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Compositionally graded epitaxial barium strontium titanate thin films derived from pulsed laser deposition

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Abstract

Epitaxial graded barium strontium titanate $(Ba_xSr_{1-x})TiO_3$ ($x = 0.75$, 0.8, 0.9, 1.0) thin films were prepared through pulsed laser deposition method on the $(La_{0.7}Sr_{0.3})MnO_3$ (LSMO)/$LaAlO_3$ (LAO) substrate. XRD analysis indicated the graded film had a broadened 2θ peak at 45° for the (2 0 0) peak. The energy dispersive analysis of X-ray (EDAX) showed a gradient change of Ba/Sr composition. P–E loop measurement gave a remnant polarization about $2\,\mu C\,cm^{-2}$, and without big up offset observed. A big room temperature dielectric constant as high as 1600 was obtained and has an approximately linear relationship with temperature from room temperature to 130 °C. All these results can be ascribed to the epitaxial and graded structure of BST thin films.

Keywords: BST; Compositional gradient; Thin films; PLD; Dielectric constant

1. Introduction

The rapid development of mobile communication has created a strong demand for dielectric materials and devices used in the radio frequency (RF) and microwave frequency [1]. A large number of dielectrics have been fabricated, including BST based [2]; $PbZrO_3$ based [3]; $BaO–MeO–TiO_2$, Me = Bi, Ca, La, Nd, Pr, Sm, W, Zr, etc. [4]; $CaTiO_3–La(Mg_{1/2}Ti_{1/2})O_3$,–$LaAlO_3$ [5]; $BaZrO_3–Ba(Zn_{1/3}Ta_{2/3})O_3$ [6]; $ZrO_2–SnO_2–TiO_2$ [7]; $MeO–Al_2O_3–TiO_2$, Me = Ba, Ca, Sr, etc. [8]. In principle, higher dielectric constant, low loss tangent and almost zero temperature coefficient of the resonant frequency are favored for microwave resonator application [9]. Those materials agile to electric field are suitable for tunable device [10]. Functional graded materials have demonstrated good properties with very small capacitance temperature coefficient over a wide temperature range, and high *Q*-factor, so they are potential candidates of microwave dielectrics [11]. Barium strontium titanate ($(Ba_xSr_{1-x})TiO_3$—BST) are basic but very important materials [12]. They have been studied extensively for the application of DRAM [13]. It is well known that BST has a high dielectric constant and low loss tangent. So there are lots of investigations on BST film for microwave application. For the BST used here, x ranges from 75, 80, 90 to 100%, its Curie temperature changes from 41.4, 57.1, 88.6 to 120 °C in a relationship 120–2200$(1 - x)$/7 [14]. It is expected that the dielectric constant have a broad distribution over a wide temperature range, which gives the temperature coefficient of the dielectric constant to have a small variation. In addition, the pulsed laser deposition (PLD) is a convenient method to fabricate graded materials [15–17]. Especially, PLD method can be used conveniently to fabricate multilayer structures which can derive a lot of novel designs to enhance the properties of microwave devices. In this paper, a graded ferroelectric BST thin film was fabricated by the PLD method. The structure and dielectric properties are characterized by XRD and impedance analyzer.

2. Sample preparation

In this work, four kinds of $(Ba_xSr_{1-x})TiO_3$ ($x = 0.75$, 0.8, 0.9, 1) targets and the bottom electrode target LSMO were formed by use of a conventional solid state reaction process. For the BST targets, the raw materials were $BaCO_3$, $SrCO_3$, TiO_2 with AR grade of purity. Before the sintering, the ball milled powder was calcined at a temperature of 1100 °C to form uniform BST crystallites. The final sintering temperature was 1350 °C, and soaking for 2 h. These sintered samples had a brown color. A hole was drilled at the center of the ceramic disc so as to form the PLD rotating targets.

