Structural and Electrical Characters of Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ /La$_{0.5}$Sr$_{0.5}$CoO$_3$ Thin Films by Plus Laser Deposition

Wen-Feng Qin, Jun Zhu, Jie Xiong, Jin-Long Tang, and Xiao Feng

Abstract—Epitaxial Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ (BST) thin films were deposited on LaAlO$_3$ (LAO) substrates with the conductive metallic oxide La$_{0.5}$Sr$_{0.5}$CoO$_3$ (LSCO) film as a bottom electrode by pulsed laser deposition (PLD). X-ray diffraction $\theta$-20 and $\Phi$ scan showed that the epitaxial relationship of BST /LSCO /LAO was [001] BST// [001] LSCO//[001] LAO. The atomic force microscope (AFM) revealed a smooth and crack-free surface of BST films on LSCO-coated LAO substrate with the average grain size of 120 nm and the RMS of 1.564 nm for BST films. Pt/BST/LSCO capacitor was fabricated to perform Capacitance–Voltage measurement indicating good insulating characteristics. For epitaxial BST film, the dielectric constant and dielectric loss were determined as 471 and 0.03, respectively. The tunability was 79.59% and the leakage current was $2.63 \times 10^{-7}$ A/cm$^2$ under an applied field of 200 kV/cm. Furthermore, it was found that epitaxial BST (60/40) films demonstrate well-behaved ferroelectric properties with the remnant polarization of 6.085 $\mu$C/cm$^2$ and the coercive field of 72 kV/cm. The different electric properties from bulk BST (60/40) materials with intrinsic paraelectric characteristic are attributed to the interface effects.

Index Terms—BST, electrode, LSCO, thin film.

1. Introduction

Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ (BST) thin films, which take advantage of strong tunability under an external dc electric field, the high dielectric constant of BaTiO$_3$ and the structure stability of SrTiO$_3$, are promising dielectric materials for ultra-large-scale integrated dynamic random access memories (DRAM), microwave tunable devices, and field effect transistors$^{[11]}$. In these applications, it is essential to fabricate high quality BST thin films. Many growth techniques, such as radio-frequency (RF) magnetron sputtering, pulsed laser deposition (PLD), and plasma-enhanced metal organic chemical vapor depositions have been applied to fabricate BST films of high quality$^{[4]-[6]}$.

In previous investigations, it was found that the electrical properties of BST thin films are strongly influenced by the structure properties such as phase structure and interface layer between an electrode and a film. To fabricate high performance BST film capacitors, proper bottom electrode has to be utilized, which requires low resistivity, good thermal stability and strong adhesion to the substrate. The bottom electrode layer influences not only the microstructure of BST films directly, but also the dielectric and ferroelectric properties. Therefore, the use of the perovskite-type metallic oxide electrodes, for example, La$_{0.5}$Sr$_{0.5}$CoO$_3$ (LSCO), SrRuO$_3$ (SRO), (Ba, Sr) RuO$_3$ (BSR), LaNiO$_3$ (LNO) and La$_{0.5}$Sr$_{0.5}$MnO$_3$ (LSMO) seems to be reasonable$^{[7]-[11]}$. Various kinds of electrode materials have been aimed at improving the electric properties of ferroelectric thin films, including BST. The epitaxial LSCO and BST have been fabricated on LAO by pulsed laser deposition$^{[12]}$. B. Nagaraj et al. reported the leakage current mechanism of LSCO/BST/LSCO capacitors on Si/SiO$_2$/Ti/Pt substrates by RF sputtering is dominated by Poole–Frenkel mechanism$^{[13]}$. However, there has been little systematically report about electric properties of Pt/BST/LSCO capacitors on LAO substrates for microwave tunable devices. This prompted our current study to fabricate BST thin films with perovskite oxide electrodes such as La$_{0.5}$Sr$_{0.5}$CoO$_3$ (LSCO) as electrode because that LSCO films and BST films are almost lattice matched and LSCO enhances the phase stability of BST. Thus, the fabrication of epitaxial BST films on LSCO-coated LAO and detailed understanding of the relation between the films structure and its properties are both of scientific and technological significance.

In this paper, we report an investigation of the electric properties of Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ films on conductive La$_{0.5}$Sr$_{0.5}$CoO$_3$ bottom electrodes deposited by pulsed laser deposition and the good properties has been obtained.

