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Dielectric tunability of barium strontium titanate films prepared by a sol–gel method

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Abstract

The electric field tuning property of the 100-kHz dielectric constant of $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) thin films deposited on Pt/Ti/SiO_2/Si substrates by a hydroxide–alkoxide-based sol–gel method was investigated by varying the annealing temperature, the thickness and the precursor solution concentration. The tunability and dielectric constant of the BST thin films increased with increasing annealing temperature, indicating the dependence of the tunability on parameters of the film quality, such as crystallinity and grain size. A ~235-nm film annealed at 700 °C showed tunability of approximately 48%. Variation of the precursor solution concentration resulted in a different microstructure, which in turn affected the tunability of the film. The dielectric tunability of the film showed a small increase as the film thickness increased; in contrast, the figure of merit decreased because of the increase in dielectric loss. Experimental results showed that increases in dielectric constant and tunability are always associated with larger dielectric loss, which effectively decrease the figure of merit. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Barium strontium titanate; Dielectric properties; Electrical properties and measurement

1. Introduction

Barium strontium titanate, $Ba_{1-x}Sr_xTiO_3$ (BST), is a continuous solid solution of ferroelectric $BaTiO_3$ and paraelectric $SrTiO_3$. As a result, the Curie temperature of the BST linearly decreases with increasing Sr concentration. The transition temperature, and hence the properties of BST, can be tailored by changing the composition according to the requirement of the electronic device under consideration. This property of BST thin films, along with the high dielectric constant, makes it suitable for many microelectronic applications. The majority of research on BST thin films has been directed to study their feasibility in thin-film integrated storage capacitors in gigabit dynamic random-access memory (DRAM). This is mainly due to their high dielectric constant, low dielectric loss, low leakage current, low temperature coefficient for the dielectric constant and the composition-dependent Curie temperature [1]. In addition to DRAM applications, BST thin films have been identified for a variety of other applications that are currently being studied, such as hydrogen gas sensors [2], pyroelectric sensors [3,4] and as a dielectric layer in electroluminescent display devices [5,6]. Recently, the non-linear dielectric property of BST thin films has been investigated for the development of high-performance microwave tunable devices, which include phase shifters, tunable filters, steerable antennas, varacters and frequency triplers [7–17]. In these devices, it is desirable to have a large change in dielectric constant under a certain electric field, accompanied by a small dielectric loss. Thin films of tunable, non-linear dielectric materials offer the advantages of lower processing temperature, compactness, lower operating voltages and compatibility with silicon processing technology [17]. The critical properties that need to be optimized are the magnitude of the change in dielectric constant as a function of applied electric field, and the dielectric loss at microwave frequencies [7]. The dependence of the tunability of BST on composition, processing parameters and the thin-film stress state have been studied by various

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authors [7–17] at different frequencies by employing thin films prepared from various methods, such as DC magnetron RF sputtering, laser ablation and chemical solution deposition on various substrates, most often on low-loss $LaAlO_3$ or MgO.

In the present study, we investigated the annealing temperature, the thickness and the precursor solution concentration dependence of the dielectric tunability of $Ba_{0.5}Sr_{0.5}TiO_3$ thin films in the parallel capacitor geometry fabricated by a sol–gel method. We observed a strong dependence of tunability on process parameters, such as annealing temperature, film thickness and the microstructure of the thin film.

2. Experimental

$Ba_{0.5}Sr_{0.5}TiO_3$ thin films were prepared following a procedure similar to the method used by Burhanuddin et al. [18]. A multi-component BST precursor solution was prepared using high-purity $Ba(OH)_2 \cdot 8H_2O$, $Sr(OH)_2 \cdot 8H_2O$ and titanium (IV) isopropoxide $[Ti(OC_3H_7)_4]$ as the starting materials and 2-methoxy ethanol as the solvent. The required amounts of barium and strontium hydroxides were separately mixed in 2-methoxy ethanol and refluxed at 120 °C for 3–4 h. Similarly, a stoichiometric amount of titanium isopropoxide was mixed with 2-methoxy ethanol separately and refluxed at 120 °C for 3 h. These three solutions were mixed after cooling to room temperature and refluxed at 120 °C for 3 h to form a homogeneous mixture of BST complex precursor, and then concentrated by solvent evaporation to form the stock solution. Thin films of approximately the same thickness were prepared by spin coating using three different concentration solutions of 0.28 M, 0.15 M and 0.08 M after appropriate dilution using 2-methoxy ethanol. The solution was syringed through a 0.2-μm filter onto Pt/Ti/SiO_2/Si substrates. Each layer was spin-coated at 5000 rev./min for 30 s. As-deposited films were then dried in oven at 140 °C for solvent evaporation for 10 min, followed by pyrolysis at 500 °C for 30 min. After obtaining the required thickness, films were post-annealed at different temperatures in the range of 500–800 °C. Substrates were prepared by depositing 1000 Å of Pt by DC sputtering over a 1000-Å Ti buffer layer on a Si wafer with a 932-Å thermal SiO_2 barrier layer.

