

Structural and dielectric properties of Fe-substituted BST thin films grown by laser ablation

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Abstract

BST thin films are grown by pulsed laser deposition technique at different temperatures and different oxygen deposition pressures. X-ray diffraction studies confirm the perovskite phase of the films. From the ϵ' - V characteristic tunability is calculated and the films grown at lower oxygen deposition pressure is found have higher tunability which is explained in terms of stress developed in the film and oxygen vacancies formed during deposition. The ϵ' - V variation is explained in terms of Devonshire's phenomenological theory.

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1. Introduction

$\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST) is a nonlinear ferroelectric material whose dielectric properties are strongly dependent on the applied electric field. At room temperature BST can be brought in the paraelectric phase by substitution of appropriate amounts of Sr as the Curie point of the material can be controlled by varying the Sr content. In the paraelectric phase, hysteresis is very small and the dielectric properties can be tuned by an applied dc electric field. Because of these properties BST thin films are employed to develop tunable microwave devices such as voltage tunable phase shifters, capacitors, oscillators, filters, delay lines and parametric amplifiers [1,2]. By applying a dc electric field a change in the value of permittivity is produced which in turn can introduce a change in the propagation constant (phase change), and it can be tuned in real time for a particular application [3]. For the application of this material for tunable microwave devices the dielectric and insulating properties must satisfy some of the properties such as high tunability i.e. large variation of ϵ' with applied dc field, low loss tangent over the range of operating voltage, lower value of ϵ'' (<500) for better impedance

matching with the dielectric of air so as to have lower insertion loss in the device stage, low leakage current, single phase with dense microstructure and minimal defects, and surface morphology must be smooth and crack free. Various authors have reported that by using small concentration of acceptor ions such as 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 sites of the $(\text{A}^{2+}\text{B}^{4+}\text{O}_3^{2-})$ perovskite structure the loss of the BST material can be lowered [4–6]. In the present work we report on the structural, surface morphology and dielectric properties of the Fe-substituted BST thin films prepared by pulsed laser deposition (PLD).

2. Experiment

An Fe-substituted BST target of the composition $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{Fe}_{0.01}\text{Ti}_{0.99}\text{O}_3$ was made from the AR grade BaCO_3 , SrCO_3 and TiO_2 powders by solid-state reaction route reported elsewhere [7]. Thin films were deposited onto (1 1 1) oriented Pt/Ti/SiO₂/Si substrates by PLD. The output from a pulsed KrF excimer laser of wavelength 248 nm (LAMBDA PHYSIK, Compex 201) was focused onto the target with laser energy of 250 mJ and frequency of 7 Hz. Thin

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films were deposited by maintaining oxygen pressure in the deposition chamber at three different pressures of 100, 200 and 300 mTorr while the substrate temperature was fixed at 650 and 700 °C, respectively. The thickness of the films was about 0.5 μm.

Thin films were characterized for structural, surface morphological and dielectric properties. The structural characterization is done by X-ray diffraction (XRD) technique using Cu Kα-radiation (Phillips Model PW-3020). The surface morphology of the films were analyzed by atomic force microscopy (AFM, NT-MDT SOLVER P47H). The dielectric properties of the films were studied by making an MFM capacitor configuration (prepared by sputter coating 400 Å thick Au-dots on top of the surface of the films at room temperature through a shadow mask of area $\sim 1.96 \times 10^{-3} \text{ cm}^2$). The ϵ' - V characteristics of the films were measured by using a computer-controlled impedance analyzer (HP 4294A) at 100 kHz and an oscillating voltage of 100 mV.

3. Results and discussion

Fig. 1 shows the XRD patterns of the BST thin films deposited by PLD at different temperatures and pressures. It is observed that all the films crystallize in the perovskite structure and the orientation is in (1 1 1) direction, which shows that the orientation follows that of the substrate. Different conditions during the deposition do not seem to affect the structure of the films.

The AFM micrographs of a typical film grown at 300 mTorr and 700 °C are shown in Fig. 2. The films are found to be smooth and crack free. There is no significant difference in the microstructure of the different films and the grain size of films grown under different conditions seem to lie in the same range ($\sim 0.5 \mu\text{m}$).

