

## Effect of bottom electrode on dielectric property of sputtered-(Ba, Sr)TiO<sub>3</sub> films

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(Ba<sub>0.5</sub>Sr<sub>0.5</sub>)TiO<sub>3</sub> (BST) films were deposited on (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> substrates by rf sputtering. By inserting a thin layer of SrRuO<sub>3</sub> in between BST film and (111)Pt electrode, the BST films grew fully (111)-oriented without any other orientations. In addition, it enables us to reduce the growth temperature of BST films while keeping the dielectric constant and tunability as high as those of BST films directly deposited on Pt at higher temperatures. The dielectric loss of the films on SrRuO<sub>3</sub>-top substrates was comparable to that on Pt-top substrates for the same level of dielectric constant. The results suggest that the SrRuO<sub>3</sub> thin layer on (111)Pt electrode is an effective approach to growing highly crystalline BST films with (111) orientation at lower deposition temperatures.

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### I. INTRODUCTION

(Ba<sub>x</sub>Sr<sub>1-x</sub>)TiO<sub>3</sub> (BST) films have been widely investigated not only for high density capacitor applications but also for tunable capacitor applications due to their high dielectric constant and large dielectric tunability, i.e., the change in the dielectric constant with the applied electric field. Research on BST films has been performed predominantly using polycrystalline films or the preferentially oriented films, as well as epitaxially grown films, particularly with (100) orientation. It is well known that the structural characteristics such as the grain size and the strain in BST films can affect their dielectric and tunable properties as has been theoretically and experimentally demonstrated.<sup>1-5</sup> On the other hand, since the required properties for BST films in the above said applications are not driven by the spontaneous polarization in the ferroelectric phase, the impact of crystal orientation on film properties has been less clarified compared to other ferroelectric thin films.

We have recently demonstrated that it is possible to grow purely (111)- and (100)-oriented BST films on Pt(111) electrodes with SrRuO<sub>3</sub> and SrRuO<sub>3</sub>/LaNiO<sub>3</sub> thin intermediate layers, respectively.<sup>6</sup> By comparing the dielectric properties, we found out that (111)-oriented BST ( $x=0.5$ ) films showed the larger dielectric constant at 0 kV/cm and the larger tunability than the (100)-oriented films. Moon *et al.*<sup>7</sup> also reported that the dielectric properties of BST films vary with the different orientations. These results indicate that the control of the orientation of BST films would be an effective way to control their properties. In particular, the orientation control on standard metal electrodes such as Pt is clearly in demand, mainly for high frequency devices.

In this paper, we give a detailed report on how the presence of SrRuO<sub>3</sub> thin layers on (111)Pt electrodes affects the

orientation, crystallinity, and dielectric properties of the overlying BST films deposited at different temperatures. By using a thin layer of SrRuO<sub>3</sub>, the BST film grew fully (111)-oriented on Pt electrodes. In addition, it enabled us to use lower growth temperatures while keeping the dielectric constant and tunability of BST films high. The obtained results are compared to those of the BST films grown directly on (111)Pt electrodes.

### II. EXPERIMENTAL

BST ( $x=0.5$ ) films with the thickness of 200 nm were deposited on (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> [Pt-top] and (111)cSrRuO<sub>3</sub>/(111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> [SrRuO<sub>3</sub>-top] substrates by rf sputtering.<sup>6,8</sup> The total gas pressure was 10 Pa with an Ar/O<sub>2</sub> gas ratio of 9/1. A pseudocubic Miller index designated as ( $hkl$ )*c* was used for SrRuO<sub>3</sub>.<sup>9</sup>

The crystal structure of the films was characterized by x-ray diffraction (XRD). The composition of the films was ascertained by x-ray fluorescence (XRF) spectrometer calibrated using standard samples. Surface morphology of the deposited films was observed by scanning probe microscopy (SPM).

Dielectric properties were measured by making Pt/BST/SrRuO<sub>3</sub> or Pt/BST/Pt parallel plate capacitor structures and by annealing them at 500 °C in atmospheric pressure with O<sub>2</sub> flow for the duration of 30 min. Top Pt electrodes of 100 μm in diameter were prepared by e-beam evaporation method. Capacitance-voltage (*C-V*) characteristics with an oscillation level at 20 mV were measured at 100 kHz using HP 4194A.