The crystallinity of the films was probed by X-ray diffraction (XRD; Shimadzu XD-5) using a Ni-filtered CuK_α radiation source. Samples for XRD were prepared using a piece of substrate (2×2 cm^2) spin-coated at 5000 rev./min and the uniform area was cut into several pieces. The thickness and microstructure of these films were measured with a Hitachi S4700 scanning electron microscope (SEM). The thickness was found to be uniform (230 ± 22 nm). Films of identical thickness were chosen from the above pieces and annealed at different temperatures for an identical duration to study the annealing temperature dependence of the XRD pattern. Different films of the same thickness were chosen to avoid repetitive heat treatment of the same film several times, which might also result in increased crystallinity. For the electrical characterization, a metal–insulator–metal (MIM) type of structure was formed by depositing a 100-nm-thick top Pt electrode with diameters of 150, 250 and 350 μm by DC sputtering through a shadow mask. The capacitance–voltage (C–V) characteristics were measured using a Hewlett Packard (HP) 4194A impedance/gain phase analyzer at 100 kHz as a function of sweeping voltage from positive- to negative-voltage DC bias. The dielectric constant of the films was calculated using values measured for the capacitance, thickness and electrode area.

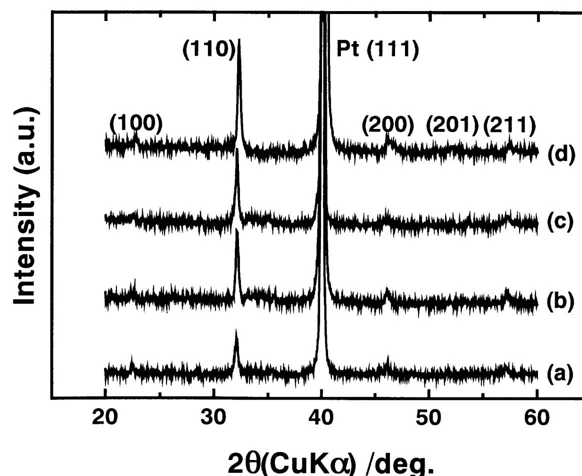

Fig. 1. XRD patterns of the $Ba_{0.5}Sr_{0.5}TiO_3$ thin films annealed at different temperature: (a) 500; (b) 600; (c) 700; and (d) 800 °C.

3. Results and discussion

Fig. 1 shows the XRD patterns of the films post-annealed at different temperatures, which indicate that reasonably well-crystallized film is obtained at a temperature as low as 500 °C. The XRD pattern shows all major peaks corresponding to perovskite BST phase, indicating the polycrystalline nature of the film, with (110) as the major peak. The intensity of the (110) peak increased with annealing temperature because of the improvement in crystallinity. The average grain size was calculated by using the full width at half-maximum of the dominant (110) peak following Scherrer's equation [19]. The 500 °C annealed sample showed an average grain size of 20 nm, which increased to 32 nm on annealing above 600 °C. The grain size of the films increased with increasing annealing temperature, as expected, because of the sintering, wherein small grains coalesce to form larger grains.

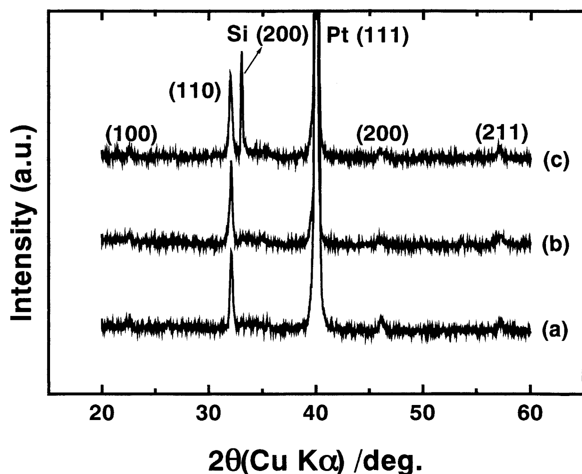

Fig. 2. XRD patterns of the $Ba_{0.5}Sr_{0.5}TiO_3$ thin films prepared using: (a) 0.08 M; (b) 0.15 M; and (c) 0.28 M precursor solutions and annealed at 700 °C for 2 h.

