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Ceramics International 35 (2009) 2761–2765
CERAMICS INTERNATIONAL
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# Dielectric properties of Fe-doped $Ba_{0.65}Sr_{0.35}TiO_3$ thin films fabricated by the sol–gel method

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Received 28 July 2008; received in revised form 29 January 2009; accepted 12 March 2009
Available online 15 April 2009

**Abstract**

Fe-doped $Ba_{0.65}Sr_{0.35}TiO_3$ (BST) thin films have been fabricated on Pt/Ti/$SiO_2$/Si substrate using the sol–gel method. The structural and surface morphology, dielectric, and leakage current properties of undoped and 1 mol% and 2 mol% Fe-doped BST thin films have been studied in detail. The results demonstrate that the Fe-doped BST films exhibit improved dielectric loss, tunability, and leakage current characteristics as compared to the undoped BST thin films. The improved figure of merit (FOM) of Fe-doped BST thin film suggests a strong potential for utilization in microwave tunable devices.


*Keywords:* Fe-doped BST thin film; Dielectric property; Tunability; Leakage current

## 1. Introduction

In recent years, the $Ba_{1-x}Sr_xTiO_3$ (BST) thin films are popularly used for applications in devices such as dynamic random access memories (DRAM) [1], thin-film capacitors [2] and ferroelectric microbolometers [3]. The properties of BST thin films are satisfactory for tunable devices: high dielectric constant, low dielectric loss factor (tan $\delta$), large-scale variations of the dielectric constant by direct current biasing field and low leakage-current density [4]. Because of the properties mentioned above, there are several previous works devoted to investigations of the capability of BST thin films for tunable microwave device applications [5–9]. However, according to the results of previous research [10,11], high tunability of BST thin films corresponds to the dielectric loss of around 0.03, which is too high for BST thin films to be of practical use in microwave tunable devices. Under DC biasing, the dielectric tunability $D$ is defined as [12]

$$D(E,T) = 1 - \frac{\varepsilon(E,T)}{\varepsilon(0,T)}$$

where the dielectric constant $\varepsilon(E,T)$ is a function of the field $E$ and temperature $T$.

It is a well-known fact that there are many effective ways to increase the tunability and lower the dielectric loss of BST thin films, including the use of donor/acceptor dopants. In the BST perovskite structure, the induced electrons derived from the oxygen vacancies can hop between different titanium ions, providing a mechanism to dielectric loss and leakage current [13]. To compensate for the oxygen vacancies, acceptor dopants that occupy the B site in the $ABO_3$ perovskite structure are used to reduce the dielectric loss and leakage-current density. In previous investigations, $Co^{3+}$, $Mn^{2+}$, $Ni^{2+}$, $Al^{3+}$, $In^{3+}$, $Cr^{3+}$, $Sc^{3+}$ [4], $La^{3+}$ [14] ions have been employed to improve the dielectric and insulating properties of BST thin films. Gong et al. [15] and Imai et al. [16] prepared Fe-doped BST thin films using the pulsed-laser deposition (PLD) method and investigated their dielectric tunability. The previous work does not provide enough information on improvement of the dielectric properties of the Fe-doped BST thin films. In this paper, we have investigated the effects of Fe dopants on the structure and dielectric properties of BST thin films by the sol–gel method.

## 2. Experimental procedure

Undoped and Fe-doped BST thin films were prepared using the sol–gel method. Barium acetate ($Ba(CH_3COO)_2$), strontium

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0272-8842/$36.00 
doi:10.1016/j.ceramint.2009.03.023

acetate ($Sr(CH_3COO)_2$), tetrabutyl titanate ($Ti(OC_4H_9)_4$), and ferric acetate basic $Fe(OH)(CH_3COO)_2$ were used as starting materials. Glacial acetic acid ($CH_3COOH$) and 2-methoxyethanol were used as solvents while acetylacetone (AcAc) was used as a chelating agent, respectively. All the above reagents were at analytic purity. Barium acetate, strontium acetate (the ratio of barium acetate and strontium acetate was 0.65:0.35) and ferric acetate basic (as a dopant precursor with concentrations of 1 and 2 mol%) were initially dissolved in heated acetic acid, and tetrabutyl titanate was added into the mixed solvent of 2-methoxyethanol and acetylacetone (AcAc). Both starting solutions were mixed to prepare the undoped and Fe-doped BST solutions. Finally, the solutions were refluxed in a reflux condenser at a temperature of about 80 °C for 4 h to obtain stoichiometric, transparent, and stable precursors. The viscosity of the solution was adjusted by adding 2-methoxyethanol. All the prepared precursors were syringed using a 0.2 μm syringe filter. The concentration of BST in precursor solutions is 0.1 M.

