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Structure and dielectric properties of Ca-doped ($Ba_{0.7}Sr_{0.3}$)TiO_3 thin films fabricated by sol–gel method

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Abstract A wide range of Ca-doped ($Ba_{0.7}Sr_{0.3}$)TiO_3 (BST) thin films (from 0 to 20 mol%) have been prepared on Pt/Ti/SiO_2/Si (100) substrates by sol–gel technique. The structural and dielectric properties of BST thin films were investigated as a function of Ca dopant concentration. The results showed that the microstructure and dielectric properties of the BST films were strongly dependent on the Ca contents. With the Ca dopant concentration increasing, the grain size, dielectric constant and dielectric loss of the BST thin films decreased. As the content of Ca dopant reaches 10 mol%, the dielectric constant, dielectric loss, tunability, the value of FOM and the leakage current density are 281, 0.0136, 16.7%, 12.3 and 5.5×10^{-6} A/cm^2, respectively.

Keywords BST thin films · Ca-doped · Sol–gel · Dielectric properties

1 Introduction

Barium strontium titanate (BST) thin films have been intensively studied for applications in the high density dynamic random access memories, monolithic microwave integrated circuit decoupling capacitors, tunable microwave filters, and phased array antennas [1–3]. For BST to be employed in tunable device applications the dielectric and insulating properties must satisfy several critical requirements. These requirements are: (1) a moderate-to-low dielectric constant at microwave frequencies, (2) a low dielectric loss factor, and (3) a large variation in the dielectric constant in an applied dc bias field. In addition, the thin film must also possess low leakage current characteristics [4–6]. Undoped BST thin films offer tunabilities upward of 50% at bias voltages of less than 10 V, which is compatible with the voltage requirements of present semiconductor based systems. Unfortunately, the tradeoff for such high tunabilities are high loss tangents, that is, loss tangents much larger than 0.02. It is well documented that small concentration of dopants can dramatically modify the properties of ferroelectric materials such as BST. In particular, Fe^{2+}, Fe^{3+}, Co^{2+}, Co^{3+}, Mn^{2+}, Mn^{3+}, Ni^{2+}, Mg^{2+}, Al^{2+}, Ga^{3+}, In^{3+}, Cr^{3+}, and Sc^{3+}, which can occupy the B site of the ($A^{2+}B^{4+}O_3^{2-}$) perovskite structure, have been known to lower dielectric loss [7–11].

In this paper, we report the influence of the cationic substitution of Ca in A site such as Ba or Sr site of the ABO_3 perovskite structure on the structure and dielectric properties of BST thin films. X-ray diffraction and field emission scanning electron microscopy were used to characterize the phase structural and microstructure evolution of the thin films. Dielectric measurements with different Ca concentration were also performed on the films at room temperature.

2 Experimental details

The precursor solution for both undoped and Ca-doped $Ba_{0.7}Sr_{0.3}TiO_3$ were prepared by the sol–gel method using barium acetate [$Ba(CH_3COO)_2$], strontium acetate [$Sr(CH_3COO)_2$], terabutyl titanate [$Ti(OC_4H_9)_4$], and calcium acetate [$Ca(CH_3COO)_2$] as the starting materials. Glacial acetate acid was used as a solvent. The barium acetate, strontium acetate, and calcium acetate (as a dopant precursor with concentrations ranging from 0 to 20 mol%) were initially dissolved in heated acetate acid and mixed together.

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After cooling to room temperature, the mixture of titanium butoxide and acetylacetone were added. The concentration of the final solution was adjusted to about 0.3 M. After aging the hydrolyzed solution for 24 h, thin film deposition was carried out on the Pt/Ti/SiO_2/Si (100) substrates by spin coating at 3,000 rpm for 20 s each layer. Each spin-coated film was subsequently heat treated at 500 °C for 15 min to remove the organic concentrations. The coating and heat treatment procedures were repeated several times until reaching the desired thickness (about 450 nm). Then the pre-baked films were annealed at 700 °C for 30 min in air for crystallization.