Similarly, XRD patterns were obtained for the films prepared from different concentrations of solution (0.08 M, 0.15 M and 0.28 M) (Fig. 2) onto platinized Si wafer; these showed only diffraction signals corresponding to BST. The average grain size calculated was approximately 32 nm.

The dielectric properties of the BST films were measured at room temperature. The maximum dielectric constant and loss are listed in Table 1, which show an increase in the dielectric constant of the film with increasing annealing temperature. The 800 °C annealed film shows a maximum dielectric constant of approximately 650; that of the film annealed at 500 °C is the lowest, approximately 350 at zero bias. Dielectric loss is maximum for film annealed at 500 °C (0.14 at zero bias). The lowest loss is observed for the BST films annealed at 600 and 700 °C (~0.03). Increase in the annealing temperature to 800 °C elevated the loss tangent to a higher value (~0.06 at zero bias) than for the film annealed at 600/700 °C. However, the loss is much lower than for the film annealed at 500 °C.

The larger dielectric constant of the films annealed at higher temperature is due to the increase in grain size and crystallinity of the thin film. XRD patterns showed that, as the annealing temperature increased, the crystallinity improved and the grain size increased. The improvement in crystallinity and grain size in turn increases the dipole density, which is responsible for the increased dielectric constant.

The dielectric loss originates from two mechanisms: resistive loss and relaxation loss [20]. In the resistive loss mechanism, energy is consumed by mobile charges in the film. In the case of the relaxation loss mechanism, it is relaxation of the dipoles that dissipates the energy. If there are very few mobile charges in the film, then the latter mechanism dominates. The resistive loss mechanism is directly connected to the leakage current of the film: if the leakage current is higher, the loss is also higher. Alternatively, if the dielectric constant of the film is higher, then an increase in the dielectric loss is obvious, due to the contribution from the second mechanism. Enhanced polarization increases the energy dissipation during relaxation.

Table 1
Effect of annealing temperature on the dielectric, tunability and figure of merit (K) of $Ba_{0.5}Sr_{0.5}TiO_3$ thin films

Annealing temperature (°C)	ε_r (max)	tanδ	Tunability (%) at 200 kV/cm, 100 kHz	K
500	350	0.14	17	1.2
600	481	0.03	38	12.7
700	550	0.03	48	16.0
800	650	0.06	49	8.2

The large dielectric loss, despite a small dielectric constant, for the 500 °C annealed film arises from the resistive loss mechanism, as indicated by the large leakage current (9.5×10^{-6} A/cm^2) in comparison to the films annealed at higher temperatures. The leakage behavior of this film might be because of the presence of an impurity phase in the form of embedded amorphous decomposition products, which require a higher temperature to burn off. The lowest leakage current (1.3×10^{-6} A/cm^2 at 100 kV/cm) was observed for the films annealed at 600 and 700 °C, and hence these films show lower dielectric loss. The increase in the dielectric loss of the 800 °C annealed film is a combined effect of the two mechanisms, as indicated by the slight increase in leakage current (2.6×10^{-6} A/cm^2 at 100 kV/cm) and due to the increase in dielectric constant. An increase in dipole density increases the loss due to dipole relaxation.

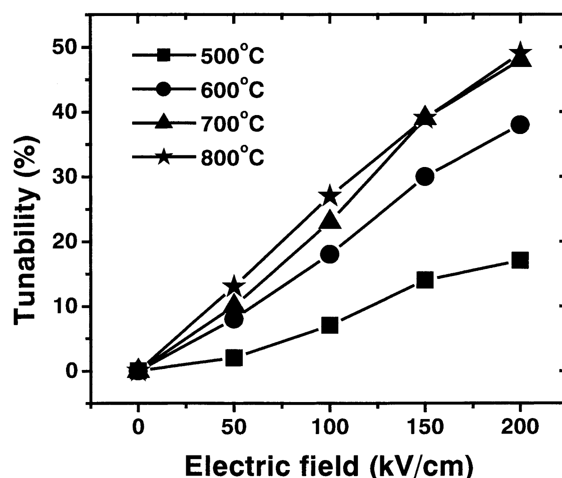

Fig. 3. Variation of the tunability as a function of applied electric field for the BST thin films annealed at different temperatures.