2. Experiment

The 3 in. ceramic BST and LSCO targets have been used to deposit films by PLD, using KrF ($\lambda = 248$ nm) excimer laser (LAMBDA PHYSIK). The average energy density was adjusted to $3.1 \text{J/cm}^2$ at a repetition of 3 Hz. LaAlO$_3$ (100) substrates were selected for this experiment, and were in situ annealed about 30 min at the temperature of 800 °C to get a...
clean and high-crystallinity surface before deposition. The about 100 nm thicknesses La_{0.5}Sr_{0.5}CoO_{3} films were fabricated on LaAlO_{3} (100) single-crystal substrate under flowing oxygen pressure 20 Pa at substrate temperature of 650°C. BST films were subsequently deposited in the same condition as that of LSCO films. After deposition, the samples were in situ annealed for 30 min under 5×10^{4} Pa oxygen pressure at the same temperature at which they were grown to improve the quality of films and decrease the oxygen vacancy. The typical deposition time of 90 min. gave film thickness of 300 nm for BST films.

The structural and dielectric properties of BST thin films were characterized by various techniques. X-ray diffraction (XRD) profiles were obtained in a Bede diffractometer using Cu Kα radiation to determine the phase formation, the crystallinity, and the orientation of the films. The surface morphologies of the films were analyzed by atomic force microscope (AFM SPM-300HV, SEIKO). For dielectric measurements, Pt top electrode was deposited on the film by direct current sputtering though a shadow mask to form the metal-insulator-metal (MIM) capacitor configuration. Dielectric constant, tunability, and loss were measured using an HP 4284 impedance analyzer. The P–E hysteresis loop measurements were carried out with a TF Analyzer2000 standardized ferroelectric test system. The leakage current through the capacitors was measured using by Agilent 4155B Semiconductor Parameter Analyzer at room temperature.

### 3. Results and discussion

Fig. 1 shows X-ray diffraction (XRD) θ–2θ scans of BST/LSCO bilayers on LAO substrate. As shown in Fig. 2, the BST and LSCO films are (100) oriented with respect to substrate, indicating that pure perovskite films are formed. The epitaxial nature of the BST and LSCO is confirmed by the in-plane alignment with respect to the major axes of the LAO substrate through XRD phi (Φ) scans of the (202) BST, LSCO, and LAO reflections. The out-of-plane and in-plane epitaxial relationships are found to be (001) BST/ (001) LSCO/ (001) LAO and (100) BST/ (100)/LSCO/ (100) LAO, respectively. These reflections clearly demonstrate a good epitaxial growth of the BST film and the LSCO bottom electrode on the (100) LAO substrate. Both the BST film and the LSCO bottom electrode show a four-fold symmetry, indicating a cube-on-cube epitaxial growth. The good lattice matching at the interface of substrate and film helps to orient the grain growth of the deposited film. The LSCO films on LAO (100) show clear (100) orientation because of similarity of lattice parameters between LAO (a_{0}=3.789 Å) and LSCO (a_{0}=3.805 Å) structures. It can be thought that the highly oriented (100) LSCO thin film on LAO substrate could help to exhibit (100) textured BST thin films. The crystallization and growth of the BST films were further facilitated by the (100) textured LSCO film due to well matching of lattice parameter between LSCO and BST (a_{0}=3.965 Å) as well as both having a similar perovskite structure.

![Fig. 1. X-ray diffraction patterns of the BST thin film.](image)

It is well known that the electrical properties of BST thin films are strongly influenced by the microstructure of the film such as the grain size, crack, pinhole and roughness. If the grain size of the BST thin films is large, the dielectric constant may be similar to that of the bulk BST, but the roughness will increase with the grain size increase\[14\]. Excessive roughnesses would be deleterious in situations where the ferroelectric is either integrated into a complex multilayer structure or used in an electronic device. It is necessary to solve these problems before any practical uses of the films can be made. The average grain size and the surface roughness of the BST thin films were analyzed with AFM using tapping mode. The typical surface AFM morphologies for the thin films are shown in Fig. 2. The AFM micrographs reveal that the BST thin film is very smooth, well crystallized, crack free, and pinhole free. The root-mean-square (RMS) roughness and the grain size on the BST film surface are estimated to be about 1.564 nm and 120 nm in an area of 5μm×5 μm, respectively.

![Fig. 2. AFM micrographs of the BST thin film.](image)

To measure the dielectric properties of the BST films, we fabricated plane capacitors by depositing platinum on top of the film surface. The dielectric properties of the BST films were measured at 10 kHz using a HP4284A impedance analyzer at room temperature. The dielectric constant of the BST layer can be calculated based on the measured capacitance. Capacitance–voltage (C–V) characteristics measured for a Pt/BST/LSCO (MIM) capacitor are shown in Fig. 3. The C–V characteristics represented double peaks corresponding to the hysteresis loop. It exhibits clear regions...
of accumulation, depletion and inversion. This curve was simultaneously measured with the cycling of bias voltage up and down. The slight asymmetry of this curve was associated with the difference between the bottom electrode LSCO and top electrode Pt. From the variation of capacitance with applied field, the value of tunability is determined for the film. The tunability \((T)\) is defined as

\[
T(\%) = \frac{C_0 - C_v}{C_0} \times 100
\]