Prior to the coating procedure, the substrates were cleaned by adopting a standard chemical procedure. The sols were deposited by spin-coating technique at 5000 rpm for 20 s to form wet films. After the spin-coating procedure, the films were kept on a hot plate at 120 °C to remove volatile liquids, and then pyrolyzed at 400 °C for half an hour to form inorganic thin films. The above process was repeated to reach the desired thickness. The samples were then annealed at 650 °C for 60 min in $O_2$ atmosphere for crystallization, and the BST and Fe-doped thin films were thus obtained. The final thickness of both undoped and Fe-doped BST thin film was about 300 nm.

To determine the microstructure of the thin films, Ni-filtered Cu $K_\alpha$ radiation was performed by X-ray diffraction (Philips Xpert X-ray diffractometer). The surface morphology of the film was analyzed by atomic force microscope (AFM) (SPA–300HV). Dielectric measurements were carried out using the metal–insulator–metal (MIM) capacitor configuration. Au top electrode with a diameter of 0.5 mm was deposited by direct current sputtering. Capacitance–voltage characteristics, as well as dielectric constant and dielectric loss, were measured using a HP 4284A LCR meter.

## 3. Results and discussion

The crystalline structure of undoped and Fe-doped BST thin films at room temperature was determined by XRD. The results are shown in Fig. 1. The X-ray diffraction patterns for each sample annealed at 650 °C indicated that the (1 0 0), (1 1 0), (1 1 1), (2 0 0), (2 1 0), and (2 1 1) peaks corresponding to the BST perovskite phase were obtained in all films and these films were polycrystalline. The secondary phase, the pyrochlore phase, which causes the decrease of the dielectric constant and the increase in leakage-current density, is apparently absent in the XRD pattern. A further analysis of the XRD data showed that the lattice parameters of undoped, 1% Fe- and 2% Fe-doped BST thin films are 3.9862, 3.9812, and 3.9783 Å, respectively. The doped Fe element obviously accounts for the slight change in the lattices parameter of the BST thin film, which may be attributed to the ionic radius charge. Because the

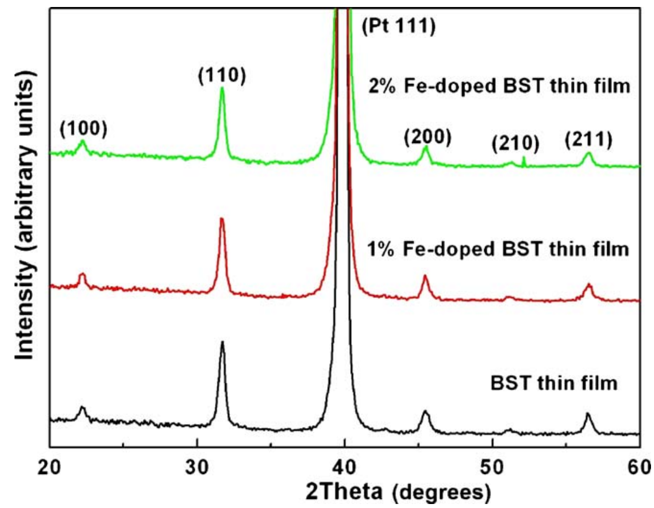


Fig. 1. XRD patterns of the undoped and Fe-doped BST thin films annealed at 650 °C.

ionic radii of $Ba^{2+}$, $Sr^{2+}$, $Ti^{4+}$, $Fe^{3+}$ are 1.34, 1.12, 0.68, and 0.64 Å, respectively, the slightly decreased lattice parameters imply that Fe ion is substituted onto the B site of the $ABO_3$-type perovskite BST materials. This phenomenon has also been reported in dielectric Fe-doped BST thin films prepared by the PLD technique as presented by Gong et al. [15].