The PLD system used here has been described elsewhere [18]. The targets were sequenced in LSMO, BST75

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($x = 0.75$), BST80, BST90, and BTO. The thin films were grown on LAO (0 0 1) substrates by pulsed laser deposition using a 248 nm KrF excimer laser with a repetition rate of 10 Hz. The energy density of the laser irradiated on the rotating LSMO and BST, BTO targets was 6 J cm^{-2}. The distance between the target and substrate was 50 mm. The rotating rate of the target was 0.1 Hz. For uniformly heating, the substrate was put on a stainless steel plate and affixed to the sample holder and heater with conductive silver paste. A small part of the substrate was painted with silver paste to act as a contact to the bottom electrode. Before the deposition, the chamber was evacuated by a rotary pump and a cryopump, respectively, to reach a base pressure of 3×10^{-6} Torr. During the deposition, the oxygen pressure was controlled to 200 mTorr. The temperature was 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 in the chamber, and the oxygen pressure was adjusted to the same as the ambient.

3. Results and discussion

The morphology of the cross section of the graded BST thin film was observed by SEM (Leica Steroscan). From the observations (see Fig. 1), the thickness of the whole film was ~1.025 μm, in which LSMO was 240 nm, and the graded film was 785 nm. The bottom electrode LSMO and the BST could be distinguished, but the interfaces of the four layers of different composition of BST and BTO merged together. In Fig. 2, from left to right, accordingly from the bottom layer to the top layer of the film, the EDAX measurement of Sr, Ba, and Ti demonstrated that the compositions of Sr and Ba were gradually changed, while Ti almost had no change, confirming the compositionally graded structure. We also did the θ–2θ scan before alignment with line scan. Fig. 3 shows the result. It is clear that the (2 0 0) peak was more broadened than the (1 0 0) peak. Their FWHMs are 0.5177 and 1.0231 for (1 0 0) and (2 0 0), respectively. The reason is that the Ba/Sr compositional variation has a bigger effect on the (2 0 0) diffraction peak than the (1 0 0) one. So the

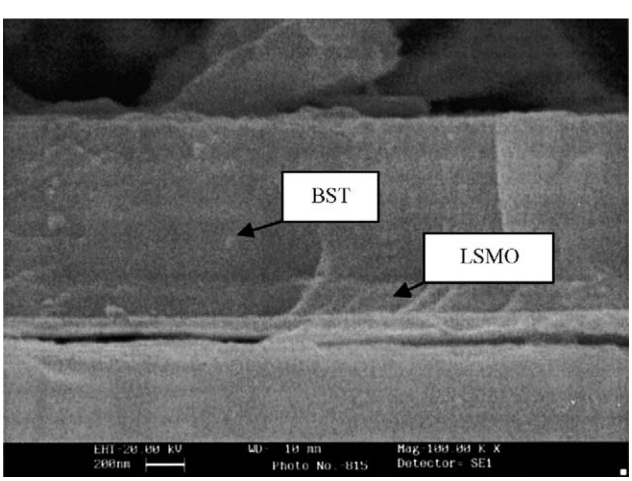

Fig. 1. Morphology of the cross section of graded BST film.

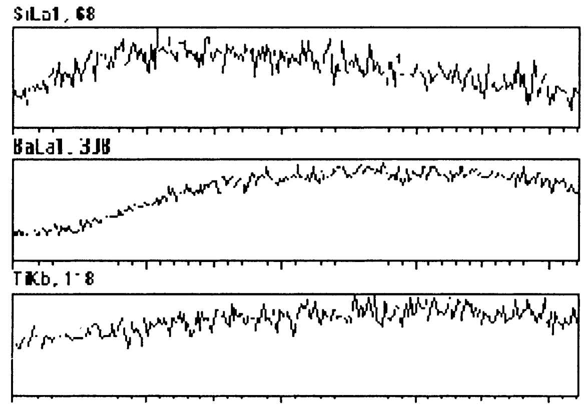

Fig. 2. Gradient Sr, Ba, Ti from EDAX.