The variation of dielectric constant (ϵ') and loss tangent ($\tan \delta$) with frequency of a typical film is shown in Fig. 3. A small frequency dispersion is observed for all the films. The variations of dielectric constant (ϵ') versus voltage (V) of the different films are shown in Fig. 4(a) and (b). From this variation it is observed that the value of dielectric constant (ϵ') decreases with the increase of applied dc field. This variation can be explained in terms of Devonshire's phenomenological theory [8–10]. According to his theory, in the perovskite cubic structure, Ti-ions oscillate in an unharmonic potential of the form $ar^2 + br^4$, where r is the position of the Ti-ion. In the case of a stress free ferroelectric subject to an electric field (E), Gibbs free energy (G) can be expanded in even powers of the polarization with coefficients, which are functions of temperature (T) only

$$G(T, P) = F(T, P) - EP \quad (1)$$

where F and P are the Helmholtz free energy (F) of a strain-free ferroelectric and polarization, respectively.

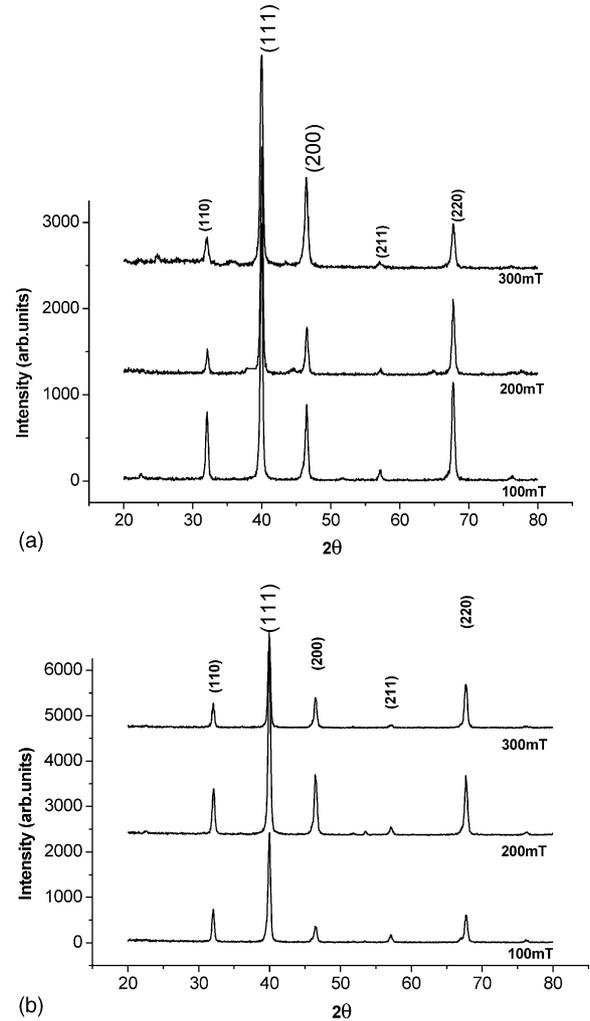


Fig. 1. XRD patterns for the $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{Fe}_{0.01}\text{Ti}_{0.99}\text{O}_3$ thin films deposited at substrate temperature (a) 650 °C and (b) 700 °C.

For a ferroelectric film subjected to stresses (X), the Helmholtz free energy can be expanded in terms of strain (x) as [11]

$$F(T, P, x) = F_0 + \left(\frac{1}{2}\right)\alpha P^2 + \left(\frac{1}{4}\right)\beta P^4 + \left(\frac{1}{6}\right)\gamma P^6 - PE + Cx^2 \quad (2)$$

where α , β , γ are the free energy expansion coefficients. But $\partial F/\partial P = 0$ for a stable state of the ferroelectric at a constant temperature. Then we get from Eq. (2) as

$$\alpha P + \beta P^3 - E = 0 \quad (\text{neglecting higher orders of } P) \quad (3)$$

$$\text{for small } P, E \approx \alpha P \quad (4)$$

$$\text{now } \frac{1}{\epsilon'} = \frac{\partial E}{\partial P} = \alpha + \beta P^2 \approx \alpha + 3\beta \left(\frac{E^2}{\alpha^2}\right) \quad (5)$$

The experimental plot of dielectric constant with the bias field fits well with Eq. (5), which explains the variation of dielectric constant with electric field.

