Dielectric properties of $Ba_{0.6}Sr_{0.4}TiO_3$ thin films using $Pb_{0.3}Sr_{0.7}TiO_3$ buffer layers

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$Ba_{0.6}Sr_{0.4}TiO_3$ (BST) thin films buffered with $Pb_{0.3}Sr_{0.7}TiO_3$ (PST) at each side of the interface contact with electrodes (PST/BST/PST) were deposited on Pt/Ti/SiO_2/Si substrates. The dielectric properties of the films were measured using planar Pt/PST/BST/PST/Pt/Ti/SiO_2/Si capacitor structures. The existence of a PST layer between the BST and Pt electrode can improve the dielectric properties of the BST film. The loss tangent of the multilayered films annealed at 750 °C was found to be 0.016 at 1 MHz and room temperature. The films showed a ~31.7% tunability of the permittivity at an applied bias field of 0.85 MV/cm. This suggests that such films have potential applications for integrated device applications. © *2007 American Institute of Physics*.
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Ferroelectric thin films, such as (Ba,Sr)TiO_3 (BST), were widely investigated for applications in integrated dynamic random access memory (DRAM) cells,[1] decoupling capacitors,[2] and microwave tunable devices, such as electrically tunable filters, voltage controlled oscillators, and phase shifters.[3–5] The restrain to practical tunable device applications of ferroelectric materials is their dielectric loss tangent.[6] In particular, Fe^{2+}, Mn^{2+}, Mn^{3+}, and Sc^{3+}, which can occupy the B sites of the ABO_3 perovskite structure, have been known to lower dielectric loss.[5,7–9] On the other hand, it was found that introducing of low dielectric loss layers into the interface of BST and electrodes could obtain tunable thin films with low loss tangent.[10] However, permittivity of such BST films decreased as the dielectric loss induced, so did the tunability. In recent years, $Pb_xSr_{1-x}TiO_3$ (PST) system was paid much attention as a potential candidate material for the future tunable microwave device components.[11–13] The Curie temperature of PST system was found to vary linearly with the concentration x and only one phase transition was observed in the PST system as compared to three transitions in the case of BST solid solutions.[14,15] The compositions of $Pb_xSr_{1-x}TiO_3$ with $x \leqslant 0.3$ have a Curie temperature below room temperature,[14] which are suitable for room temperature microwave devices.[14,16] It was reported that the tunability and loss tangent value of $Pb_{0.3}Sr_{0.7}TiO_3$ ceramics under a 20 kV/cm bias field at 10 kHz and room temperature were 70% and less than 0.1%, respectively.[11] Epitaxial PST films deposited on $LaAlO_3$ substrate showed a very high dielectric constant value of 3100 and very dielectric tunability of 48% at 40 V/cm at room temperature.[17] Therefore, polycrystalline PST films using magnetron sputtering deposition showed low dielectric loss about 1%.[18]

The stoichiometric $Ba_{0.6}Sr_{0.4}TiO_3$ and $Pb_{0.3}Sr_{0.7}TiO_3$ targets with diameter of about 60 mm were prepared via the conventional ceramic processing. The stacks of PST/BST/PST films were deposited on Pt/Ti/SiO_2/Si substrates by rf magnetron sputtering under the conditions listed in Table I. The growth rate of the PST and BST films under such condition were about 4 and 4.5 nm/min, respectively.[19] The deposition of stacks of PST/BST/PST films was carried out for 10, 60, and 10 min, respectively. A postdeposited anneal was performed for 30 min in oxygen at 700–800 °C to crystallize the films. Phase composition and crystallization of the sandwich films were characterized by x-ray diffraction (XRD). The film thickness was measured by a Talysurf FTSS2-S4C Aspherics Measuring System, the error of which was less than 3 nm for thin films. Pt top electrodes were sputtered onto the annealed sandwich films through a shadow mask. The dielectric properties were measured with a 500 mV oscillating test field using an Agilent impedance analyzer (model 4294A). All measurements were carried out after calibration without and with the probe, respectively,

TABLE I. Sputtering conditions for PST and BST depositions.