The grain size and surface roughness are the key parameters determining the electrical properties of high dielectric thin film capacitor. The AFM images, shown in Fig. 2 (a: undoped BST; b: 1% Fe-doped BST; c: 2% Fe-doped BST), were obtained using an area of 5 μm × 5 μm, and the thin films were fully crystallized, smooth, dense, and crack-free on the selected area. This is important since the dielectric properties are dependent of the well-defined microstructure. From the AFM observation, it is suggested that the crystalline grain size depends on the doped amount of Fe dopant. The estimated average sizes of undoped, 1% Fe-doped and 2% Fe-doped BST thin films are 103, 85, and 77 nm, respectively. Such result runs similar with the results of previous research [17–19] that many dopants could cause the crystalline grain size of BST thin films to decrease drastically. In fact, the small grain size leads to a low dielectric constant [20]. The grain size and the root mean square roughness (RMSR) of the samples a–c estimated by AFM are 3.9, 3.2, and 1.5 nm, respectively. The large grain size tends to increase the RMSR, and Fe dopant causes the decrease of surface roughness of BST thin film, which facilitates the improvement of electrical properties. Fukuda et al. verified that rough surfaces cause the enhancement of the local electrical field and increase the leakage current of BST thin films [21].

The dielectric constant and dielectric loss of undoped and Fe-doped BST thin films as a function operating frequency, measured at room temperature, are shown in Figs. 3 and 4. The dielectric constant of all the three samples tend to decline (but the variation is not significant) and the dielectric losses tend to ascend with increasing frequency. At the same time, the increased Fe doping content causes the decrease of the dielectric constant and the dielectric loss factor. For example, at 10 kHz, the values of dielectric constant and dielectric loss of

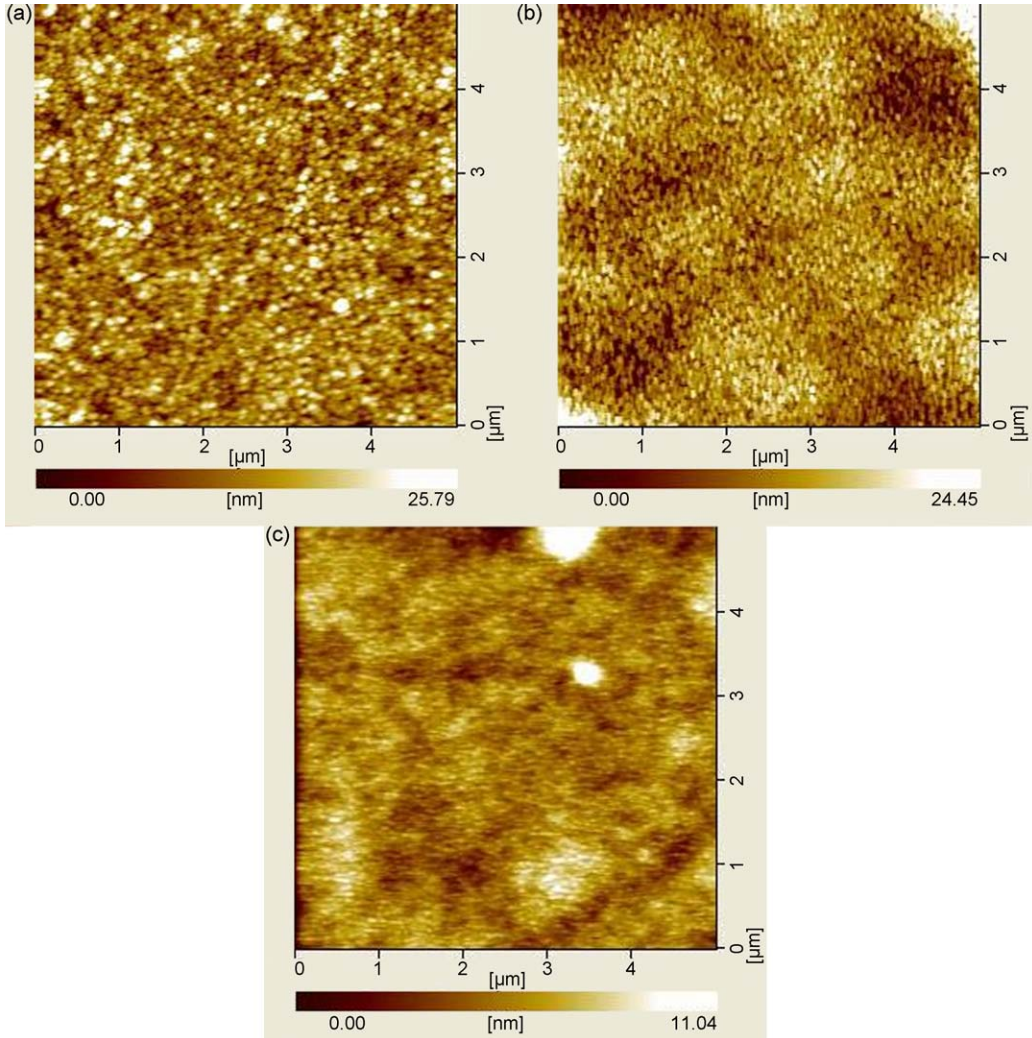


Fig. 2. AFM micrographs of the 650 °C annealed (a) undoped, (b) 1 mol%, (c) 2 mol% Fe-doped BST thin films.

