High tunability in compositionally graded epitaxial barium strontium titanate thin films by pulsed-laser deposition

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Compositionally graded barium strontium titanate $[(Ba_xSr_{1-x})TiO_3$—BST, $x=0.75$, 0.8, 0.9, and 1.0] thin films are fabricated by pulsed-laser deposition on a $LaAlO_3$ substrate with $(La_{0.7}Sr_{0.3})MnO_3$ as the bottom electrode. A high dielectric permittivity and temperature characteristic without Curie–Weiss law are obtained. A tunability of over 70% is obtained at frequency of 1 MHz, which is higher than that of single BST layer with the same compositions. All the results indicate that the graded thin films have better electrical properties than a single-layer film. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1569427]

Barium strontium titanate $[(Ba_xSr_{1-x})TiO_3$—BST] has been investigated intensively for applications in dynamical random access memory (DRAM),[1] as well as tunable microwave devices, such as filters[2] and phase shifters.[3] As the next generation of DRAM is expected to match the 50 and 35 nm of technology mode, a dielectric permittivity (ε) as high as 700 to 1500 is needed, and this poses a challenge in the fabrication of high ε BST thin films. Epitaxial template structure is regarded as a promising method to tackle this problem.[4] While for microwave devices, high tunability, low loss tangent, and good temperature stability are required. As for the origin of the high tunability of a BST thin film, some previous reports ascribed it to the anomaly of a high dielectric constant at room temperature near its Curie temperature.[5] However, for BST thin films, nanodomains with sizes as small as 5 nm have been observed by using the near-field optical technique,[6] hence, the Curie–Weiss law should be modified into the form for relaxor ferroelectrics.[7,8] The peak value of dielectric permittivity ε changes with the Ba/Sr ratio, and there is a big change in the dielectric permittivity as a function of temperature. In view of this consideration, a graded structure is expected to have a high relative dielectric permittivity as well as a flatter temperature characteristic of permittivity.[9] In this work, we report a multilayer compositionally graded structure of BST (BTO) thin film, which has a large dielectric permittivity, high dielectric tunability, and flatter permittivity–temperature characteristic.

The procedures of sample preparation are as follows. Before the deposition, four kinds of targets $(Ba_xSr_{1-x})TiO_3$ ($x=0.75$, 0.8, 0.9, and 1, abbreviated as BST75, BST80, BST90, and BTO, respectively) and bottom electrode target $(La_{0.7}Sr_{0.3})MnO_3$ (LSMO) were prepared by use of conventional solid-state reaction process. For the BST (BTO) targets, the raw materials were $BaCO_3$, $SrCO_3$, and TiO_2 with an analytic reagent grade of purity. The raw materials were ball milled, dried, sieved, and then calcined at a temperature of 1100 °C to form uniform BST (BTO) crystallites. After the second ball milling, drying, and granulating, dry pressed green pellets were sintered at a temperature ranging from 1300 to 1350 °C, and soaked for 2 h. The as-sintered samples had a brown color. A hole was drilled at the center of the ceramic so as to form the pulsed-laser deposition (PLD) rotating targets.

The PLD system used here has been introduced elsewhere.[10] The targets were sequenced in LSMO, BST75, BST80, BST90, and BTO. The bottom electrode LSMO film and BST thin films were grown on $LaAlO_3$ (001) substrates by use of a 248 nm KrF excimer laser with a repetition rate of 10 Hz. The energy density of a laser irradiated on the rotating LSMO, BST, and BTO targets was 6 J/cm^2. The distance between the target and the substrate was 50 mm. The rotating rate of target was 0.1 Hz. For uniform heating, the substrate was put on a stainless-steel plate and connected to the sample holder and heater with conductive silver paste. A small corner of the substrate was painted with silver paste to act as a contact to the bottom electrode. Before the deposition, the chamber was pumped and evacuated by a rotating pump and cryopump, respectively, to reach a base pressure of 3×10^{-6} Torr. During the deposition, the oxygen pressure was maintained at 200 mTorr. The substrate temperature was fixed to 650 °C. For each layer of BST (BTO), the deposition time was 5 min, and the final annealing time was 30 min. After annealing, the samples were cooled down with the chamber, and the oxygen pressure was adjusted to the same as the ambient. For single-layer thin films, the deposition time was 20 min and the other conditions were the same as just mentioned.