where \(C_0\) and \(C_v\) are the capacitance values at zero and maximum dc bias voltages. The tunability is 79.58%, while the applied voltage changed from 0 V to 6 V and the loss tangent is 0.03 at zero dc bias voltage. The tunability value of BST/LSCO films was higher than BST/Pt films in the literature. L. Kinder et al. \([15]\) observed that the tunability values and maximum dielectric loss values of \(\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3\) films grown Pt were estimated to be about 44.45% and 0.03 at 10 kHz, respectively. Several reasons are possible for increased tunability of BST/LSCO film. Firstly, the reduction of dielectric constant in BST/Pt thin film can be explained by the existence of Pt hillocks \([16]\). The BST film grown on LSCO electrode can avoid influence by Pt hillocks, which have an adverse effect on the BST dielectric properties. Secondly, BST film with a LSCO electrode has higher compressive stresses than BST thin film grown on Pt electrode \([17]\). High compressive stresses promote the polarization of electric dipoles, which increases the dielectric constant. This interpretation is consistent with several reports on the study of stress on the dielectric constants for ferroelectrics \([18]\).

For tuning application, both tunability and loss tangent must be considered when comparing the relative merits of different film and varactor configurations. A figure merit \((\kappa)\) is given by:

\[
\kappa = \frac{C_0 - C_v}{C_0 \tan \delta}
\]

where \(\tan \delta\) is measured under zero dc bias. Then the \(\kappa\) factor is 26.53. The value made the film suitable for low frequency tunability device, which are operated at room temperature. Using the expression \(C = \varepsilon \varepsilon_0 A / t\), the dielectric constant of the film was calculated to be 471 assuming 0 V and 10 kHz. Here, \(C\) is the capacitance, \(\varepsilon_0\) is the permittivity of free space, \(\varepsilon\) is the dielectric constant of BST film, \(A\) is the area of the top electrode and \(t\) is the thickness of BST film. The relatively higher dielectric constant measured in this work could be due to the big grain of the film.

Fig. 4 shows the frequency dependence of the capacitance and loss tangent for the epitaxial BST/LSCO films (Pt was used as the top electrode). The measurements were carried out at zero bias fields and the ac field does not address the polarization state. In the lower frequency region (below 10 kHz), the capacitance shows a slight decrease with increasing frequency, while the loss tangent increases slowly. The average values are about 7.7 nF for the capacitance and dielectric loss tangent is 0.0275, respectively. At higher frequencies, the capacitance and loss tangent become variable with frequency, presenting the relaxation in this frequency range. The relaxation frequency observed is low and obviously not due to the real dielectric relaxation of the BST thin films. The possible reasons for the low relaxation frequency come from the inductance and the capacitance of the equivalent measurement circuit \([19]\).

For practical application, the leakage current passing through the insulating layer should be as low as possible. Fig. 5 shows the leakage current density characteristics of BST thin films versus the applied voltage measured at room temperature at 10 kHz. As shown in Fig. 5, the leakage current density of BST films was 2.63×10\(^{-7}\) A/cm\(^2\) under an applied field of 200 kV/cm. The result is in agreement with that of BST thin film with SRO electrode \([20]\). The value sheds light on the good insulation for the BST thin film.

The ferroelectric properties of the films were measured in a Pt/BST/LSCO capacitor. A well saturated P-E hysteresis
loop of the Ba_{0.6}Sr_{0.4}TiO_{3} thin film is shown in Fig. 6. The hysteresis loops directly show ferroelectric behavior of BST thin films. According to the measurements, the coercive field ($E_c$) and the remnant polarization ($P_r$) of BST films were 72 kV/cm and 6.085 µC/cm^2, respectively. These values are consistent with those of the Ba_{0.9}Sr_{0.1}TiO_{3} films reported by Leng et al.[21] But the composition of BST in our work is Ba:Sr of 60:40. The result shows a good ferroelectric property of the BST films on LSCO coated LAO substrates by plus laser deposition method. It is noted that the hysteresis property of the BST films on LSCO coated LAO substrates Ba:Sr of 60:40. The result shows a good ferroelectric

Fig. 6. $P$–$E$ hysteresis loop of BST thin film at room temperature.

4. Conclusions

Epitaxial Ba_{0.6}Sr_{0.4}TiO_{3} and La_{0.5}Sr_{0.5}CoO_{3} films have been successfully grown on (100) LaAlO_{3} substrate by PLD. The dielectric constant and loss tangent of the BST films were about 471 and 0.03, respectively, below 10 kHz. The ferroelectric hysteresis loop was measured for this Pt/BST/LSCO heteroepitaxial capacitor. The remnant polarization $P_r$ was coercive field $E_c$ about 6.085 µC/cm^2 and 72 kV/cm, respectively. The heteroepitaxial capacitor showed low dc leakage current of $2.63 \times 10^{-7}$ A/cm^2 under an applied field of 200 kV/cm.

References


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