Novel tunable acceptor doped BST thin films for high quality tunable microwave devices

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The materials properties of undoped and low concentration Mg doped Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ (BST) thin films are reported. The films were fabricated on single crystal (100) MgO and Pt coated Si substrates via the metalorganic solution deposition (MOSD) technique using carboxylate-alkoxide precursors and post-deposition annealed at 800°C (film/MgO substrates) and 750°C (film/Pt-Si substrates). The dielectric properties were measured at 10 GHz using unpatterned/non-metallized films via a tuned coupled/split dielectric resonator system and at 100 kHz using metal-insulator-metal capacitors. The structure, microstructure, surface morphology and film/substrate compositional quality were analyzed and correlated to the films dielectric and insulating properties. The Mg doped BST films exhibited improved dielectric loss and insulating characteristics compared to the undoped BST thin films. The improved dielectric properties, low leakage current, and good tunability of the low level Mg doped BST thin films merits strong potential for utilization in microwave tunable devices.

Keywords: Tunable microwave devices; thin films; microstructure.

1. Introduction
Thin film barium strontium titanate (BST) shows great promise as a candidate material for the fabrication of RF and microwave components, such as voltage-controlled oscillators, tunable filters, and phase shifters [1,2]. Practical realization of such tunable devices at microwave frequency requires that the paraelectric BST-based thin film possesses low microwave loss, high tunability, and good insulating properties. To date, thin film BST that simultaneously possesses both low loss and a large tunability as required for many microwave applications has not been realized. It is well documented that small concentrations of acceptor dopants can dramatically modify the material properties, that is, lower the dielectric loss of ferroelectric/paraelectric materials such as BST [1-3]. In previous studies we have investigated the effect of various acceptor dopants on the dielectric and insulating properties of BST thin films at frequencies between 10 kHz and 1 MHz and found a significant reduction of the loss tangent, enhanced film resistivity, and good dielectric tunability characteristics for acceptor doped BST thin films [3,4]. In this paper we report the microwave dielectric properties of pure and low-level Mg doped BST films prepared via the metalorganic solution deposition (MOSD) technique. The structural, microstructural, surface morphological, and film-substrate interfacial properties were characterized and correlated with the microwave dielectric and insulating properties in order to define the trade-offs between film structure, composition, dielectric loss, tunability and insulating characteristics for tunable device applications.

2. Experimental
Pure and 1 mol% Mg doped Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ thin films were fabricated by the metalorganic solution deposition (MOSD) technique. Figure 1 shows the basic steps for fabrication of pure and Mg doped thin films by the MOSD technique. In the fabrication method, barium acetate, strontium acetate, and magnesium acetate were initially dissolved in acetic acid, then mixed together to form a clear homogenous stable solution. 2-methoxyethanol was added to adjust the viscosity and surface tension of the solution. Magnesium acetate, the dopant precursor, and Ti were added to adjust the viscosity and surface tension of the solution. Magnesium acetate, the dopant precursor, and Ti
isopropoxide were the final precursors added to the solution. The precursor films were deposited on Pt-coated silicon and (100) single crystal MgO substrates by a multiplayer spin-coating approach. Particulates were removed from the solution by filtering through 0.2 µm syringe filters. Subsequent to each coating, the films were pyrolyzed at 350°C for 10 min in order to evaporate solvents and organic addenda and form an inorganic amorphous film. The spin-coating process was repeated until a nominal film thickness of 165 nm was achieved. Crystalline films were achieved via post-deposition furnace annealing in an oxygen ambience for 60 min. at 750°C and 800°C, for the films deposited on the Pt-silicon and MgO substrates, respectively.

