (100) orientation is along the surface-normal direction. X-ray pole figure measured at fixed 2θ angle corresponding to BST*110* is inserted in Fig. 1 for the case of BST film on MgO substrate. Ring structure at inclination angle *psi* of about 45° presupposes a (100) one-axis orientation of the film, and the same was determined for other three films. The XRD rocking curve full width at half maximum of BST200 was ascertained to be from 3.1° to 5.3° for all BST samples. These results suggest that the (100)-one-axis-oriented BST films have similar degree of orientation even though they have been deposited on different substrates.

Figure 2 shows the lattice spacing of BST*200* [d(BST*200*)] and Pt111 [d(Pt*111*)] planes, calculated on the basis of the data shown in Fig. 1 as a function of $\alpha_{(\mathrm{sub})}$. Both d(BST*200*) and d(Pt*111*) increased almost linearly with the increase in $\alpha_{(\mathrm{sub})}$. This implies that the change of these values with $\alpha_{(\mathrm{sub})}$ is mainly determined by the in-plane thermal stress σ_{th} defined as

$$\sigma_{\mathrm{th(film)}} = [E/(1-\nu)][\alpha_{(\mathrm{sub})} - \alpha_{(\mathrm{film})}][T_{(\mathrm{depo})} - T_{(\mathrm{RT})}],$$

where E and v represent the elastic modulus and Poisson's ratio of the films, respectively, and $\alpha_{(\mathrm{film})}$, $T_{(\mathrm{depo})}$, and $T_{(\mathrm{RT})}$ are the thermal expansion coefficients of the film, deposition temperature, and room temperature, respectively. The estimated slope of the change in d(BST*200*) with $\alpha_{(\mathrm{sub})}$ under constant $\alpha_{(\mathrm{film})}$, $T_{(\mathrm{depo})}$, and $T_{(\mathrm{RT})}$ is almost identical to the data shown in Fig. 2.[12] This suggests that the corresponding variations in the residual strain in the films with $\alpha_{(\mathrm{sub})}$ originated due to the thermal strain induced by the substrates, not due to the misfit strain. This is also supported by the fact that the residual misfit strain is almost identical for all BST films as the top portion of the buffer stacks has the same SrRuO$_3$

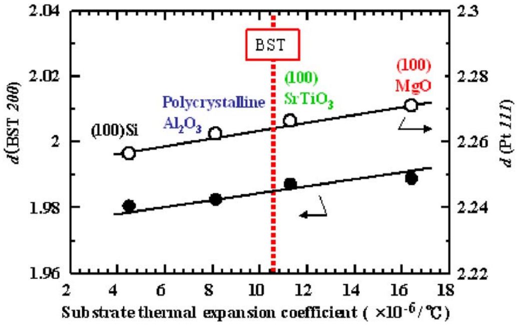

FIG. 2. (Color online) Change of the lattice spacing of BST200 [d(BST200)] and Pt111 [d(Pt111)] planes, calculated from the data, shown in Fig. 1, as a function of the thermal expansion coefficient of the substrate [$\alpha_{(\mathrm{sub})}$].

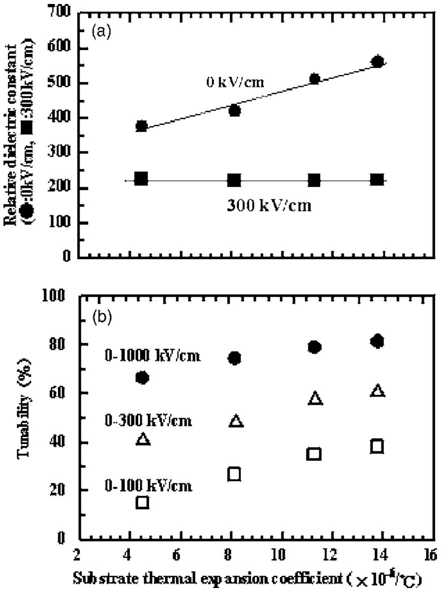

FIG. 4. (a) Relative dielectric constant at 0 and 300 kV/cm obtained from Fig. 3 and (b) the dielectric tunability measured under different applied electric fields for BST films deposited on different substrates as a function of the thermal expansion coefficient of the substrate [$\alpha_{(\mathrm{sub})}$].