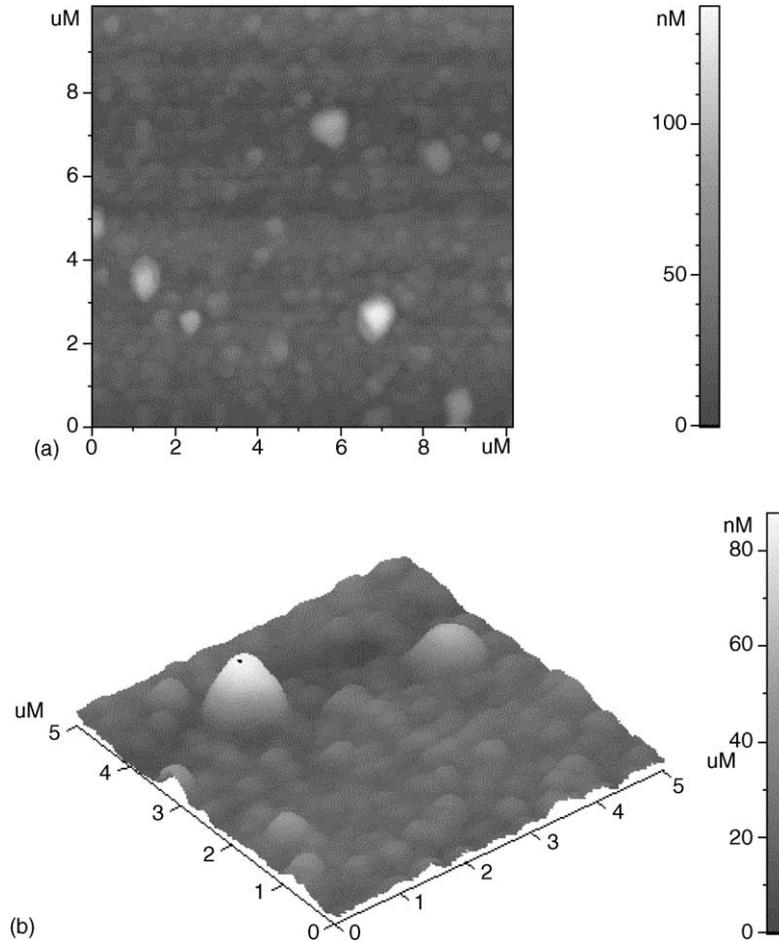


Fig. 2. AFM micrographs of a typical film deposited at 300 mTorr and 700 °C (a) 2D and (b) 3D view.

From the variation of dielectric constant with applied field, the value of tunability which is defined as

$$\text{tunability (\%)} = \frac{\varepsilon'_0 - \varepsilon'_{\max}}{\varepsilon'_0} \times 100\% \quad (6)$$

is determined for all the films. Table 1 summarizes the properties of dielectric data for the films.

From Table 1, a significant change is observed in the dielectric properties of the films deposited under different conditions although the structural and morphological properties remain almost the same. The films deposited at lower pressure for a particular substrate temperature is found to have higher value of dielectric constant and higher value of tunability. Various workers have reported the variation of dielectric constant of BST system as a function of composition [12,13], crystallinity [14,15], grain size [16–18] and stress [19]. As there is no significant difference observed on the crystallinity, grain size and surface morphology for the present films, the observed variation of the dielectric properties of the films may be attributed to the film stress. It might also be possible that the dielectric properties are dependent on the oxy-

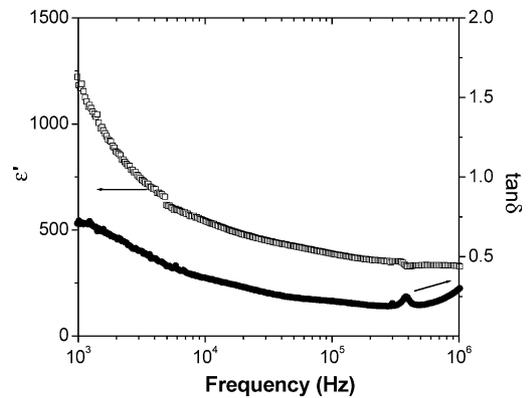


Fig. 3. Variation of dielectric constant (ε') with frequency for the films deposited at different substrate temperatures and oxygen pressures 700 °C and 200 mTorr.

gen background pressure and substrate temperature. Both of the aforementioned can be responsible for the generation of oxygen vacancies or the lack of them. With a change in the oxygen pressure during deposition, a change in the oxygen vacancy concentration is introduced; the oxygen vacancies