The epitaxial structure and gradient composition were confirmed by x-ray diffraction characterization (Philips X'pert), which was published elsewhere.[11] From scanning electron microscopy observation, the thickness was about 800 nm for BST film and 240 nm for LSMO.

The gold was sputtered on to the surface of the thin film as top electrode. The diameter of the top electrode was 0.2 mm. And a sandwich configuration was used to measure the electrical properties of the graded BST thin films. Before the measurement, the as-prepared BST graded film was bonded to a printed circuit board (PCB) with metal Al wires connecting the top and bottom electrodes to the clad copper stripes

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on the PCB board. The dielectric properties were measured using an impedance analyzer (HP 4194A). Results indicated that the graded BST film had a large dielectric permittivity (over 1660) compared to conventional BST thin film by PLD method (less than 1000)[12] and small loss tangent (less than 0.05 at 10 kHz, the smallest one reaches 1.0×10^{-2}, especially small at low frequency). The large dielectric permittivity can result from the graded BST film with different Ba/Sr ratios, which giving rise to the peak values of dielectric permittivity–temperature relations of each BST (BTO) film with different Ba/Sr ratios. For a BST film in which Ba composition is x_i, assuming its permittivity ε_i has such a distribution function with temperature,[13]

$$\varepsilon_i = \frac{\int_0^\infty \varepsilon(T, T_c) e^{-(T_c - T_{av})^2/\sigma^2} dT_c}{\int_0^\infty e^{-(T_c - T_{av})^2/\sigma^2} dT_c} \tag{1}$$

where

$$\varepsilon(T, T_c) = \begin{cases} \varepsilon_{av} & \text{for} \quad T \leqslant T_c \\ \dfrac{C}{T - T_0} & \text{for} \quad T > T_c \end{cases} \tag{2}$$

Here, T_{av} is the average phase transition temperature, T_c is the Curie temperature of the individual crystallites, C is Curie constant, T_0 is Curie–Weiss temperature, σ is the diffusive parameter of Gauss distribution.

Considering the gradient in the film is in an ideal situation, and neglecting the interfaces between the layers, then the whole film can be regarded as an ensemble containing a graded distribution of Ba^{2+} and Sr^{2+} ions normal to the growth surface. For an "up" structure (BTO layer is on the top), when the temperature decreases from a temperature higher than 120 °C, the phase transition will occur from the top layer to the bottom layer one by one. Because of the induction polarization, the "layer" with a higher permittivity will dominate the permittivity–temperature characteristics.[14] Then, the graded material demonstrates a higher average permittivity than conventional material. This is why the bulk graded BST ceramic has a higher permittivity in the whole temperature range.[9,14] In view of the foregoing reason, the polarization intensity of the whole film can be expressed into a linear combination of polarization intensity of each layer, then the permittivity of the whole film can be written as

$$\varepsilon = \frac{dP}{dE} = \frac{d\Sigma B_i P_i}{dE} = \sum B_i \varepsilon_i, \tag{3}$$

where B_i are constants, ε_i is expressed in Eq. (1). Since $T_i = 120 - 2200(1 - x_i)/7$ ($x_i \geqslant 0.3$),[15] then total ε is the superposition of each curve of permittivity versus temperature. Approximately, the ε value of the graded film approaches the shoulder value of permittivity peak of each layer. And a broadened peak will be obtained.