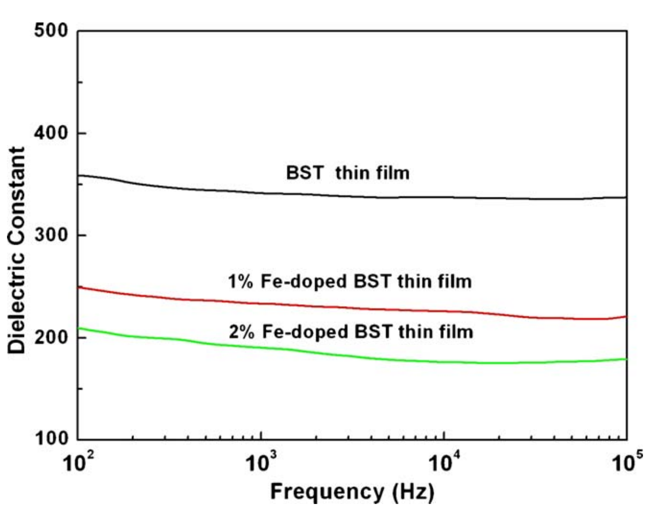


Fig. 3. Dielectric constant as a function of applied frequency for undoped and Fe-doped BST thin films.

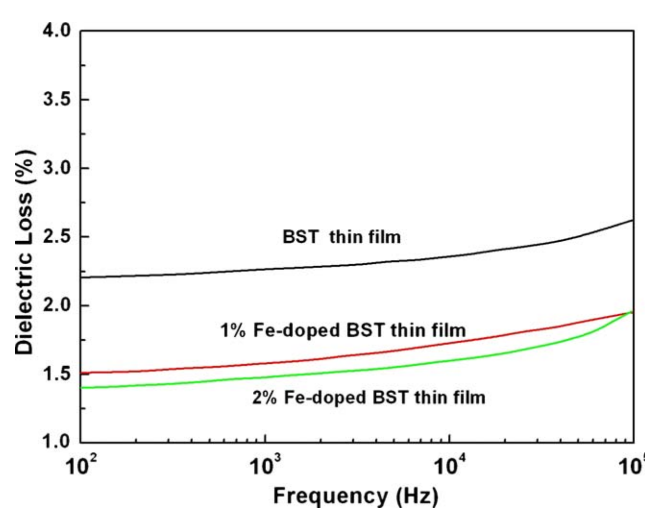


Fig. 4. Dielectric loss as a function of applied frequency for undoped and Fe-doped BST thin films.

three samples are 336, 226, 177 and 2.35, 1.72, 1.59%, respectively. The low values of dielectric constant of Fe-doped BST thin films are due to the fact that the crystalline size is visibly smaller that that of undoped BST thin film; this is known as the grain size effect [22,23]. In addition, the Fe dopant leads to a decrease in the dielectric loss factor, which improves the figure of merit of tunable devices. The figure of merit $K$ can be defined as

$$K = \left[\frac{\text{tunability}}{\tan\delta}\right]$$

According to the definition of the figure of merit, ferroelectric thin films with high tunability and low dielectric loss are required for tunable microwave applications (Fig. 5).

The dielectric loss generally comes from resistive loss and relaxation loss. The dielectric loss in resistive loss mechanism is mainly dominated by mobile charges in the film, such as oxygen vacancy [24]. The Fe dopants can pin the oxygen vacancies, which leads to the decrease in dielectric loss. The improvement of tunability of BST thin films can be achieved by adjusting the Ba/Sr ratio. However, the higher tunability of undoped BST thin films is also accompanied with higher dielectric loss and Curie temperature [25]. Furthermore, the excellent leakage current characteristic should also be considered in the production of tunable components and devices. The leakage current–voltage characteristics of the undoped and doped BST thin films are shown in Fig. 6. The leakage current of BST thin film is remarkably reduced upon addition of Fe dopant at each given electric field. The 2% Fe-doped BST film shows a slight reduction in leakage current density in comparison to the 1% Fe-doped BST film. Such result is consistent with previous investigations that many dopants significantly decrease the leakage current in a Pt/BST/Pt capacitor. Combined with Fig. 3, the tunability property of BST thin film is evidently worse than that of Fe-doped BST thin films despite the fact that the BST thin film possesses higher dielectric constant. For example, under the electric field of 400 kV/cm, the tunabilities of BST, 1% and 2%