### III. RESULTS AND DISCUSSIONS

#### A. Crystal structure and surface morphology

Figures 1 and 2 show the XRD  $\theta$ - $2\theta$  patterns of the films deposited both on Pt-top and SrRuO<sub>3</sub>-top substrates and the

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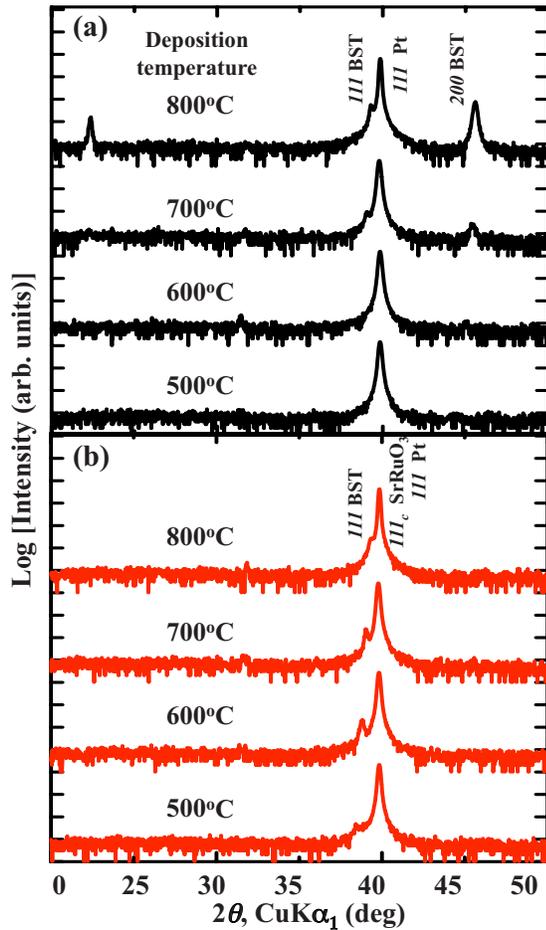


FIG. 1. (Color online) XRD  $\theta$ - $2\theta$  patterns of BST films prepared at various deposition temperatures on (a) (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> substrates and (b) (111)SrRuO<sub>3</sub>/(111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> substrates.

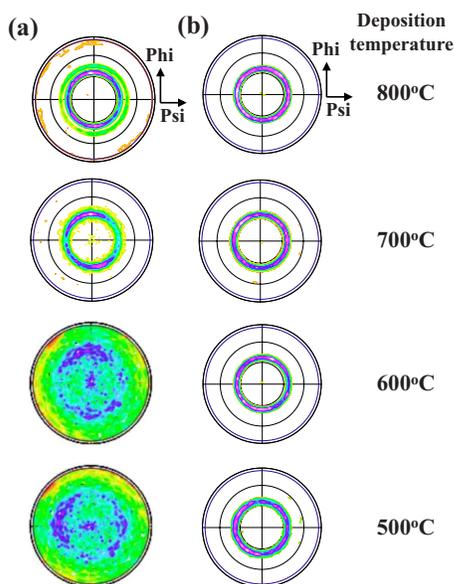


FIG. 2. (Color online) X-ray pole figures of BST films prepared at various deposition temperatures on (a) (111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> substrates and (b) (111)SrRuO<sub>3</sub>/(111)Pt/TiO<sub>2</sub>/SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> measured at the fixed  $2\theta$  angle corresponding to BST 220.

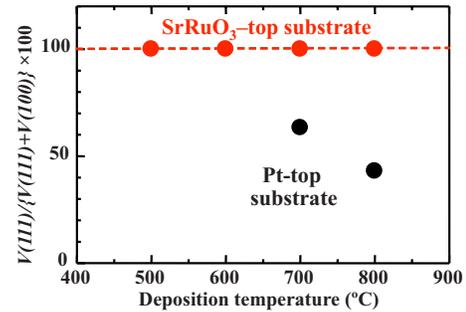


FIG. 3. (Color online) Volume fraction of (111) orientation in (111) and (100) orientations of BST films estimated from XRD  $\psi$ - $2\theta$  scans as a function of deposition temperature.

x-ray pole figures of those films measured at the fixed  $2\theta$  angle corresponding to BST 220. For the films on (111)Pt-top substrates, a low crystalline phase was obtained at 500–600 °C as well as mixed orientation of (111) and (100) was obtained at 700 and 800 °C. On the other hand, (111)-oriented BST films without any other orientations were found to be achievable at above 500 °C on (111)cSrRuO<sub>3</sub>-top substrates.