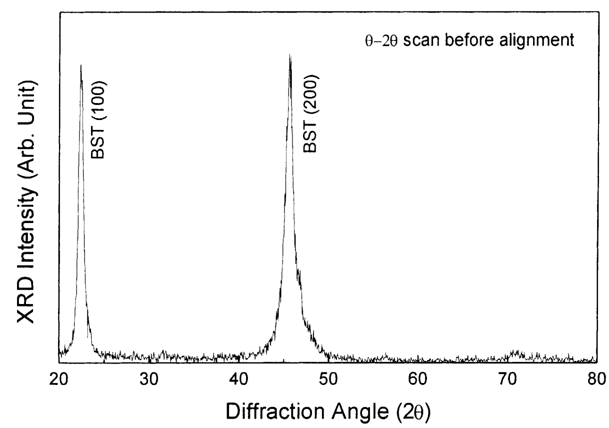

Fig. 3. The θ–2θ scan of graded BST thin film before alignment with line scan.

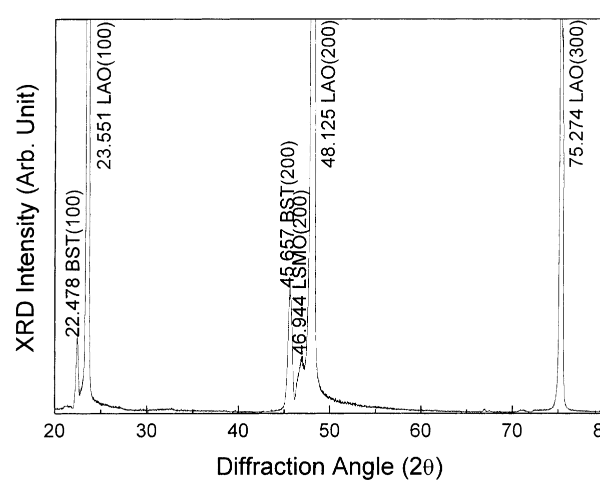

Fig. 4. The θ–2θ scan of graded BST thin film after alignment with point scan.

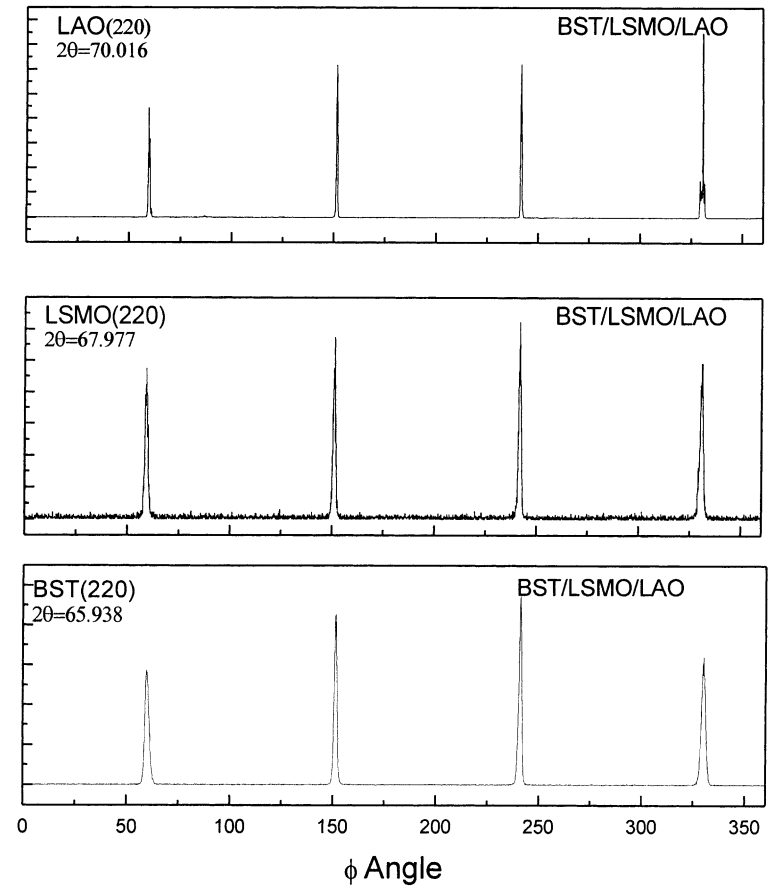

Fig. 5. The ϕ scan of BST/LSMO/LAO film.