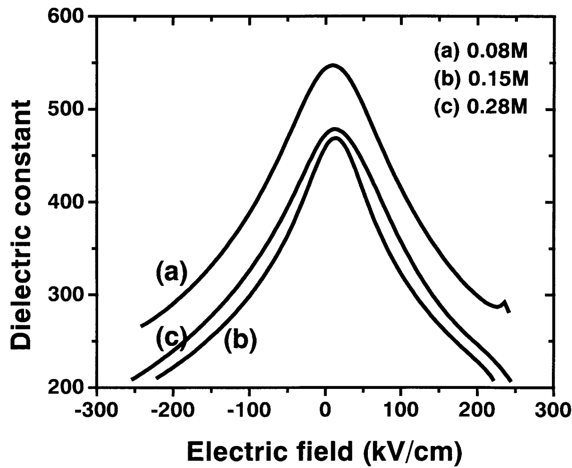

Fig. 4. Variation of the dielectric constant with applied electric field for the BST thin films prepared using precursor solutions of three different concentrations and annealed at 700 °C for 2 h in air.

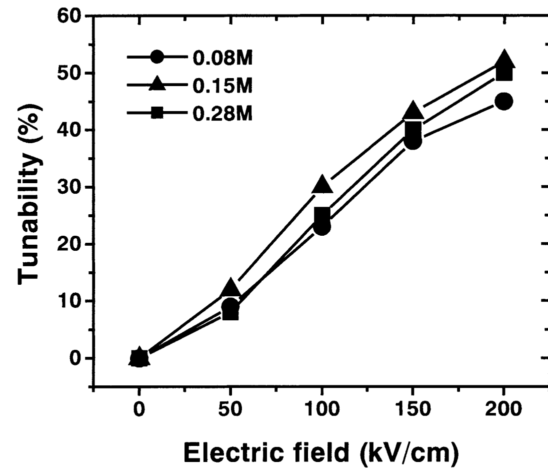

Fig. 5. Variation of the tunability as a function of applied electric field for the BST thin films prepared from different concentration precursor solutions and annealed at 700 °C for 2 h.

Fig. 3 shows the dielectric constant tunability [$=(\varepsilon_{r(max)}-\varepsilon_r)/\varepsilon_{r(max)}$] of the films annealed at different temperatures as a function of applied field. The tunability increased with increasing annealing temperature and applied electric field. The figure indicates that the tunability of the 500 °C annealed film is poor (17% at 200 kV/cm); this increased on annealing at 600 °C to 38% and increased further on annealing at higher temperatures (Table 1). Maximum tunability is observed for the sample annealed at 800 °C, although the magnitude of the difference in tunability between the 700 and 800 °C annealed sample is marginal. The figure of merit (K=tunability/loss, Table 1) is large for the sample annealed at 700 °C because of the low loss and moderately large tunability. The data listed in the table indicate that, as the annealing temperature increased, the dielectric constant, tunability and dielectric loss increased. Even though maximum tunability of 49% is observed for the film annealed at 800 °C, because of the larger dielectric constant, the figure of merit remained low by virtue of the higher loss compared to the 700 °C annealed film. Dielectric loss of the 800 °C annealed film is approximately double of the 700 °C annealed film. Hence, the figure of merit for the former reduced to half of that for the latter. The lower figure of merit for the films annealed at low temperature is because of the low magnitude of the change in dielectric constant (tunability), accompanied by a larger dielectric loss in the case of the 500 °C annealed film.

Table 2
Effect of precursor solution concentration on the dielectric, tunability and figure of merit (K) of $Ba_{0.5}Sr_{0.5}TiO_3$ thin films

Precursor solution concentration (M)	ε_r (max)	tanδ	Tunability (%) at 200 kV/cm, 100 kHz	K
0.08	550	0.03	45	15.0
0.15	468	0.03	52	17.3
0.28	480	0.04	50	12.5

The dependence of the tunability of BST films on annealing temperature originates from quality parameters of the thin films, such as crystallinity and grain size. Correlating the XRD results and the tunability of the films, we suggest that as the film crystallinity increases, the tunability increases. However, the increase in tunability alone does not decide the feasibility of the film for device application. The parameter of importance for device application is the figure of merit, which depends upon dielectric loss. Hence, moderate tunability and low loss are the key factors. Low dielectric loss is critical for voltage-tunable devices to achieve low insertion loss [7].