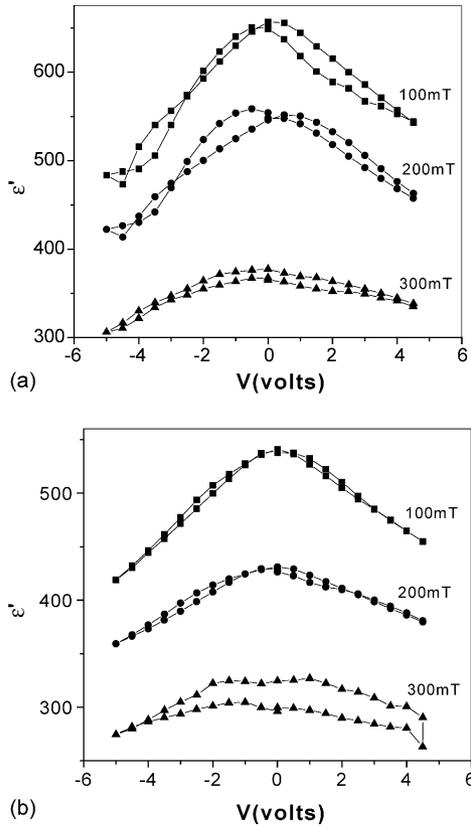
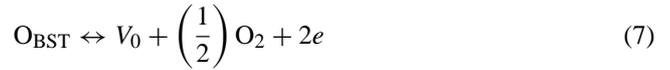


Fig. 4. Variation of dielectric constant (ϵ') vs. voltage (V) of the films deposited at substrate temperature (a) 650 °C and (b) 700 °C at different oxygen deposition pressures.

may increase, decrease, or screen the overall film stress. Different amount of stresses are produced in these films because of the lattice mismatch and thermal expansion between BST films and Pt/Si substrates. The stress was found to be lower for the films deposited at lower oxygen pressure [20].

The dielectric properties are affected by the presence of moisture, complexity of the grain boundaries, grain size, orientation and ionic space charge carriers like oxygen vacancies and other ionic defects generated during film growth. During deposition at a particular temperature (T), we can assume that the oxygen atoms in the chamber and in the BST film are in equilibrium. The oxygen vacancies act as donors in BST films and so oxygen vacancies (V_0) formed in the film can be

expressed in terms of oxygen atoms in BST (O_{BST}) as



From simple mass-action equation, the oxygen concentration can be expressed as

$$[V_0][e]^2 \propto \exp\left(\frac{-\Delta H}{kT}\right) P^{-1/2} \quad (8)$$

where $[V_0]$ is the concentration of oxygen vacancies in the BST matrix, P is the pressure of oxygen in the chamber and ΔH is enthalpy for generating oxygen vacancies. The number of oxygen vacancies in the BST matrix is quite small, so $[O_{\text{BST}}]$ is constant and $[V_0]$ is $(1/2)[e]$, the concentration of oxygen vacancies at any temperature T is

$$[V_0] \propto P^{-1/6} \quad (9)$$

Thus the films deposited at lower oxygen pressure are expected to have higher concentration of oxygen vacancies. When the number of oxygen vacancies increase, there is an increase in the total polarization because of the increase of number of defect dipoles and ionic polarization [20]. So the films deposited at lower oxygen pressure have higher dielectric constant, higher tunability and lower loss. However, films deposited at oxygen pressures below 100 mTorr showed much higher losses probably on account of increased conductivity arising due to the presence of oxygen vacancies and hence exhibiting a net reduction in dielectric properties. Although the tunability in the films was reasonable high, the dielectric needs to be reduced and further work is being done specially to address this issue.

4. Conclusions

The value of the dielectric constant (ϵ') and tunability of the BST thin films fabricated at lowest oxygen deposition pressures are found to be highest at both the substrate temperatures of 700 and 650 °C. This observed variation is explained in terms of the lower stress and higher oxygen vacancy concentration for the films deposited at lower oxygen deposition pressure. When the oxygen vacancy concentration is higher the polarization is higher because of the increase number of defect dipoles.

Table 1
Dielectric data of the films

Substrate temperature (°C)	Oxygen pressure (mTorr)	ϵ'	$\tan \delta$	Tunability (%)
650	300	365	0.567	16
650	200	548	0.252	22
650	100	649	0.3	27
700	300	300	0.38	9
700	200	426	0.207	15
700	100	538	0.238	22

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