Figure 3 plots the volume fraction of (111) orientation in the (100) and (111) orientations obtained by the  $\psi$ - $2\theta$  scan maps.<sup>10</sup> As seen from Fig. 3, the BST films deposited on SrRuO<sub>3</sub>-top substrates have complete (111)-orientation regardless of the deposition temperature in the examined range. On the other hand, the volume fraction of (111) orientation in the films on Pt-top substrates decreased with increasing deposition temperature. The present data clearly show that SrRuO<sub>3</sub>-top substrate is useful for the growth of the BST films with (111)-orientation even though the lattice mismatch between BST and SrRuO<sub>3</sub> ( $a=3.93$  Å) is almost the same as the one between BST and Pt ( $a=3.92$  Å). This indicates that the similarity in crystal structure between BST and SrRuO<sub>3</sub>, namely, the shared by both of them perovskite structure unlike the face centered structure of Pt, is a key factor in obtaining fully (111)-oriented BST films.

Figure 4 shows the full width at half maximum (FWHM) and the integrated intensity of the rocking curve for the BST110 of (111)-oriented BST films on SrRuO<sub>3</sub>-top substrates. The FWHM was decreased by increasing the deposition temperature from 500 °C. It is interesting to notice that

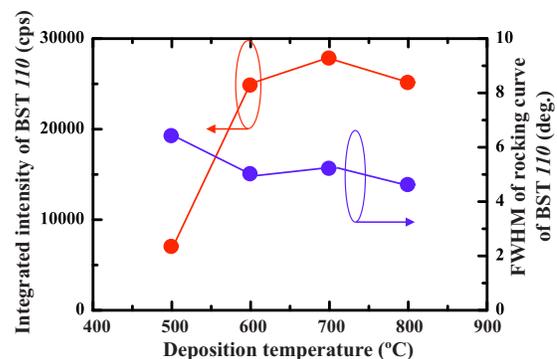


FIG. 4. (Color online) FWHM and integrated intensity of the rocking curves of BST110 obtained from (111)-oriented films on SrRuO<sub>3</sub>-top substrates as a function of deposition temperature.

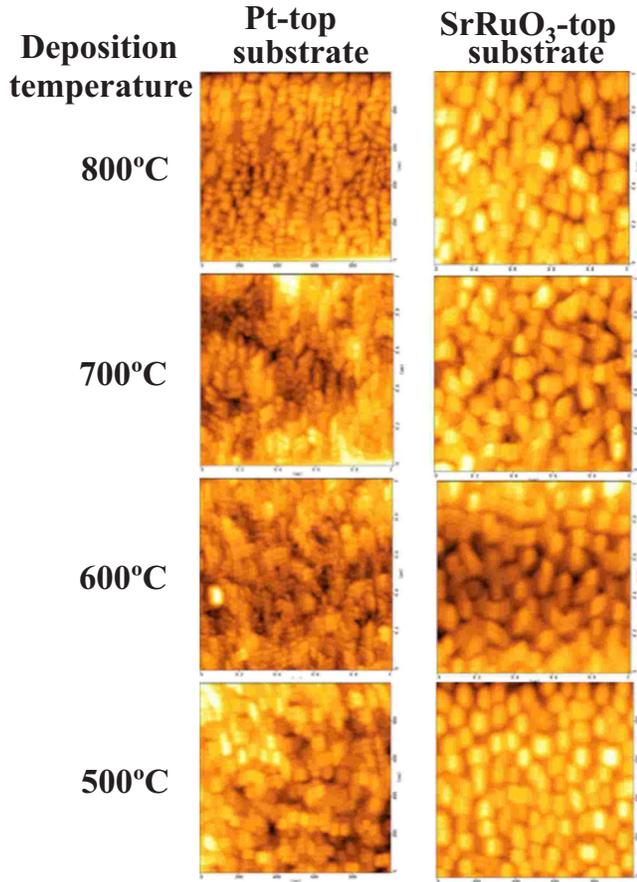


FIG. 5. (Color online) SPM images ( $1 \times 1 \mu\text{m}^2$  area) of BST films prepared on Pt-top and SrRuO<sub>3</sub>-top substrates at different deposition temperatures.

the integrated intensity jumped up at the deposition temperature from 500 to 600 °C; however, it did not further increase above 600 °C. The results indicate that the high crystallinity of BST films can be achieved on SrRuO<sub>3</sub>-top substrates regardless of the deposition temperature unless it is less than 600 °C. On the other hand, 700 °C or more is required for highly crystalline BST films on Pt-top substrates as shown in Figs. 1(a) and 2(a). The higher crystallinity of BST films on SrRuO<sub>3</sub>-top substrates compared to that of films on Pt-top substrates may be also attributed to the same perovskite structure between BST and SrRuO<sub>3</sub>,<sup>11,12</sup> namely, the epitaxial growth with the same crystal structure promotes not only the film orientation but also the crystallization process even at low temperatures during the growth.

