J Electroceram (2006) 17:141–144
DOI 10.1007/s10832-006-9734-2

Thickness dependent ferroelectric properties of BSTO thin films deposited by RF magnetron sputtering

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Received: 27 June 2005 / Revised: 21 June 2006 / Accepted: 10 July 2006

Abstract The thickness dependence of ferroelectric permittivity of (Ba, Sr)TiO_3 has been investigated. The BST films could be obtained to have a simple cubic perovskite structure, space group Pm3m, and practically c-axis epitaxial structure deposited at 800°C. Through post-annealing process, we have improved the dielectric properties; dielectric permittivity, dielectric loss, and tunability. The change in dielectric properties before and after annealing is attributed to the change in film strain and the contraction in film lattice. As the thickness of BST films increases from 55 nm to 350 nm, the dielectric constant of BST films increases from about 100 to above 670 due to the reduction of interfacial dead layers with low dielectric constant between films and top electrodes. The dielectric loss of BST thin films decreased as the thickness increases. The existence of interfacial dead layers in a thinner film had a larger effect on the effective dielectric constant than tensile strain between the BST films and MgO substrate.

Keywords BST · RF sputtering · Ferroelectric · Microwave · Tunable devices

1 Introduction

The dielectric properties of high dielectric (Ba, Sr)TiO_3 (BST) thin films are dependent on the film stress, thickness and the fabrication process [1–3]. Notably, when metal electrodes are used, the dielectric constants of a BST film, measured at zero bias, decrease dramatically with decreasing BST film thickness. This is believed to be due to the presence of certain low-dielectric interfacial layers between the films and the electrodes. Even when the interfaces do not contain any nonperovskite phases or contaminates, an interfacial low-dielectric layer exists as a result of the intrinsic size effect of dielectric polarization [4]. Through the thickness dependence of the dielectric constant, it has been shown that there is an interface "dead layer effect" that reduces the effective dielectric constant in ferroelectric constant.

When the epitaxial layer of ferroelectric thin film was grown on the MgO substrates, it is strained due to lattice mismatch [3]. Strain is a very significant factor to effect dielectric properties. The effect of the strain on the dielectric constant is due to the fact that ionic positions and vibrations in a ferroelectrics are modified by the strain, and these changes are coupled to the polarization mechanism in the ferroelectrics [5]. Sputtered BST thin films have been investigated by several researchers [6–8]. The role of annealing process has been specifically studied for its influence on strain, and dielectric properties [9].

In this study, the effects of thickness and post-annealing on ferroelectric properties of the BST thin films deposited by the RF magnetron sputtering were investigated.

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2 Experimental procedures

$(Ba_{0.5}Sr_{0.5})TiO_3$ (BST) thin films were deposited on (100) MgO single crystal substrate at 800°C by RF magnetron sputtering. The sputtering chamber was evacuated to a base pressure of 5×10^{-6} Torr. All of the BST films were deposited at fixed power of 100 W and a constant pressure of

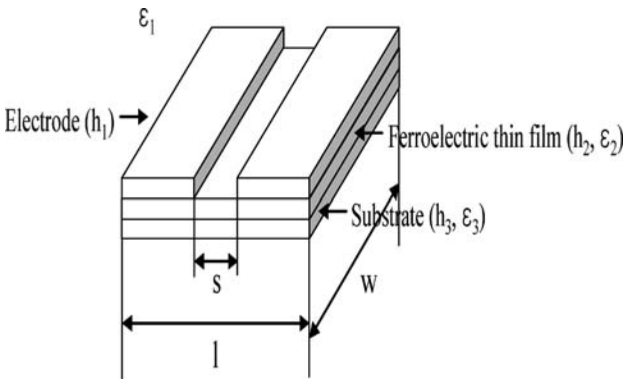

Fig. 1 Diagram of a planar capacitor consisting of an insulating substrate, a ferroelectric thin film layer, and conducting electrodes separated by a gap of width s

10 mTorr which was maintained by a mixture of Argon and oxygen (Ar/O_2 : 75/25) set by individual mass flow control valves and substrate temperature of 800°C. The target and substrate separation was about 7 cm. BST films have the various thickness from 55 nm to 350 nm. The deposited films were post-annealed in box furnace at 1100°C for 1h in air.

