

Effect of the Strain from the Substrate on Tunability of (100) One-axis Oriented (Ba_{0.5}Sr_{0.5})TiO₃ Thin Films

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Abstract — The impact of the residual strain induced by the thermal strain on the dielectric tunability was systematically studied for (100)-one-axis-oriented polycrystalline (Ba_{0.5}Sr_{0.5})TiO₃ films. These films were grown on various substrates with different thermal expansion coefficients [$\alpha_{(sub.)}$] covered with a stack of (100)_cSrRuO₃/(100)_cLaNiO₃/(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})TiO₃ 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})TiO₃ films can be achieved by using residual thermal strain.

INTRODUCTIONS

Thin films of (Ba,Sr)TiO₃ have been extensively studied for tunable capacitor applications employing their large capacitance change characteristics under an applied electric field, so called the dielectric tunability [1, 2]. The origin of the dielectric tunability is pointed out to be caused by the electrostrictive strain of the film [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})TiO₃ 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})TiO₃ [$\alpha_{(film.)}$], the tunability of the films can be modulated.

An experimental trial was reported by *Taylor et al.* [5], in which the effect of the stress applied to the RF sputtered (Ba_{0.24}Sr_{0.76})Ti_{0.96}O₃ film on the tunability was investigated by changing $\alpha_{(sub.)}$. 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 be also mentioned that the composition of the films produced by them is (Ba_{0.24}Sr_{0.76})Ti_{0.96}O₃, and with corresponding tunabilities somewhat different from the widely investigated (Ba_{0.5}Sr_{0.5})TiO₃ or (Ba_{0.7}Sr_{0.3})TiO₃. 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})TiO₃ 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})TiO₃.

In the present study, the dielectric tunability was investigated using (100)-one-axis-oriented (Ba_{0.5}Sr_{0.5})TiO₃ 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.

EXPERIMENTAL

(Ba_{0.5}Sr_{0.5})TiO₃ [BST] films 200 nm in thickness were deposited at 800°C by RF magnetron sputter deposition method. The total gas pressure was 2.7×10^1 Pa with Ar/O₂ 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 O₂ 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 Al₂O₃, (100) SrTiO₃, and (100) MgO. Amorphous SiO₂ layer was firstly deposited to make a discontinuation layer and to eliminate the substrate crystal structure mismatch dependence. After that, (100)_cSrRuO₃ (20nm)/(100)_cLaNiO₃(100 nm)/(111)Pt (100 nm) layers [SrRuO₃ and LaNiO₃ labeled with pseudo cubic Miller index designation (hkl)_c] were deposited on SiO₂ [7, 9][see Fig.1(a)], where RF sputtered LaNiO₃ has self (100)_c-orientation characteristics on (111)Pt [10],[see Fig.1(b) and (c)]. Finally, (100)_cSrRuO₃ was RF

sputtered on (100)_cLaNiO₃ layer to promote the crystallinity enhancement of the BST films[11]. Common (100)_cSrRuO₃ 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.

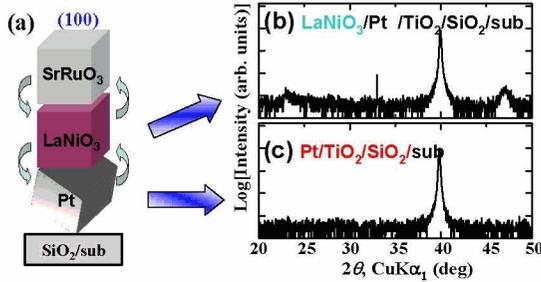


Fig.1 (a) Schemin drawing of the substrates for BST deposition and their XRD patterns. (b) LaNiO₃/Pt/TiO₂/SiO₂/substrate, (c) Pt/TiO₂/SiO₂/substrate

The crystal structure of the BST films was characterized by X-ray diffraction (XRD). By using wavelength dispersion X-ray fluorescence spectrometer (XRF), calibrated with standard samples, the composition of the films was ascertained to be Ba/(Ba+Sr)=0.5 and (Ba+Sr)/Ti=1.0.

The electrical properties of Pt/BST/SrRuO₃ capacitor were characterized after making 25μm × 25 μm square 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 was measured using a HP 4194A impedance analyzer.

RESULTS AND DISCUSSIONS

Fig.2 shows the XRD patterns of the films deposited on four kinds of substrates. *h00* 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 BST110 is inserted in Fig. 2 for the case of BST film on MgO substrate. Ring structure at inclination angle *psi* of about 45 degree 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 (*FWHM*) of BST200 was ascertained to be from 3.1 to 5.3 degree 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.

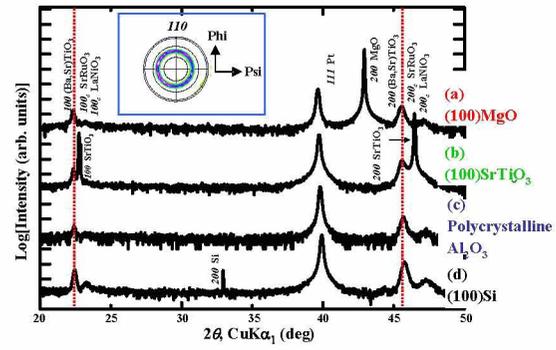


Fig.2 XRD patterns of the BST films, deposited on: (a) (100) MgO, (b) (100) SrTiO₃, (c) polycrystalline Al₂O₃, and (d) (100) Si substrates. The insert shows the X-ray pole figure data, measured at fixed 2θ angle, corresponding to BST110 for the film on (100) MgO substrate.