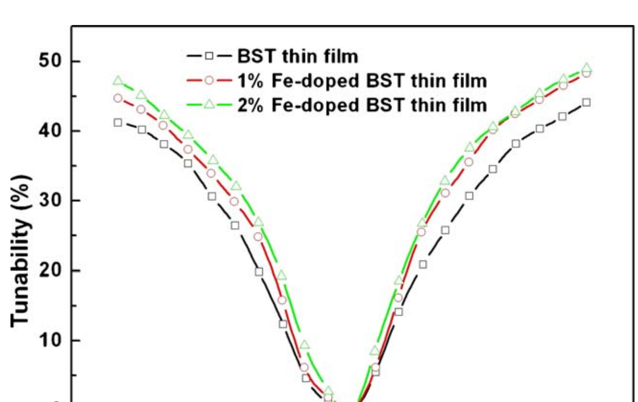


Fig. 5. Tunability of the undoped and Fe-doped BST thin films as a function of applied electric field.

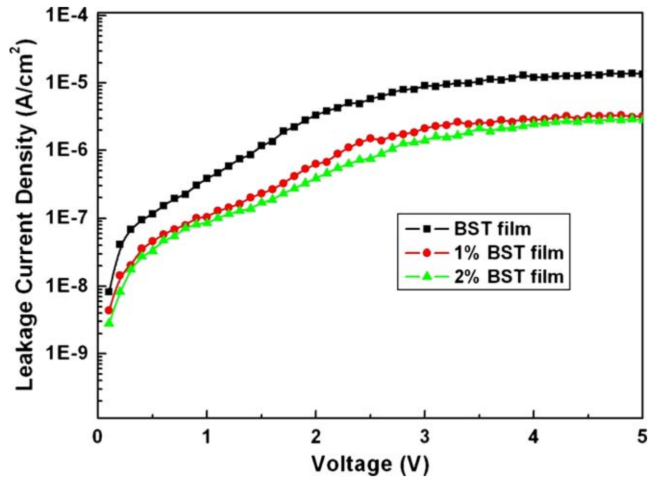


Fig. 6. Leakage current–voltage characteristics of the undoped and doped BST thin films.

Fe-doped BST thin films are 40.5, 44.6, and 45.5%, respectively. The introduced Fe dopant visibly improved the tunability property of BST thin films, by adding acceptor dopants to obtain high tunability; this is not, however, a novel idea, and previous references [26–28] have presented similar results for doped BST thin film. As a result, considering the tunability, dielectric loss, and leakage current, the Fe-doped BST thin films appear to be excellent potential candidates for tunable device applications.

The decreased leakage current density of Fe-doped BST films could be similar to that of Ce-doped BST films explained by Wang et al. [29]. The charge balance compensation mechanism when $Ti^{4+}$ is replaced by $Fe^{3+}$ is depicted in the following defect reaction equation:

$$BaO + Fe_2O_3 \rightarrow Ba_{Ba} + 2Fe'_{Ti} + 4O_O + V''_O$$

where $V''_O$ is an extrinsic oxygen vacancy controlled by the Fe content. The inherent oxygen vacancies are usually formed at the top electrode/BST interface, and acceptor $Fe^{3+}$ dopants prohibit the formation of charge carriers.

$$O_O \leftrightarrow V''_O + \frac{1}{2}O_2 + 2e'$$

where $O_O$ and $e'$ represent the oxygen ion on its normal site and free electron, respectively. In addition, the decreased leakage current also is dependent on grain size of the film, and this study refers to a previous similar work [14].

## 4. Conclusions

Using the sol–gel method, we have deposited undoped and Fe-doped BST films annealed at 650 °C on Pt/Ti/$SiO_2$/Si substrates and investigated the influence of Fe doping on the microstructure, surface morphologies, dielectric, tunability, and leakage current of the BST thin film. The investigation demonstrates that the Fe dopant had a noteworthy influence on the material properties of BST thin films. The Fe dopant leads to the decrease in grain size, dielectric constant, and dielectric loss of BST thin films and evidently improves the tunability and leakage current properties, which is suited for the improvement of FOM. These results suggest that the Fe-doped BST films are suitable for tunable microwave devices.

## Acknowledgements

This work was supported by the Science Foundation of the Fujian Province, China (Grant No. A0420001) and the Doctoral Foundation of Fuzhou University, China (Grant No. 826369).

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