DC sputtering was applied for the deposition of copper electrode on the BST thin films. The copper electrode patterns were materialized by chemical etching. The crystal structure of the films was examined by X-ray diffraction (XRD), medium energy ion scattering (MEIS), and reflection high energy electron diffraction (RHEED) measurements. The BST film thickness was determined from Scanning Electron Microscope (SEM). Atomic force microscopy (AFM) was used to determine the surface roughness and microstructure. The dielectric characteristics and tunability of the ferroelectric films were measured using a HP 4294A impedance analyzer at the 1 MHz. The dielectric properties of BST films were extracted using a modified conformal-mapping partial capacitance method with the dimension of the capacitors [10, 11].

Models are needed which can calculate the capacitance of a planar structure formed by a ferroelectric thin film on an insulating substrate with metal planar electrodes with allowance for the fringing fields in the ambient free space(air). Such a calculation is based on the method of conformal mapping, which can transform the field in a planar structure into the field of a sandwich capacitor. The planar structure in question consists of three components parts: the ferroelectric film, substrate, and air. A separate calculation of the capacitance of each of the component parts with subsequent summation constitutes the basis of the partial capacitance method. This method was implemented in works of Kochanov [12]. Consider a planar capacitor in Fig. 1. Its capacitance is formed by the capacitance of the stray fields in the ambient space(air) with dielectric constant $\varepsilon_1 = 1$, the capacitance of the ferroelectric thin film layer of thickness h_2 with dielectric constant ε_2, and the capacitance of the substrate of thickness h_3 with dielectric constant ε_3. We represent the composite layered capacitor as three simple planar capacitors with homogeneous filler connected in parallel, and seek its capacitance as the sum of the three partial capacitances where C_1, C_2, and C_3 Eq. (1) are the capacitances of the component parts of the planar capacitor, which are the fringing field in air, the ferroelectric film, and the substrate respectively [11]. From the Eq. (1) and (2), the dielectric constant of BST films was calculated.

$$C = C_1 + C_2 + C_3 \tag{1}$$

$$\begin{aligned} C_1 &= w\varepsilon_0 \frac{2}{\pi} \ln\left(4\frac{l}{s}\right) \\ C_2 &= \frac{w\varepsilon_0\,(\varepsilon_2 - \varepsilon_3)}{s/h + (4/\pi)\ln 2} \\ C_3 &= w\varepsilon_0\,(\varepsilon_3 - 1)\,\frac{1}{\pi}\ln\left(16\frac{h_3 - h_2}{\pi s}\right) \end{aligned} \tag{2}$$

3 Results and discussions

The ferroelectric thin film had practically epitaxial structure as shown in the RHEED pattern of the BST thin films on MgO substrates at 800°C of deposition temperature presented in Fig. 2. Figure 3 shows the example of MEIS spectra measured on the BST/MgO film grown in the process of RF cathode reactive sputtering in the Laboratory of Layered structures (ETU, S-Petersburg). The BST film thickness is 180 nm. Physical modeling of the experimental spectra was implemented with an account of the dechanneling ions