The crystalline phase of the thin films was identified by X-ray diffraction (BRUKER D8 Advance diffractometer). F20 filmetrics was employed to measure thickness of the films. The surface morphology was determined by FESEM (FEI Quanta 200 FEG). Dielectric measurements were carried out using the metal–insulator–metal (MIM) capacitor configuration. Au top electrode having a diameter of 0.5 mm was deposited by direct current sputtering to measure electrical properties. Dielectric constant and loss were measured using an HP4284A impedance analyzer. The leakage current characteristics were measured using a Keithley 6517A.

3 Results and discussion

Figure 1 shows the XRD patterns of BST thin films with various Ca-doping ratios in the range of 0–20 mol% annealed at 700 °C. It can be seen that all the films were perovskite and polycrystalline structure with no evidence of secondary phase formation. The polycrystalline nature in the films was due to a lattice mismatch between BST thin film and the Pt/Ti/SiO_2/Si (100) substrate [12]. There was no apparent change in peak intensity resultant of the Ca doping indicating that all films were well developed at this annealing temperature and time.

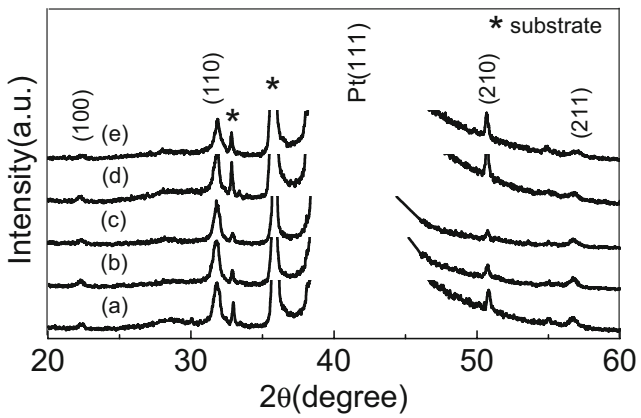

Fig. 1 XRD patterns of BST thin films with different Ca content (*a*) Ca 0 mol% (*b*) Ca 2 mol% (*c*) Ca5mol% (*d*) Ca 10 mol% (*e*) Ca 20 mol%

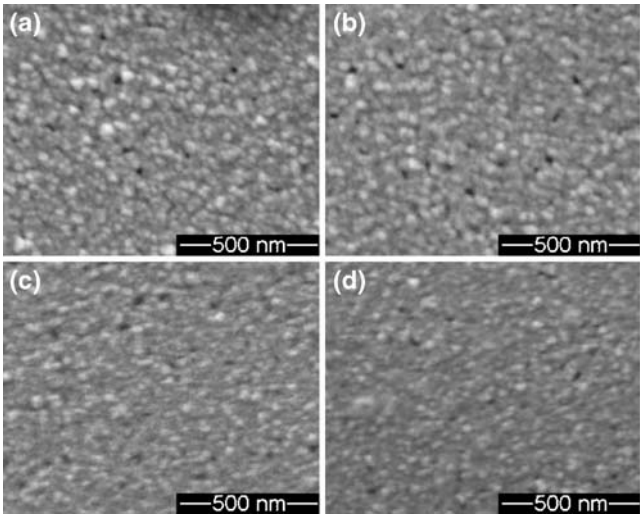

Fig. 2 FESEM images of BST thin films (**a**) Ca 0 mol% (**b**) Ca 5 mol% (**c**) Ca 10 mol% (**d**) Ca 20 mol%

Figure 2 shows FESEM images of the BST films. The surface morphological features of the films appeared to be quite sensitive to the amount of Ca content. Through an analysis of these FESEM images, it can be observed that the average grain size of the BST films significantly decreased with the increase of the Ca content.