The films were characterized for dielectric, insulating, structural, compositional, and surface morphological properties. The dielectric properties, of the post-deposition annealed films were characterized utilizing both microwave and low frequency measurement techniques. The microwave dielectric properties were measured at 10 GHz using unpatterned (no metal electrodes) undoped and Mg doped BST thin films grown on MgO substrates via a tuned coupled/split dielectric resonator system. Figure 2 displays a schematic diagram of the split dielectric resonator system. This measurement technique is noncontacting and nondestructive. The measurement process is a two phase: First the permittivity and dielectric loss of the MgO substrate is determined and then the permittivity and dielectric loss of the thin film is determined by the differences in resonant frequencies and Q-factors of the MgO substrate and the MgO substrate + thin film. The microwave measurement frequency is determined by the geometry and permittivity of high Q, temperature-stable dielectric resonators. In this method the electric field is tangential to the plane of the sample. Numerical methods are used to analyze these measured data. The measurement capabilities of this technique are currently from 1 – 30 GHz and the uncertainty in permittivity is approximately twice the uncertainty in the thickness of the film. The low frequency (100 kHz) dielectric and insulating measurements were conducted on the undoped and Mg-doped BST thin films deposited on Pt-Si substrates in the metal-insulator-metal (MIM) capacitor configuration. MIM capacitors were formed by sputter depositing 0.2 mm Pt dots with 0.5 mm spacings, through a shadow mask covering a 1 × 1 cm² area. The film capacitance (Cp) and dissipation factor (tan δ) were measured with an HP 4194A impedance/gain analyzer. The insulating properties of the films were evaluated via I-V measurements using a HP 4140B semiconductor test system. The film crystallinity was assessed by glancing angle x-ray diffraction (GAXRD) using a Rigaku diffractometer with CuKa radiation at 40 kV. Cross-sectional film microstructure was examined using a Hitachi S4500 field emission scanning electron microscope (FESEM). The surface morphology of the films was assessed by a Digital Instrument’s Dimension 3000 atomic force microscope (AFM) using tapping mode. The elemental distribution within and across the film-substrate interface was assessed using a Perkin-Elmer 660 scanning Auger microprobe.

3. Results and discussion

The room temperature thin film dielectric properties, measured at 10 GHz and 100 kHz, are summarized in Table I. A comparison of the data tabulated in Table I clearly demonstrates that amounts as low as ~1 mol% of the Mg dopant have a noticeable influence on the dielectric and insulating properties of the BST thin films. The 1 mol% Mg-doped BST thin film possessed a lower dielectric loss with respect to that of the undoped BST thin film at both low and microwave frequencies. The permittivity of the 1 mol% Mg-doped BST...
thin film was notably lower than that of the undoped BST at 100 kHz and 10 GHz. The permittivity for both the undoped and 1 mol% Mg-doped thin films, at both frequencies, is well within the requirement for device impedance matching purposes, i.e. \( \varepsilon_r < 500 \), [5,6] thereby allowing efficient power transfer in the device. The electrical quality, that is, the insulating nature, of a dielectric film is determined by the value of leakage current or resistivity of the film. The Mg-doped BST thin film possessed an enhanced film resistivity, \( 0.55 \times 10^{12} \Omega \text{-cm} \), (low leakage current/high resistivity) value with respect to that of the undoped BST thin film, \( 0.40 \times 10^{12} \Omega \text{-cm} \). Capacitance-voltage measurements, conducted on the MIM capacitors, were used to analyze the effect of Mg doping on the dielectric tunability of the BST thin films. The dielectric tunability (in %) is defined in terms of \( \Delta C/C_0 \), where \( \Delta C \) is the change in capacitance relative to zero-bias capacitance \( C_0 \). The tunability, measured at 200 kV/cm, for the undoped and Mg doped thin films was 28.1 % and 23.0 %, respectively. Thus, the tunability, decreased with the addition of the Mg dopant. The improvement in the permittivity and dielectric loss values at the expense of decreasing dielectric tunability has been noted in other studies involving acceptor doped thin films [3-5]. It must be kept in mind that the BST film stoichiometry, i.e., the Ba/Sr ratio of 60/40 was designed to position the \( T_c \) at room temperature. However, it has been demonstrated for 5 mol % Mg doped BST thin films that the addition of the Mg causes the \( T_c \) to shift to a lower temperature [3,4]. According to Wu and Barnes the tunability reaches its maximum value near the \( T_c \) [7]. Thus, the fact that the tunability values were measured at room temperature (for both film compositions), combined with the temperature down shift in \( T_c \) for Mg doped films explains the slightly lower tunability of the Mg doped BST film.

In order to select the film composition best suited for reliable tunable microwave device applications the films’ dielectric and insulating properties must be carefully considered and weighed against one another in terms of relative importance. The material property requirements for tunable device applications include:

a) low dielectric loss, i.e., less than 0.03;

b) a permittivity less than 500;

c) high dielectric tunability (goal of 50%), and

d) low leakage current/high resistivity, \( \sim 10^{11} \Omega \text{-cm} \).