	Target	
	$Pb_{0.3}Sr_{0.7}O_3$	$Ba_{0.6}Sr_{0.4}TiO_3$
Target diameter (mm)	60	60
Target-substrate distance (mm)	65	65
RF power (W)	120	90
Substrate temperature (°C)	300	500
Overall gas pressure (Pa)	4	5
Ar/O_2 flow rate ratio	60/40	60/40

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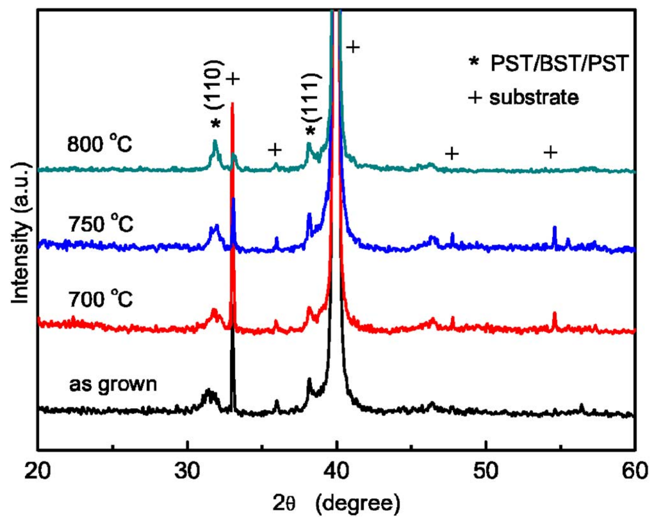

FIG. 1. (Color online) XRD patterns of the PST/BST/PST films.

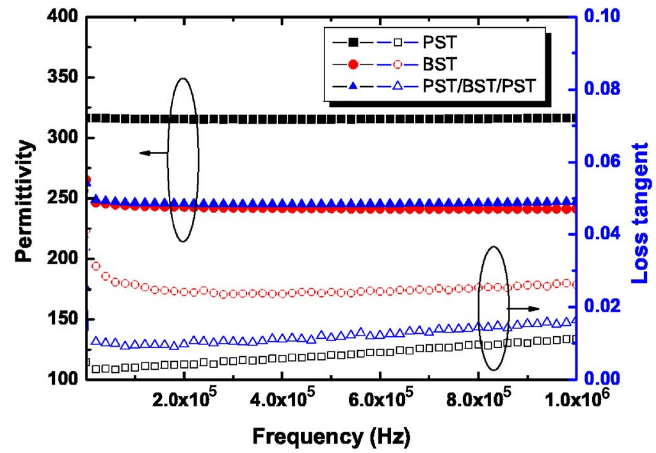

FIG. 2. (Color online) Permittivity and loss tangent of PST/BST/PST and one type of PST and BST films annealed at 750 °C as a function of frequency at zero-bias and room temperature.

before each measurement. The relative permittivity ε_r was calculated from capacitors defined by 0.3 mm diameter top electrodes $[\varepsilon_r = C \times t/(\varepsilon_0 \times A)$, where t was the total stack of PST/BST/PST film thickness, ε_0 the vacuum permittivity, and A the capacitor area]. The relative tunability was defined as $(\varepsilon_{\max} - \varepsilon_{\min})/\varepsilon_{\max}$, where $\varepsilon_{\min}$ is the minimum permittivity measured permittivity at the maximum applied field and $\varepsilon_{\max}$ is the dielectric constant at zero bias.

Before depositing the stacks of PST/BST/PST films, one type of PST and BST films were deposited and annealed under the same conditions, as Table I showed. Here, the thickness of PST stack and central layer of BST of the PST/BST/PST films were about 40 and 270 nm. The XRD patterns of PST/BST/PST films before annealing and as a function of annealing temperature are shown in Fig. 1. Polycrystalline PST/BST phase can be seen in the composite films. The XRD patterns of one type of PST and BST films deposited under the same conditions with the composite films demonstrated the same oriented polycrystalline PST and BST phase, as Fig. 1 shows, which was not shown in this letter.

Dielectric properties of the PST buffered BST films annealed at different temperature were measured at room temperature and 1 MHz. Permittivity of the films as grown and annealed at 700, 750, and 800 °C were about 145, 174, 247, and 308, respectively. The values of the dielectric constants of the thin films are similar to some other groups researched on BST thin films reported.[20] Dielectric loss tangent corresponding such films were about 0.02, 0.018, 0.016, and 0.028, respectively. 750 °C maybe the proper temperature for the PST/BST/PST films annealing. Figure 2 shows the zero-bias dielectric properties of the PST/BST/PST film and one type of PST and BST films annealed at 750 °C measured in the 1 kHz–1 MHz range at room temperature. The measured capacitance of the metal-insulator-metal (MIM) is the series connection of the capacitance of one BST and two PST layers if the electric field is applied along the thickness direction.[18] Thus, the nominal permittivity of the PST/BST/PST films can be expressed as

$$\frac{d_{\text{total}}}{\varepsilon_{\text{PBP}}} = \frac{d_{\text{bottom-PST}}}{\varepsilon_{\text{bottom-PST}}} + \frac{d_{\text{BST}}}{\varepsilon_{\text{BST}}} + \frac{d_{\text{top-PST}}}{\varepsilon_{\text{top-PST}}}, \quad (1)$$

where d_{total}, d_{BST}, $d_{\text{bottom-PST}}$, and $d_{\text{top-PST}}$ represent the thickness of the total film, BST, bottom PST, and top PST, respectively. Since the thickness and permittivity of stacks of PST/BST/PST films were known, the average permittivity of the PST/BST/PST films could be calculated. According to Eq. (1), permittivity of the PST/BST/PST films was calculated to be 254, which was near the experiment value of 247, as shown in Fig. 2. Dielectric loss tangent of BST films without PST buffers was about 0.026, as Fig. 2 shows. When PST buffer layers were introduced, dielectric loss tangent of BST films decreased sharply. Obviously, PST buffer layers were effective to decrease the dielectric loss tangent of the BST films.