This assumption can be further proved by the temperature relation of dielectric permittivity (Fig. 1). One can see that there is no steep variation occurring in the range of high temperatures for conventional ferroelectric material, usually occurring in the form of Curie–Weiss law, but a rather flat variation within a wide range of temperature. In addition, two broad peaks appear, indicating some change associated with the broadened phase transition process. These two
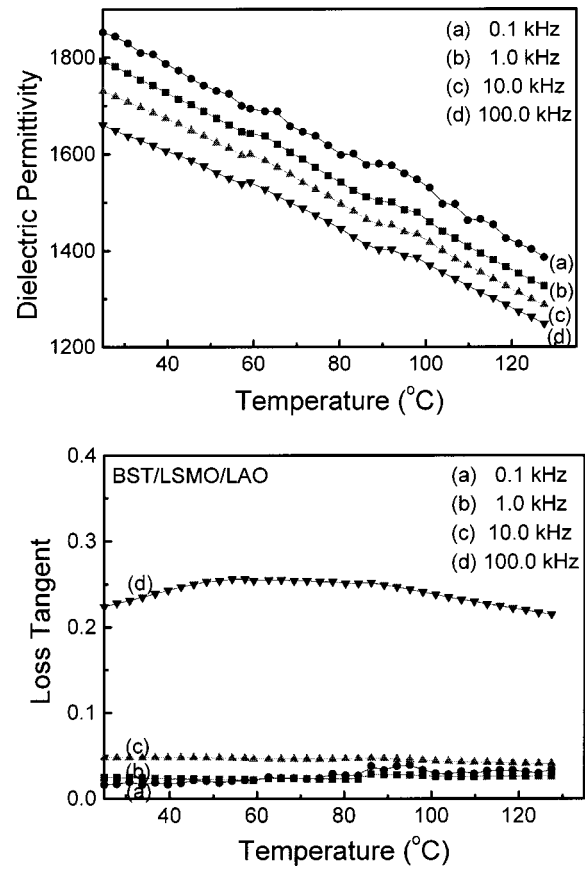

FIG. 1. Temperature relations of dielectric permittivity and loss tangent in BST (BTO) graded thin film.

peaks occur at about 59 °C and 92 °C, near the phase transition temperatures of $Ba_{0.80}Sr_{0.20}TiO_3$ (57 °C) and $Ba_{0.90}Sr_{0.10}TiO_3$ (89 °C), respectively. There are also very broadened peaks observed in the loss tangent versus temperature characteristics. But they are not very clear. Especially for the 10 kHz loss tangent, almost no peaks can be found. The bigger loss tangent value for 100 kHz may be associated with our measuring system. The two broadened peaks may be regarded as the incomplete diffusion of Ba^{2+} and Sr^{2+} ions, resulting in the trace of BST90 and BST80 compositions. The whole film, however, is still a graded structure.

Figures 2 and 3 show the tunability of dielectric permittivity with an electric field at 1 kHz for a single-layer film and graded film, respectively. The single-layer film has a smaller tunability percentage. For the graded BST film, the tunability ratio is defined as $\varepsilon_r(T,0)/\varepsilon_r(T,E)$ for the downfacing semicircle is 4.66:1, while for the up-facing semicircle, it is 4.45:1. For different frequencies, the tunability ratio is different. Figure 2 and inset of Fig. 3 show the relationship of tunability percentage defined as $[\varepsilon_r(T,0) - \varepsilon_r(T,E)]/\varepsilon_r(T,0)$ versus frequency. The phenomenon which occurred here can be qualitatively interpreted by Johnson proposed simplified formula,[16]

$$\varepsilon_r(T,E) = \frac{\varepsilon_r(T,0)}{[1 + (\varepsilon_0 \varepsilon_r(T,0))^3 B(T) E^2]^{1/3}}. \tag{4}$$