Considering the tradeoff’s between tunability and the values of dielectric loss, permittivity and film resistivity, the 1 mol% Mg-doped BST film possessed better overall material properties with respect to that of undoped BST film for tunable device applications. It must be kept in mind that good dielectric and insulating properties are not stand-alone device requirements. Other material properties such as film structure, microstructure, surface morphology and nature of the film-substrate interface will strongly influence device performance and reliability. It is well documented that the variations in the dielectric properties of the BST based material system are strongly influenced by sample composition, crystallinity, grain size, stress, and the quality of the film-substrate interface [3,4,8,9]. Therefore, the influence of low level Mg doping on the structural, microstructural, interfacial, and surface morphological properties of the BST-based films must be evaluated and correlated with the films microwave dielectric and insulating properties.

In order to insure optimum and reliable dielectric properties, long term device reliability and film fabrication reproducibility the films must be well crystallized and possess a single phase structure. The as-pyrolysed undoped and 1 mol% Mg-doped BST thin films were amorphous thus post deposition annealing was required to impart crystallinity, increase the overall grain size of the film, and to remove film strain by filling oxygen vacancies. These factors are particularly important since the dielectric loss in ferroelectric thin films has been reported to be strongly influenced by stoichio-

![Figure 3. X-ray diffraction patterns of the (a) undoped and (b) 1 mol% Mg doped Ba\(_{0.6}\)Sr\(_{0.4}\)TiO\(_3\).](image-url)
metric deficiencies, which create vacancies, film strain, and the presence of a large grain boundary to grain ratio [3,10]. Therefore, in order to reduce the microwave dielectric loss the as-pyrolysed films on MgO substrates were post-deposition annealed for 1h in the temperature range of 600 to 800°C in an oxygen atmosphere. Glancing angle x-ray diffraction (GAXRD) was utilized to assess film crystallinity and to determine whether or not the films possessed a single phase structure. Figure 3 displays the glancing angle x-ray diffraction patterns of the undoped and 1 mol% Mg doped BST films deposited on MgO substrates. The absence of diffraction peaks in the x-ray diffraction patterns for both film compositions annealed at 600°C indicated that these films were amorphous in nature. Partially crystallized undoped and Mg-doped films were obtained at an annealing temperature of 650°C with no evidence of secondary phase formation. As the annealing temperature was increased the x-ray peak intensity increased and the full-width-half-maximum (FWHM) decreased indicating enhanced crystallinity and an increase in grain size with increasing annealing temperature up to 800°C. Based on the x-ray characterization results, 800°C was determined to be the optimum annealing temperature for both film compositions, i.e. the films were fully developed at this temperature. The 800°C annealed undoped and doped films were cubic, and possessed a non-textured polycrystalline structure with no evidence of secondary phases. Direct comparison of the GAXRD data for the undoped and doped films showed that the FWHM of the Mg doped film was larger than that of the undoped BST films at all annealing temperatures which indicates a smaller grain size for the Mg doped BST films with respect to that of the undoped films.

The cross-sectional FESEM analyses of the as-deposited undoped and doped films showed them to be amorphous. Figures 4 and 5 display the microstructural evolution of the undoped and doped thin films, as a function of annealing temperature from 600 to 800°C, respectively. The FESEM analyses supports the x-ray results in that the 600°C annealed films were amorphous and that the microstructure became
Figure 6. AFM plan-view micrographs of the (a) undoped and (b) 1 mol% Mg doped BST thin film surfaces post-deposition annealed at 800°C. The corresponding three-dimensional AFM images of the (c) undoped and (d) 1 mol % Mg doped BST thin film surfaces showing surface roughness in response to postdeposition annealing at 800°C.

Figure 7. Grain size of the undoped (solid line) and 1 mol% Mg doped (dashed line) BST thin films as a function of annealing temperatures from 650 to 800°C.

The surface morphology of the films was assessed via tapping mode AFM over a $1 \times 1 \mu m^2$ scan area. The AFM images of the films annealed at 800°C displayed in Fig. 6, show that both the undoped and Mg-doped films exhibited a well crystallized, dense microstructure with no cracks or defects observed. The surface roughness as quantified by AFM, was found to increase with increasing annealing temperature resulting in an average surface roughness ($R_{av}$) of 2.25 nm at 800°C for both film compositions. The para-
ter of film surface roughness is extremely important for device performance since the dielectric properties depend not only on a well-defined microstructure, but also on the quality of the electrode-film interface [11]. A rough film surface will contribute to the conductor loss of the device, which in turn manifests into a higher device insertion loss. Thus, in order to maintain a low device insertion loss a smooth film surface is required. It has been reported that surface roughness also has a strong influence on the value of leakage current or film resistivity [12,13], thus, the fact that the undoped and Mg doped MOSD films are extremely smooth is consistent with the excellent film resistivity values achieved in this investigation. The AFM results demonstrated that the Mg dopant had no appreciable effect on the films surface roughness; however, the AFM results did show a grain size difference between the annealed undoped and doped films. The average grain size was determined via the line-intercept method using the AFM plan-view data over a 1×1 µm scan area on the film surface. Figure 7 displays a plot of grain size as a function of annealing temperature for both the undoped and Mg doped films. The results support the GAXRD findings suggesting that even a small amount of Mg dopant added to BST depresses the grain size relative to that of undoped BST. This result was also observed for 5 mol% Mg doped films deposited on Pt-Si substrates [3]. The grain size of the fully crystallized films was 75 nm and 67 nm for the undoped and Mg doped films, respectively. The grain size difference between the undoped and Mg doped films accounts for the reduced permittivity of the Mg doped film. In general, a larger polarization, hence higher permittivities are expected for larger grain size materials since the volume of dielectric polarization is proportional to the size of the grain.