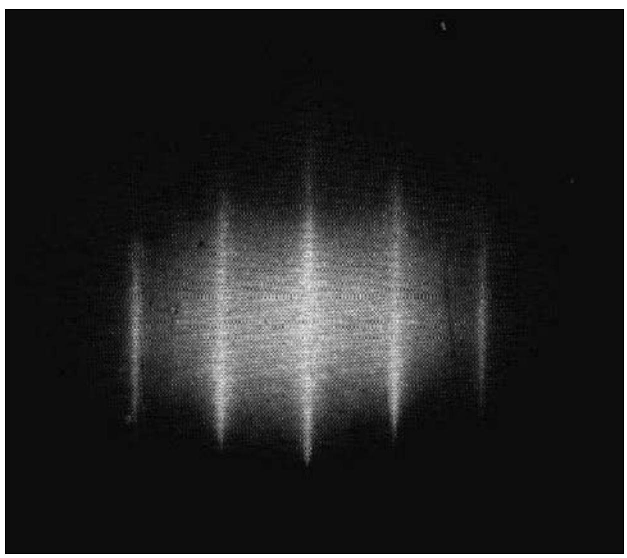

Fig. 2 The RHEED pattern of the BST/MgO heteroepitaxial structure

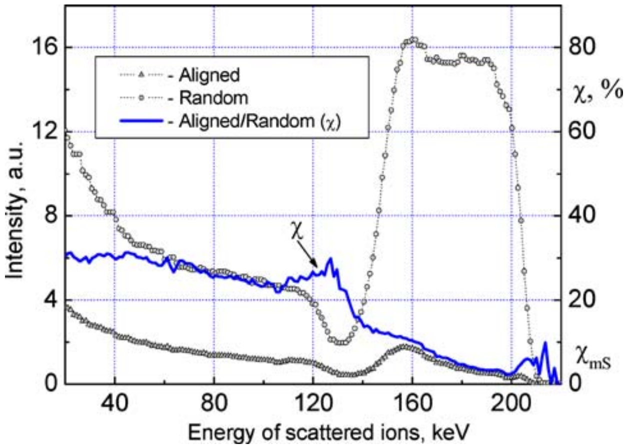

Fig. 3 The MEIS spectra of the BST/MgO heteroepitaxial structure

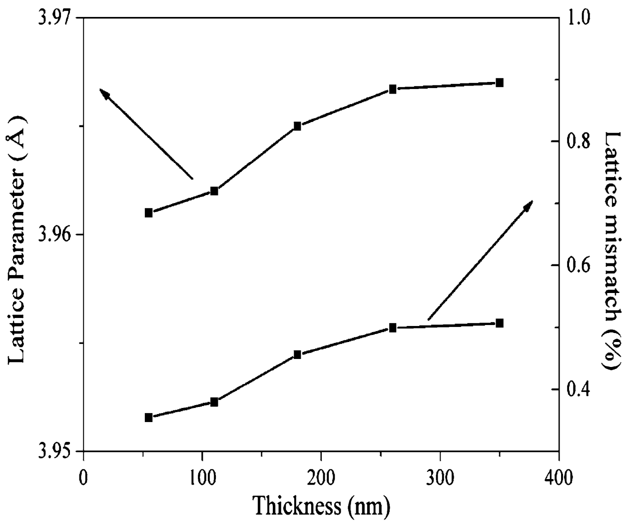

Fig. 4 The variation of the lattice parameter according to the thickness of the BST thin films with post-annealing at 1100°C

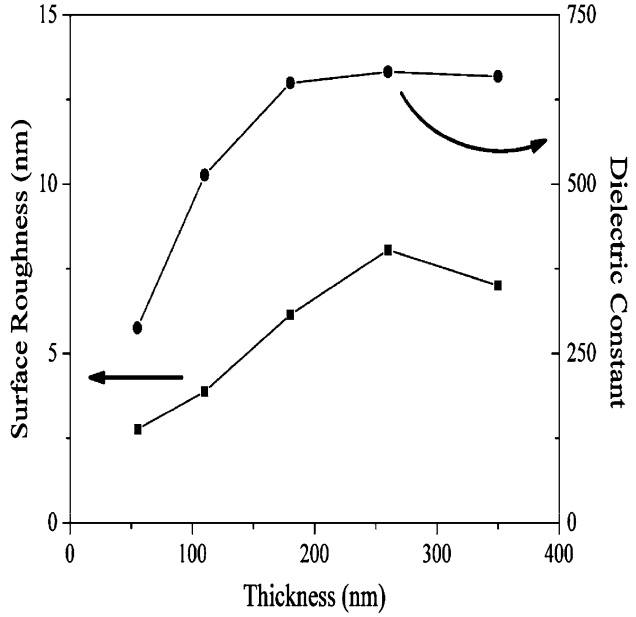

Fig. 5 The variation of dielectric constant and surface roughness as a function of the BST thin film thickness with post-annealing at 1100°C

formed in the investigated sample on the way up to the scattering event. The MEIS spectrum was measured under an action of H + ions with the energy 234 keV. The film sample had practically epitaxial structure that one can see in the RHEED pattern presented in the same figure. The film had the maximal relative yield of the scattered ions $\chi_{mS} \approx 0.025$. The BST films could be obtained to have a simple cubic perovskite structure, space group Pm3m, and practically *c*-axis epitaxial structure under all thickness at 800°C of deposition temperature. Through post-annealing in box furnace, the (100) peak of the films gradually increased and slightly shifted to lower angle(2θ) as the BST film thickness increases from 55 nm to 350 nm. This result indicated that the lattice parameter of BST films increased slightly shown in Fig. 4. The mismatch between BST films and MgO substrate was calculated. When the BST thin films were as-deposited for 2 h, the normal lattice parameter of the films was 2.48% greater than the lattice parameter ($a = 3.947$Å) of the corresponding bulk BST material. The observation of the lattice expansion of the BST films is due to lattice and thermal coefficient mismatch between the BST film and substrate, and oxygen vacancies in the films [5]. Through post-annealing, the normal lattice parameter of the film decreased from 2.48% to 0.5% at with Ar/O_2 (75/25) ratio of sputtering gas. This phenomenon could explain remove of the strain between the BST films and MgO substrate. The mismatch between BST films and MgO substrate tended to increase from 0.35% to 0.5% with an increase of thickness of the BST thin films.