The dielectric properties of the BST thin films in an Au/BST/Pt configuration were measured at room temperature as a function of the applied frequency and electric field. Figure 3 shows the dielectric constant and the dielectric loss of the BST thin films as a function of Ca content at a frequency of 100 kHz. It was found that the dielectric constant and the dielectric loss of the BST thin films decreased from 366, 0.021 to 256, 0.0135, when the Ca content increased from 0 to 20 mol%. The decreasing dielectric constant factor of the sample with small grain size may be attributed to the increasing amounts of grain boundaries [13].

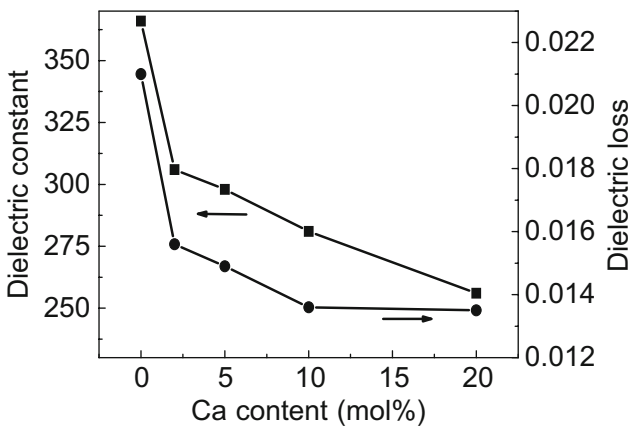

Fig. 3 Dielectric constant and dielectric loss of the BST thin films with different Ca content

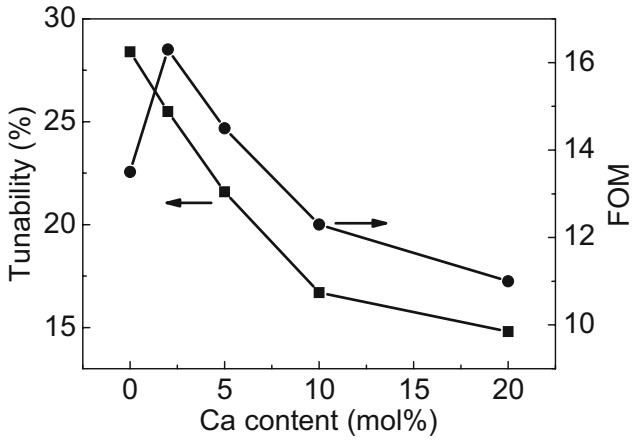

Fig. 4 Tunability and the FOM of the BST thin films with different Ca content

The tunability (k) was calculated by using the expression:

$$k = \frac{\varepsilon(0) - \varepsilon(\mathrm{E})}{\varepsilon(0)} \quad (1)$$

where $\varepsilon(0)$ and $\varepsilon(E)$ represent the dielectric constant at zero and a certain E field, respectively. The figure of merit (FOM) is calculated based on the expression below:

$$FOM = \frac{k(\%)}{\tan\delta(\%)} \quad (2)$$

where dielectric loss is given as a percentage scale. This figure of merit reflects the fact that a tunable microwave circuit cannot take full advantage of high tunability if the loss factor is high [14]. Figure 4 shows the tunability (at 200 kV/cm) and FOM of BST thin films with different Ca content. It was clear that the tunability of the films decreased from 28.4 to 14.8% as the Ca content increased from 0 to 20 mol%. However, the change of the value of FOM had a different tendency. It increased from 13.5 to 16.3 with Ca content increasing from 0 to 2 mol%, and then decreased to11 as the Ca content reached 20 mol%.