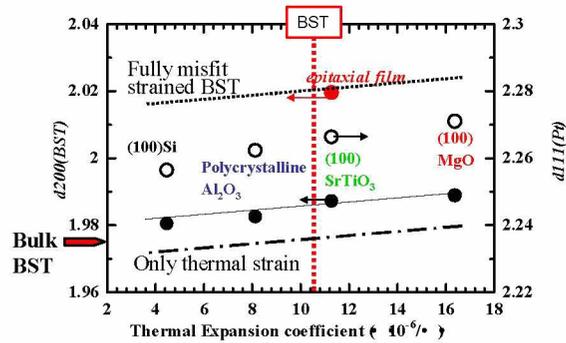


FIG. 3 Change of the lattice spacing of BST200 [*d*(BST200)] and Pt111 [*d*(Pt111)]_planes, calculated from the data, shown in Fig. 2, as a function of the thermal expansion coefficient of the substrate [α_{sub}].

Fig.3 shows the lattice spacing of BST200 [*d*(BST200)] and Pt111 [*d*(Pt111)] planes, calculated on the basis of the data shown in Fig. 2 as a function of α_{sub} . Both *d*(BST200) and *d*(Pt111) increased almost linearly with the increase in α_{sub} . This implies that the change of these values with α_{sub} is mainly determined by the in-plane thermal stress σ_{th} , defined as:

$$\sigma_{th(film)} = [E/(1-\nu)] \times [\alpha_{(sub.)} - \alpha_{(film)}] \times [T_{(depo.)} - T_{(R.T.)}],$$

where *E* and ν represent the elastic modulus and Poisson's ratio of the films, respectively, and $\alpha_{(film)}$, *T*_(depo.) and *T*_(R.T.) are the thermal expansion coefficient of the film, deposition temperature and room temperature, respectively. The estimated slope of the change in *d*(BST200) with α_{sub} under constant $\alpha_{(film)}$, *T*_(depo.), and *T*_(R.T.) is almost identical to the data shown in Fig. 3 [13]. This suggests that the corresponding variations in the residual strain in the films with α_{sub} originated due to the thermal strain induced by the substrates, not due to

the misfit strain. Estimated lines are also shown in Fig.3 when the misfit strain under the film deposition at the deposition temperature is perfectly remain in the film (fully misfit-strained films) and when the misfit strain was perfectly released (perfectly misfit strain-relaxed films). In both case, thermal strain applied under the cooling process after the deposition are take into account. In other words, fully misfit strained films is strained by both of misfit and thermal strains, while perfectly misfit strain-relaxed films are strained only by the thermal strain. Fig.3 shows that about 20% misfit strain was remained for all films. 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 SrRuO₃ layer with relatively large lattice mismatch between the BST and SrRuO₃ (*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. 2 and 3, is presented in Fig. 4. Fig.5 summarizes the relative dielectric constants at 0 and 1000 kV/cm, obtained from Fig.4 as a function of $\epsilon_{\text{thermal}}$.

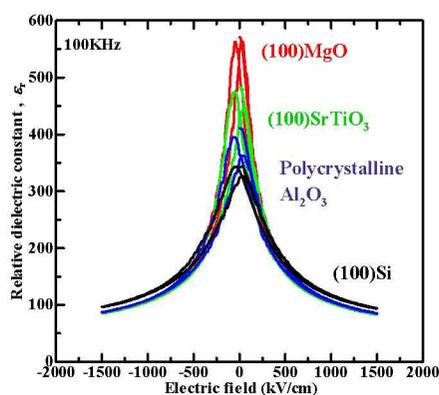


Fig. 4 The change of the relative constant under the applied electric field for the BST films, shown in Figs. 2 and 3.

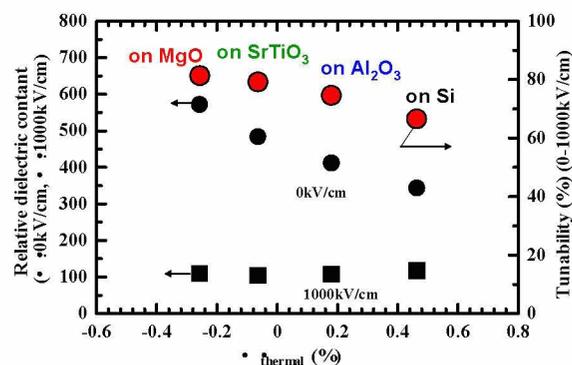


Fig.5 (a) The relative dielectric constant at 0 and 1000 kV/cm, obtained from Fig.4 and (b) the dielectric tunability measured under different applied electric fields

for BST films deposited on different substrates as a function of the thermal strain [$\epsilon_{\text{thermal}}$].

The relative dielectric constants at 0 kV/cm were found to be strongly dependant on the kind of the substrate used and to almost linearly increase with the increase in $\epsilon_{\text{thermal}}$, while those at high electric field of 1000kV/cm were nearly independent of the substrate. The dielectric tunability measured under any applied electric field almost linearly increased with the increase in $\epsilon_{\text{thermal}}$ 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 0kV/cm and 1000kV/cm was in the range of 0.4% to 1.2% (100 KHz).

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.*, SrRuO₃) of the multilayer buffer stack [8].

SUMMARY

In summary, (100)-one-axis-oriented BST films were prepared on four kinds of substrates with different $\alpha_{(\text{sub.})}$, covered by (100)_cSrRuO₃/(100)_cLaNiO₃/(111)Pt layers. Surface-normal lattice spacing of (Ba_{0.5}Sr_{0.5})TiO₃ and Pt linearly increased with the increase in $\alpha_{(\text{sub.})}$, which is indicative of a monotonous increase of the residual strain. Tunability of the capacitance also linearly increased with the increase in $\alpha_{(\text{sub.})}$. 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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