The dielectric properties of the BST films at 1 MHz as a function of various thicknesses of the BST thin films by post-annealing are shown in Fig. 5. The dielectric permittivity of the as-deposition film was below 100 because of high tensile strain between the BST films and MgO substrate Fig. 5 [9]. Through post-annealing, the dielectric constant of BST films remarkably increasing from about 100 to above 670 due to get rid of the strain in the films and increase the grain size. The RMS value of BST thin films tended to increase with an increase of thickness of BST thin films. According to Lee et al. [13] that means, the dielectric permittivity of the BST films having a relatively large grain size is higher than that of one with a small grain size. The dielectric constants of the BST thin films tended to increase from 280 to 670 with an increase of thickness of the BST thin films. This result may be attributed to interfacial dead layers between BST thin films and top electrode with low dielectric constant [14, 15]. In other words, the existence of interfacial dead layers in a thinner film had a larger effect on the effective dielectric

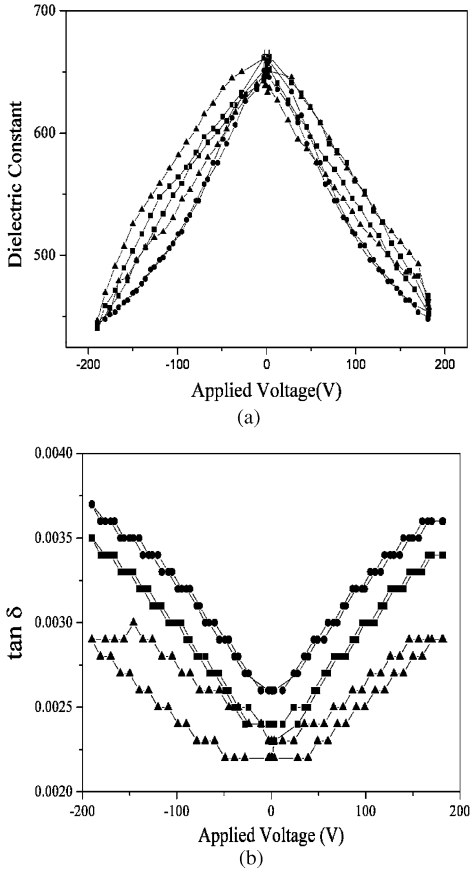

Fig. 6 The tunability and dielectric loss of BST thin film with post-annealing at 1100°C : ▲:180 nm ●: 260 nm ■: 350nm)

constant than tensile strain between the BST films and MgO substrate.

The tunability of 180–350 nm thickness BST films with post-annealing was shown in Fig. 6(a). The tunability of the as-deposited BST films was not measured because of high tensile strain between BST films and MgO substrate. The tunability of the BST films through post-annealing remarkably increased up to 35% at 180–350 nm BST films. One possible explanation for this observed improvement is that the tensile stress was decreased remarkably by annealing process. The dielectric loss of 180–350 nm BST films with post-annealing was shown in Fig. 6(b). The dielectric loss of as-deposited BST film measured at 1 MHz was 0.008. The dielectric loss of BST films with post-annealing remarkably decreased to 0.0024 without applied bias.

4 Conclusions

In this paper, we have researched the high dielectric permittivity BST films deposited by RF magnetron sputtering. Through post-annealing process, we have improved the dielectric properties; dielectric permittivity, dielectric loss, and tunability. The change in dielectric properties with and without post-annealing is attributed to the change in the film strain and the contraction in the film lattice [9]. As the thickness of the BST films increased from 55 nm to 350 nm, the dielectric constant of BST films increased from about 100 to above 670 due to the reduction of interfacial dead layers with low dielectric constant between films and top electrodes and the dielectric loss. The existence of interfacial dead layers in a thinner film had a larger effect on the effective dielectric constant than tensile strain between the BST films and MgO substrate.

Acknowledgement This research has been supported by Korea-Russia Joint Research Project.

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