The bias-field dependence of the normalized dielectric constant and loss tangent at the measurement frequency of 1 MHz for the BST films and PST/BST/PST films annealed at 750 °C is shown in Fig. 3. It is found that the relative dielectric constant and dielectric loss of the films nonlinearly decrease with increasing applied dc field. Such nonlinearity had been explained in the literature.[21] Asymmetry of the curve could be seen in Fig. 3. The lattice of $Ba_{0.6}Sr_{0.4}TiO_3$ (a=0.396 nm)[9] thin films is a little more than that of $Pb_{0.3}Sr_{0.7}TiO_3$ (a=0.392 nm)[17] thin films. It was reported that lattice distortion could induce strains and strains can be impacted to thin films and have previously been used to alter the ferroelectric transition temperature (T_c) of ferroelectric

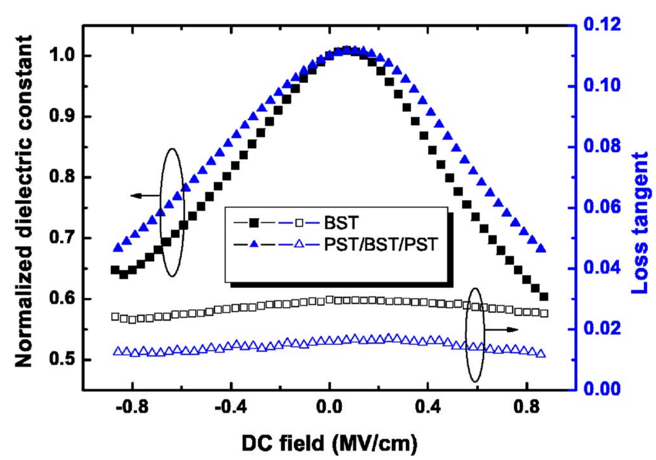

FIG. 3. (Color online) Normalized dielectric constant and loss tangent of PST/BST/PST and BST films as a function of applied dc electric fields at room temperature. The measurement frequency was 1 MHz.

TABLE II. Dielectric, tunability, and FOM of BST and PST/BST/PST films

	ε_r at zero field	tan δ at zero field	Tunability (%) at 0.85 MV/cm	FOM
PST/BST/PST	247	0.016	31.7	19.8
BST	241	0.026	36	13.8

materials.[22–24] Therefore, misfit dislocations and interfacial space charge also could cause the asymmetry of the *C-V* curve.[25] The dielectric constant of PST/BST/PST films changed by about 31.7% under a bias of 0.85 MV/cm while that of the BST films changed by about 36% under the same applied dc field. In the case of a layer composite, e.g., passive layer at the ferroelectric-electrode interface, the tunability can be suppressed. This is particularly important for thin films. In fact, the behavior of a layered ferroelectric composite is very close to that of a pure ferroelectric with a decreased Curie temperature.[26] Here, the decrease of tunability of the PST/BST/PST films should be more studied. The dielectric properties and tunability of the BST and PST/BST/PST films are listed in Table II. The zero-electric permittivity of the PST/BST/PST film is 247, with a dielectric tunability of 31.7% at an applied dc bias field of 0.85 MV/cm. Its dielectric loss tangent value is 0.016. In comparison, the pure BST deposited with the same processing parameters has a relative dielectric permittivity of 241, a dielectric tunability of 36% at the same dc field and a dielectric loss tangent of 0.026. However, the parallel plate structure is not suitable for high frequency measurement here. High frequency performances of the thin films are planned to be characterized by appropriate structure such as interdigital patterns. Though tunability of the PST/BST/PST decreased slightly, figure of merit [FOM, which is defined as FOM =(tunability/loss tangent) × 100%] of the PST/BST/PST increased sharply because of the dielectric loss tangent decreased a lot. The increase of the FOM and reduction of the dielectric loss tangent of the PST/BST/PST film were attributed to the PST buffer layers. From a phase shifter applying point view, a low dielectric loss tangent and high FOM are desirable to reduce the insertion loss and, hence, increase the phase shifter per decibel of loss. In this respect, introducing PST buffer layers to the interfaces between BST films and metal electrodes is feasible to obtain materials for integrated device applications.

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