The precursor solution concentration dependence of the dielectric constant, dielectric loss, tunability and figure of merit was studied by depositing films of approximately the same thickness (~320 nm) using different concentrations of precursor solution, followed by post-deposition annealing at 700 °C for 2 h. The results indicate that the dielectric constant and loss tangent varied with the precursor solution concentration. Fig. 4 shows the variation of the dielectric constant with electric field for these films. The dielectric constant of the film prepared from the dilute solution (0.08 M) is larger than that of films prepared from 0.15 M and 0.28 M solutions. At zero bias, the dielectric constant of the BST film prepared from 0.08 M solution is approximately 550, whereas the values for 0.15 M and 0.28 M solutions are approximately 468 and 480, respectively (Table 2). Films prepared from both 0.15 M and 0.28 M solutions showed almost similar variation in dielectric constant and loss tangent with the bias DC field.

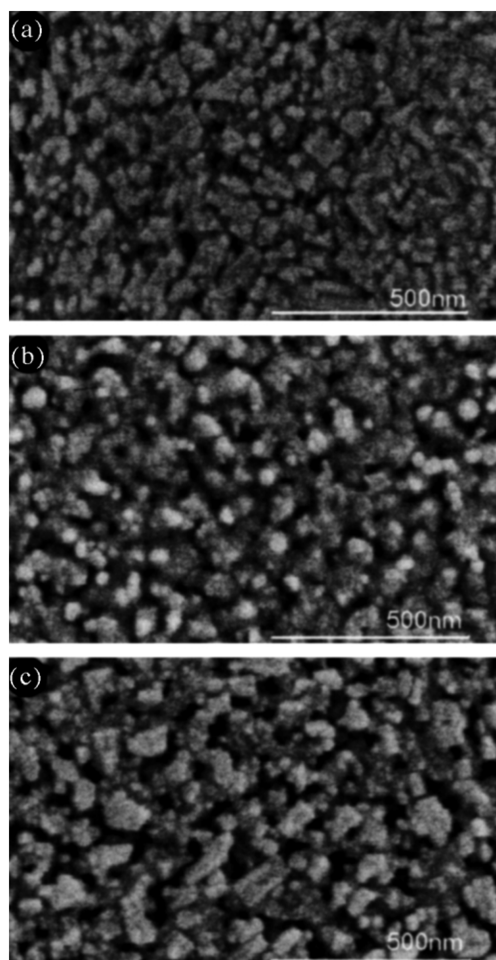

Fig. 6. SEM micrographs of the BST thin films prepared from: (a) 0.08 M; (b) 0.15 M; and (c) 0.28 M precursor solutions and annealed at 700 °C for 2 h in air.

The tunability variation of the above films with applied electric field is plotted in Fig. 5. The films show small change in the tunability. Highest tunability is observed for the sample prepared from 0.15 M solution and the lowest is observed for the 0.08 M solution. The important observation is that, even though the film prepared from the 0.08 M precursor solution has a higher dielectric constant, the magnitude of the change in dielectric constant is lower, resulting in the lower tunability for this film. On the other hand, the film prepared from 0.15 M solution has a lower dielectric constant among these films, but higher tunability, and hence a larger figure of merit. The dielectric loss is larger for the film prepared from 0.28 M solution and the figure of merit is lowest.

The difference in the properties of films prepared from three different concentrations of precursor solution can be explained on the basis of microstructure. Fig. 6 shows SEM micrographs of the films prepared from different concentrations and annealed at the same temperature (700 °C for 2 h), which showed a distinctly different microstructure. The film prepared from 0.08 M solution shows irregular-shaped grains of 40–70 nm in size, whereas the films prepared from 0.15 M solution show agglomerated spherical grains in the same size range and those of the 0.28 M solution shows more plate-like, elongated grains. The remarkable difference between these films is in the grain morphology and the porosity. The film prepared from 0.08 M precursor solution is less porous and the film prepared from 0.28 M solution is highly porous. These results indicate that as the solution concentration increases, the porosity in the film also increases. This affects the dielectric and electrical properties of the film. The lower porosity in the film deposited using dilute solution is due to the fact that each thin layer is individually pyrolysed and thermally cycled more times than the film prepared from the concentrated solution, which requires a lower number of layers to attain the same thickness. The individual layers are thicker than the film prepared from the dilute solution and leave behind more carbonaceous decomposition products after pyrolysis. On annealing at 700 °C, these embedded impurities burn off, leaving behind pores in the film. Films prepared from three different concentrations of precursor solution differed in their microstructure, in particular in porosity and morphology. The film prepared from the dilute solution showed lower porosity than the films from more concentrated solutions. This reduced porosity increases the polarization density, thereby increasing the dielectric constant. The above results indicate that the microstructure plays an important role in determining the voltage tunability of the thin films. The microstructure can be tailored by changing the precursor solution concentration.