Although the composition is graded, the whole structure can be treated as a ferroelectric whose dielectric permittivity–temperature relation should be modified thor-
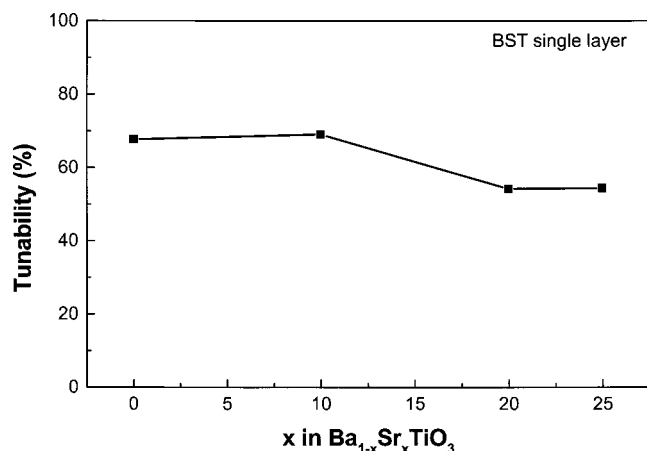
FIG. 2. Tunability as a function of composition "*x*" for a one-layer BST (BTO) thin film. The measuring frequency is 1 MHz.

ough considering the gradient template. For the graded structure, the dielectric permittivity will be larger in the whole temperature range, so the numerator in the Eq. (4) will be larger than that without graded structure. For a large $\varepsilon_r(T,0)$, assuming the $B(T)$ and E are constants, and $\varepsilon_r(T,0)/\varepsilon_r(T,E) \geqslant 4$, Eq. (4) can be rewritten as

$$\frac{\varepsilon_r(T,0)}{\varepsilon_r(T,E)} \approx \varepsilon_0 \varepsilon_r(T,0)[B(T)E^2]^{1/3}, \tag{5}$$

so, in general, the higher the dielectric permittivity at zero-electric field, the larger the tunability. Because the BST has a higher dielectric permittivity at room temperature, the tunability of the BST thin film also has a very large value
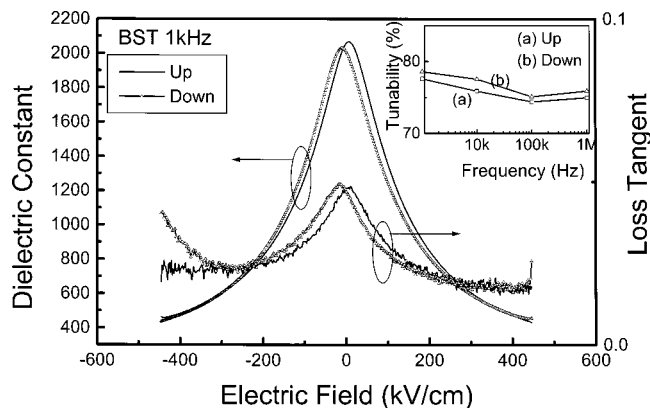

FIG. 3. Electric-field dependence of the dielectric permittivity of BST graded thin film at 1 kHz. Inset is the relationship of tunability vs measuring frequency.

under a dc field. We may do a simple numerical estimation. At room temperature and at 1 MHz, $\varepsilon_r(T,0) \sim 10^3$, $\varepsilon_0 \sim 1$, $B(T) \sim 3 \times 10^{-22}$ m^2/V^2,[5] $E = 4 \times 10^7$ V/m, then $\varepsilon_r(T,0)/\varepsilon_r(T,E) \approx 7.83$, which is larger than what we obtained experimentally.

On the other hand, Diamond[13] accounted the high tunability not for the domain alignment or rotation processes, but for the randomly oriented domains, and the external electric field could induce the crystallites in the grain into a ferroelectric state in the phase transition regime. In a BST thin film, because of the compositional fluctuation, usually, the BST demonstrates the relaxor properties.[6,7] As in PMN, one grain is composed of nanosized domains. So under a dc bias, the nanodomains may be affected by the external field through changing the nonferroelectric states into ferroelectric ones. Statistically, the tunability is dominated by the dielectric characteristic of every nanodomain. Since either BTO or STO has a high permittivity at room temperature under a small ac field without dc bias, so it is reasonable that the BST has a high tunability. And the graded BST will also have a high tunability over a wide temperature range.

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