Figure 5 shows the SPM images of the deposited films. The average grain size of the BST films on SrRuO<sub>3</sub>-top substrates was larger than that on Pt-top substrates. No obvious change in grain size with the alternation of deposition temperature was detected.

## B. Electrical properties

Figure 6 shows the deposition temperature dependence of the dielectric constant  $\epsilon_r$  and the dielectric loss ( $\tan \delta$ ) measured at 100 kHz and at 0 kV/cm. Both  $\epsilon_r$  and  $\tan \delta$  increased with the increase in the deposition temperature regardless of the kinds of substrates. Nevertheless, the BST

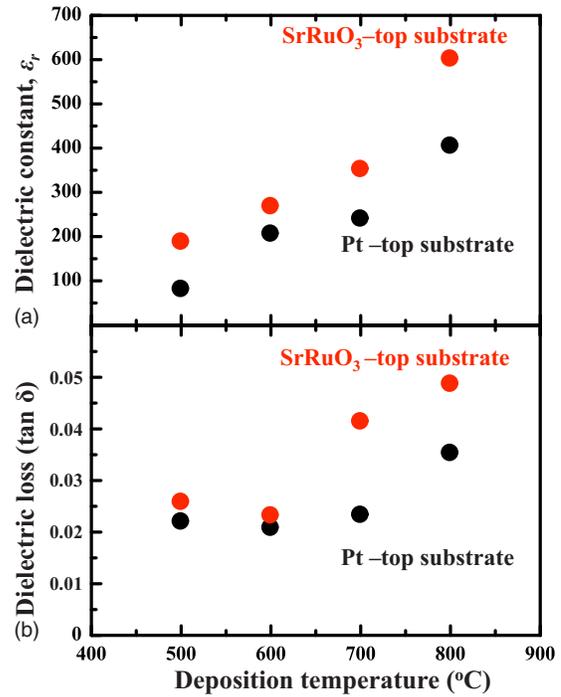


FIG. 6. (Color online) (a) Relative dielectric constant  $\epsilon_r$  and (b) dielectric loss ( $\tan \delta$ ) of BST films prepared on Pt-top and SrRuO<sub>3</sub>-top substrates as a function of deposition temperature.

films on SrRuO<sub>3</sub>-top substrate always showed higher  $\epsilon_r$  and  $\tan \delta$  compared to the films on Pt-top substrates at the same deposition temperatures.

The higher  $\epsilon_r$  for the films on SrRuO<sub>3</sub>-top substrate compared to  $\epsilon_r$  for films on Pt-top substrate can be basically due to higher crystallinity and larger grain size of BST films achieved by adding SrRuO<sub>3</sub> thin layers as discussed above. However, the increase in  $\epsilon_r$  for the films on SrRuO<sub>3</sub>-top substrate with the increase in deposition temperature above 600 °C is not clearly understood since the crystallinity and grain size of the films grown at these temperatures are quite similar as shown in Figs. 4 and 5. Although the reduction in the FWHM of the rocking curves with the increase in the deposition temperature may influence the dielectric response of the material, there might be additional influencing factors such as the strain in the films. The BST films deposited at higher temperatures are more stretched in the in-plane due to the mismatch of thermal expansion coefficients between films ( $\approx 10 \times 10^{-6}/^\circ\text{C}$ ) and substrates ( $\approx 8 \times 10^{-6}/^\circ\text{C}$ ). Indeed, the larger  $\epsilon_r$  (along out-of-plane direction) with the larger in-plane tensile strain in (111)BST films has been theoretically predicted.<sup>13</sup> Further investigation of the impact of the thermal strain on the dielectric properties in (111)BST films is required to fully clarify the observed phenomenon.

As for  $\tan \delta$  of the films, a higher  $\epsilon_r$  led to a higher  $\tan \delta$ , which is typical for many ferroelectric materials. The monotonous relationship between  $\epsilon_r$  and  $\tan \delta$  can be clearly found in Fig. 7. In addition, the observed data seem to be rather independent of the substrates used. This fact implies that the inserted SrRuO<sub>3</sub> layer did not have a noticeable influence on the dielectric loss behavior of the BST films at the conditions examined in this study; however other influences