The tunability is known to be a function of applied dc electric field. To withstand large electric field, the leakage current of BST films should be low. Figure 5 shows the leakage current characteristics of undoped and Ca-doped BST thin films measured at room temperature. It could be found that the leakage current density decreased from 2.4×10^{-4} A/cm^2 to 1.7×10^{-6} A/cm^2 with Ca content increasing from 0 to 20 mol% at applied electric field of 200 kV/cm. The decrease in leakage current may be due to that the grain size decreased with increasing Ca content for BST thin film, which could be seen from FESEM measurements. The undoped BST film with large grain size had short conduction paths along the highly resistive grain boundary, which caused a higher leakage current than that of Ca-doped BST thin films with smaller grain size [15]. In Fig. 3, it is also indicated that the dielectric loss of the BST thin films decreased with the increasing in Ca content, which is consistent with the result of the leakage current shown in Fig. 5. The leakage current characteristics were distinctly different in positive and negative electric field regions. It could be seen from Fig. 5 that the reverse currents at negative bias regions were much different from forward current at positive bias regions. The different reverse current

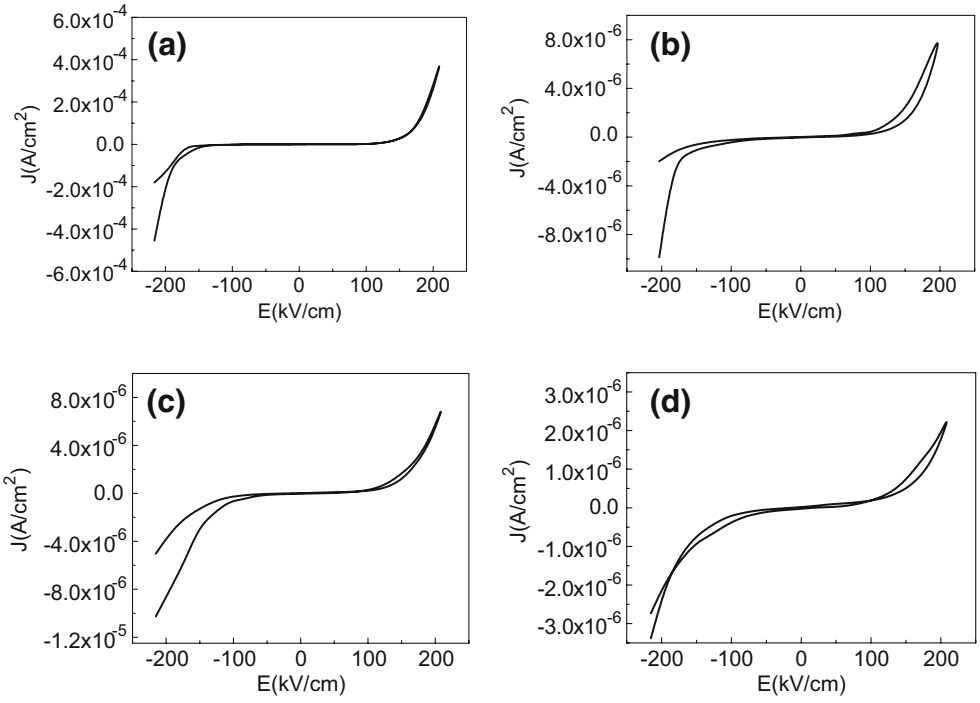

Fig. 5 Leakage current characteristics of the BST thin films with different Ca content (**a**) Ca 0 mol% (**b**) Ca 5 mol% (**c**) Ca 10 mol% (**d**) Ca 20 mol%

might be caused by generation of a different amount of oxygen vacancy at top Au/BST interface and at the bottom Pt/BST interface [16].

4 Conclusion

In this article, undoped and Ca-doped BST thin films were successfully fabricated by sol–gel technique on Pt/Ti/SiO_2/Si (100) substrates at an annealing temperature of 700 °C. The XRD patterns revealed that all films were polycrystalline and single phase. The FESEM images showed that the average grain size significantly decreased with the increase of the Ca content. The dielectric constant, dielectric loss, the tunability and the leakage-current density were found to decrease with increase in Ca content. The maximum value of the FOM=16.3 was found when the Ca content reached 2 mol%. Our results demonstrated that Ca dopant concentration had a strong influence on the microstructure and dielectric properties of the BST thin films. The improved dielectric properties such as dielectric loss and leakage current density of Ca-doped BST thin films suggested their suitability for tunable microwave applications.

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