The variation of the dielectric constant and loss with the thickness of the film is plotted in Fig. 7. As the film

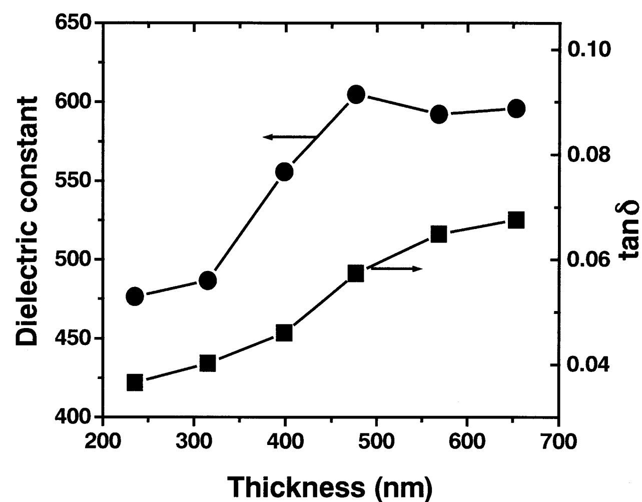

Fig. 7. Variation of 100-kHz dielectric constant and loss tangent of the BST thin film prepared from 0.28 M solution as a function of thickness.

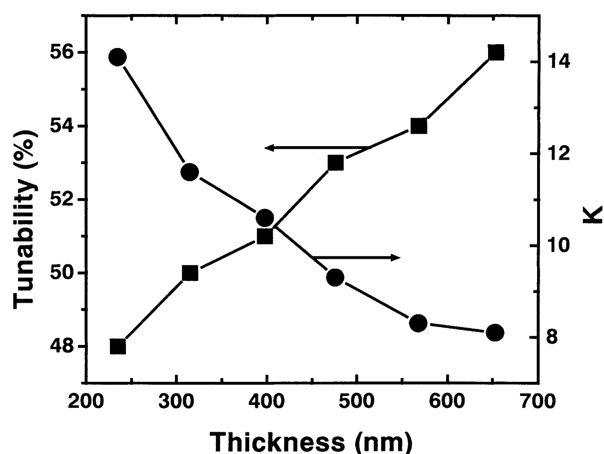

Fig. 8. Variation of tunability and figure of merit with film thickness for $Ba_{0.5}Sr_{0.5}TiO_3$ thin films.

thickness increases, the dielectric constant also increases and saturates above a thickness of 500 nm. The increase in dielectric constant with film thickness is due to the increase in grain size, film crystallinity and film density. In the sol–gel method of preparation, as the number of layers increases, the film porosity decreases because subsequent layers coated on the first pyrolysed layer cover up the pores and bulk defects left behind by the burn-off of organic material. The saturation in dielectric constant above a certain thickness might be due to the limitation in grain size that can be achieved by this method of preparation. Similar to the dielectric constant, the loss tangent also increased with increasing film thickness. The increase in loss tangent is due to the increased dipole relaxational loss because of the larger dipole density, which is also a reason for the increased dielectric constant.

The tunability and figure of merit of the film also showed variation with the thickness (Fig. 8). Tunability varies similarly to the dielectric constant, increasing with an increase in film thickness. On the contrary, the figure of merit decreases with increasing film thickness. The reason for this decrease can be derived from Fig. 7, which shows an increase in the dielectric loss with the increase in film thickness. The figure of merit and the dielectric loss have an inverse relation.

4. Conclusions

This study highlights the effect of film processing parameters, and in turn the film crystallinity and microstructure, on the dielectric tunability and the figure of merit. The tunability of the film increases with increasing crystallinity, grain size and film thickness. However, the increase in tunability also leads to an increase in the dielectric loss, thereby decreasing the figure of merit, a parameter of importance for use of the material in device fabrication. Hence, it is essential to have optimum dielectric constant tunability and low dielectric loss. The study also indicated that the dielectric tunability property of BST thin films can be varied by changing the microstructure, which in turn can be tailored by changing the precursor solution concentration at a given annealing temperature.

Acknowledgments

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