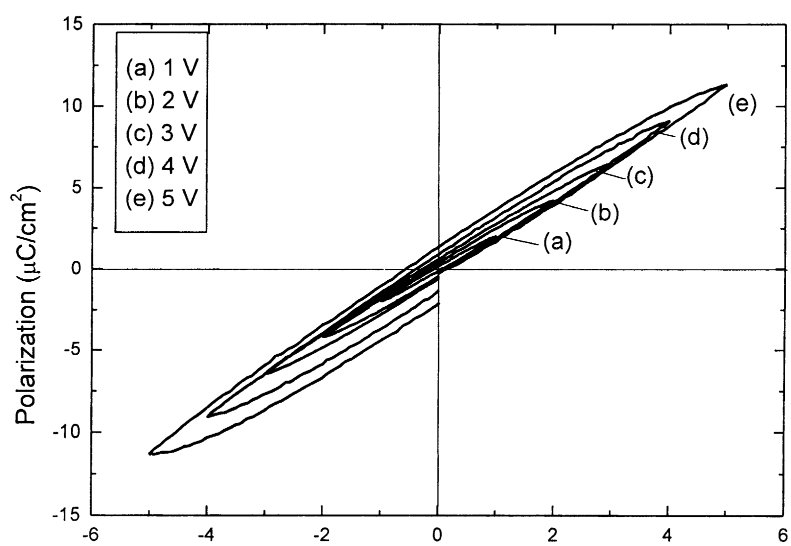

Fig. 6. P–E loop of BST graded thin film.

width of (2 0 0) peak can be used to detect the widening extent from different Ba/Sr compositions.

Figs. 4 and 5 show the XRD profile—θ–2θ scan and ϕ scan after alignment with point scan (usually the X-ray incident beam is slightly off from the normal direction) and filtered with Ni (Philips X'pert). The rocking curve was also obtained. XRD–scan rocking curves on the BST (2 0 0), LSMO (2 0 0) and LAO (2 0 0) reflections yielded a full width at half maximum (FWHM) of 0.7410, 1.3943, 0.2639°, respectively, showing that the graded BST film has epitaxial structure. Like the situation before alignment, the FWHM (2 0 0) (0.42) is larger than FWHM (1 0 0) (0.25). And further, it is larger than that of single layer BST film, for instance ∼0.22 in [19], and 0.36 in [20].

The polarization–electric field (P–E) loop was measured by use of a RT66A Standardized Ferroelectric Test system (Radiant Technologies). Before the measurement, gold top electrodes with a diameter of 0.2 mm were sputtered onto the top film. Fig. 6 shows the P–E measurement results. From the figure, we can see that the ferroelectricity of the BST graded film still exists. When the applied voltage increases, the remanent polarization P_r has a small increase. For the graded BST thin film, P_r is about 2 $\mu C\,cm^{-2}$, which is smaller than that of PZT thin film (25 $\mu C\,cm^{-2}$ [18]). No obvious dc offset was observed in the P–E loops.

The dielectric properties were measured using an impedance analyzer (HP 4194A). The results are shown in Fig. 7. The graded BST film has a large dielectric constant (over 1600) compared to conventional BST thin film by PLD method (less than 1000 for different Ba/Sr ratios) and small loss tangent (less than 0.2, the smallest one reaches 7.5×10^{-2}). The small loss tangent is favored for application in RF and microwave dielectrics. The permittivity and loss tangent versus temperature relationships at different frequencies were also measured. The results are shown in Fig. 8. It is seen that there is no abrupt variations in temperature ranged from 25 to 130 °C. The permittivity decreases almost linearly with temperature instead of having a resonance peak as in BST of single composition which makes the temperature compensation much easier.