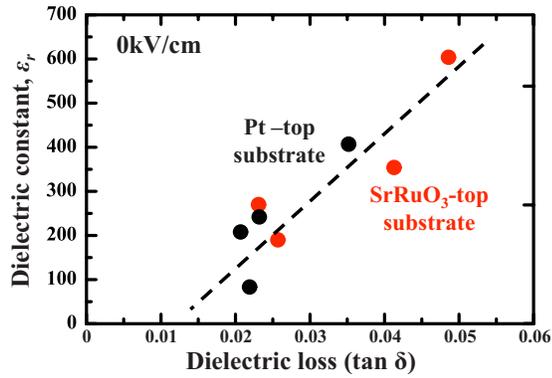


FIG. 7. (Color online) Relationship between the relative dielectric constant  $\epsilon_r$  and the dielectric loss ( $\tan \delta$ ) of BST films prepared on Pt-top and SrRuO<sub>3</sub>-top substrates at different deposition temperatures.

such as the difference in interfacial structure and the interdiffusion on those dielectric properties cannot be fully excluded.

Figure 8 shows the field dependence of  $\epsilon_r$  of the deposited BST films. As described above,  $\epsilon_r$  at 0 kV/cm increased with the increase in the deposition temperature. On the other hand,  $\epsilon_r$  under high applied electric fields tends to become saturated to almost the same value irrespective of the deposition temperature except for films with very low crystallinity deposited at 500 °C on Pt-top substrate. This is because  $\epsilon_r$  of a ferroelectric under sufficiently high dc field would become constant as described by  $\epsilon(E) \approx \beta^{-1/3} E^{-2/3} / (3\epsilon_0)$ , where  $\beta$  is the coefficient of the dielectric nonlinearity and  $\epsilon_0$  is the permittivity of vacuum.<sup>14</sup> Therefore, a higher  $\epsilon_r$  at 0 kV/cm would result in a higher tunability of the films.

Figure 9 shows the relative tunability at 400 kV/cm as a function of the deposition temperature. Tunability monotonously increased with the increase in the deposition temperature, namely, the increase in  $\epsilon_r$  (at 0 kV/cm) of the films as expected. At the same deposition temperature, the tunability of BST films on SrRuO<sub>3</sub>-top substrate was higher than that on Pt-top substrates in the same manner as  $\epsilon_r$ .

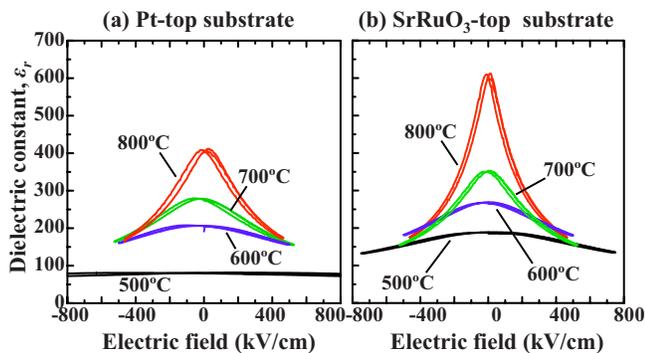


FIG. 8. (Color online) Field dependence of the relative dielectric constant  $\epsilon_r$  of BST films prepared on (a) Pt-top and (b) SrRuO<sub>3</sub>-top substrates at different deposition temperatures.

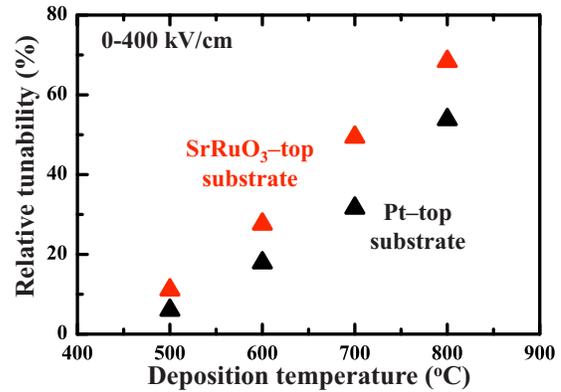


FIG. 9. (Color online) Relative tunability under the external electric field of 400 kV/cm of BST films on Pt-top and SrRuO<sub>3</sub>-top substrates as a function of the deposition temperature.

#### IV. CONCLUSIONS

Present results suggest that the SrRuO<sub>3</sub> thin layer on (111)Pt electrode is an effective approach to growing highly crystalline BST films with (111) orientation at low deposition temperatures. In particular, higher dielectric constant and tunability were obtained at lower deposition temperature than those for the BST films directly grown on Pt-top substrates. The dielectric loss of the BST films on SrRuO<sub>3</sub>-top substrates was comparable to that on Pt-top substrates for the same level of dielectric constant, although further investigations at higher frequencies will be needed for certain applications. The approach applied lets us achieve high quality ferroelectric films on highly conductive commonly used metal electrodes.

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