The Auger electron spectroscopy (AES) depth profiles for both film compositions are displayed in Fig. 8. The AES depth profiles revealed a sharp interface with no interdiffusion of constituent elements between the dielectric film and the MgO substrate. The depth profiles also revealed that each element component of the film possessed a uniform distribution from the film surface to the film-substrate interface. These data substantiate the fact that the undoped and Mg doped BST films on MgO substrates maintain chemical and thermal stability at processing temperatures up to 800°C (annealing temperature). The fact that no impurities were observed in the AES elemental depth profile, without doubt, contributed to the films good dielectric and insulating properties.

Results of this investigation have demonstrated that Mg doping as low as 1 mol% had a notable influence on the films microstructure, dielectric, and insulating properties. The exact mechanism by which Mg altered the film properties is not fully understood. We suggest that the Mg doping (composition alteration) is the parameter, which is responsible for the modification of the BST thin film material properties. Material doping has been reported to modify and control thin film dielectric and insulating properties by reducing the oxygen vacancy concentration [3-5,14,15]. Acceptor type dopants can prevent the reduction of Ti⁴⁺ to Ti³⁺, by neutralizing the donor action of the oxygen vacancies. Because the electrons resulting from the generation of oxygen vacancy can hop between different titanium ions and provide a mechanism for dielectric losses, the compensation for oxygen vacancy with the correct amount of acceptor dopant such as Mg²⁺, should in theory, help to lower the loss tangent. We further speculate that the Mg dopant served to enhance the insulation re-

\[\text{Table I. Dielectric properties of the undoped and 1 mol% Mg doped BST thin films.}\]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Frequency</th>
<th>(\varepsilon_r) (Zero bias)</th>
<th>(\tan \delta) (Zero bias)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO subst.</td>
<td>10 GHz</td>
<td>9.71</td>
<td>2.85 \times 10^{-5}</td>
</tr>
<tr>
<td>BST/MgO</td>
<td>10 GHz</td>
<td>406</td>
<td>0.025</td>
</tr>
<tr>
<td>1 mol% Mg-BST/MgO</td>
<td>10 GHz</td>
<td>348</td>
<td>0.024</td>
</tr>
<tr>
<td>BST/PtSi</td>
<td>100 GHz</td>
<td>450</td>
<td>0.013</td>
</tr>
<tr>
<td>1 mol% Mg-BST/PtSi</td>
<td>100 GHz</td>
<td>423</td>
<td>0.008-0.01</td>
</tr>
</tbody>
</table>

\[\text{Figure 8. AES elemental depth profiles of the 800°C annealed}\]

(a) undoped and (b) 1 mol% Mg doped \(\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3\) deposited on MgO substrates.
sistance (excellent film resistivity values listed in Table I) of the BST based film, by suppressing the concentration of oxygen vacancies, and growth of potential barrier at grain boundaries.

4. Conclusions

This investigation demonstrated that Mg doping as low as 1 mol% had a noteworthy influence on the material properties of BST thin films. The annealed undoped and 1 mol% Mg-doped BST films were single phase, possessed a dense defect free microstructure with a thermally stable film-substrate interface, and smooth continuous surface morphology. Improved dielectric and insulating properties were achieved for 1 mol% Mg-doped BST thin films with respect to that of pure BST films. The 10 GHz measured values of permittivity and dissipation factor of BST thin films doped with 1 mol% Mg were 348 and 0.024, respectively. The film resistivity was also enhanced as a result of the Mg doping. The compensation for oxygen vacancies via low amounts of Mg acceptor doping was suggested to be responsible for the enhanced material properties of the 1 mol% Mg doped BST thin film.