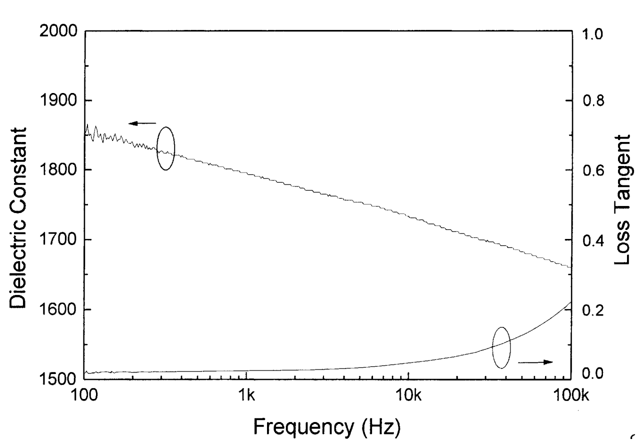

Fig. 7. Dielectric constant of BST graded thin film vs. frequency.

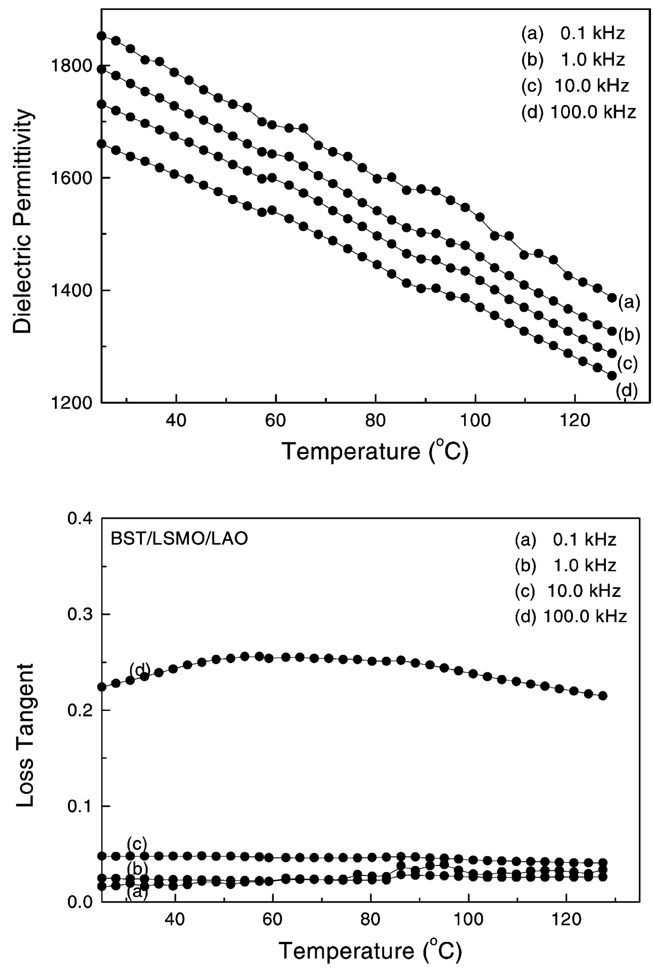

Fig. 8. Dielectric constant of BST graded thin film vs. temperature.

4. Conclusion

In this work, epitaxial compositionally graded barium strontium titanate thin films were prepared on the LSMO/LAO substrate. The remnant polarization is about 2 $\mu C\,cm^{-2}$. A big room temperature dielectric constant as high as 1600 was obtained and has an almost linear relationship with temperature from 25 to 130 °C.

Acknowledgements

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