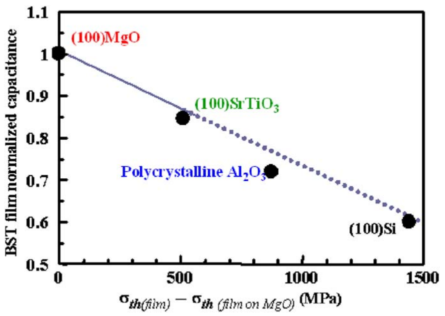

FIG. 5. (Color online) Normalized capacitance of BST films at 0 kV/cm as a function of the predicted difference of tensile stress in the BST film on MgO substrate vs the stress on other substrates. The solid line corresponds to the data reported by *Shaw et al.* [see Ref. 16] and the dashed line is its extrapolation.

layer with relatively large lattice mismatch between the BST and SrRuO$_3$ (i.e., about 6.5%) as well as by the fact that the deposition process induced stress is also identical, since all BST films were deposited within the same batch.

The dependence of the relative dielectric constants on the applied electric field for the BST films, shown in Figs. 1 and 2, is presented in Fig. 3. The capacitance-voltage (C-V) curves were obtained under applied bias voltages from −30 to +30 V, and because the film thickness approximated 200 nm in all samples, the corresponding electric field was ±1500 kV/cm. It must be noted that the existence of a small hysteresis in the C-V curves could be due to the electric-field-induced ferroelectricity and/or to slow capacitance relaxation taking place with change of dc bias.[13,14] The latter phenomenon is associatable with redistribution of the oxygen vacancies or other space charges and near-electrode charging/discharging processes[14] or could as well be attributed to Maxwell-Wagner-type dielectric relaxation.[15]

Figure 4(a) summarizes the relative dielectric constants at 0 and 300 kV/cm obtained from Fig. 3 as a function of the $\alpha_{(\mathrm{sub})}$. The relative dielectric constants at 0 kV/cm were found to be strongly dependent on the kind of the substrate used and to almost linearly increase with the increase in $\alpha_{(\mathrm{sub})}$, while those at high electric field of 300 kV/cm were nearly independent of the substrate [see Fig. 4(a)]. The dielectric tunability measured under any applied electric field almost linearly increased with the increase in $\alpha_{(\mathrm{sub})}$ as obtained from capacitors made from the BST films deposited on different substrates [see Fig. 4(b)]. This result supports the data by *Taylor et al.*[5] It must be noted that the dielectric loss of all the BST films between 0 and 1000 kV/cm was in the range of 0.4%–1.2% (100 kHz).

Figure 5 shows the normalized capacitance of BST films at 0 kV/cm as a function of the predicted difference of tensile stress in the BST film on MgO substrate versus the stress on other substrates, assuming an elastic modulus of $E=200$ GPa and Poisson's ratio of $\nu=0.23$ as values of the bulk BST material.[5] Normalized capacitance almost linearly decreased with the difference of tensile stress in the BST film on MgO substrate versus the stress on other substrates. The straight line in Fig. 5 corresponds to the data measured by *Shaw et al.* for the capacitor change with the applied mechanical load for the BST films deposited on (100) Si substrate.[16] This line is in good agreement with the present results.

There is strong experimental evidence that the strain applied to the film is an important factor for determining the tunability of BST films and that it is in good agreement with the reported prediction of the static strain data. In addition, the tunability of the BST films is recognized to be modulated by the residual strain, which is induced by the various interactions, such as the thermal stress under cooling and the misfit stress strongly influenced by the crystalline structure of the immediate adjacent layer (i.e., SrRuO$_3$) of the multilayer buffer stack.[8]

In summary, (100)-one-axis-oriented BST films were prepared on four kinds of substrates with different $\alpha_{(\mathrm{sub})}$, covered by $(100)_c$SrRuO$_3$/$(100)_c$LaNiO$_3$/(111)Pt layers. Surface-normal lattice spacing of (Ba$_{0.5}$Sr$_{0.5}$)TiO$_3$ and Pt linearly increased with the increase in $\alpha_{(\mathrm{sub})}$, which is indicative of a monotonous increase of the residual strain. Tunability of the capacitance also linearly increased with the increase in $\alpha_{(\mathrm{sub})}$. The experimental evidence clearly shows that the tunability can be tailored by the residual strain and that it is in good agreement with the reported prediction of the static strain data.

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