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Correlation of Microwave Dielectric Properties and Microstructure of Unpatterned Ferroelectric Thin Films

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ABSTRACT

The influence of low concentration (1 mol%) Mg doping on the structural, microstructural, surface morphological and dielectric properties of $Ba_{1-x}Sr_xTiO_3$ thin films has been measured and analyzed. The films were fabricated on MgO and Pt-Si substrates via the metalorganic solution deposition technique using carboxylate-alkoxide precursors and post deposition annealed at 800 °C (film/MgO substrates) and 750 °C (film/Pt-Si substrates). The structure, microstructure, surface morphology and film/substrate compositional quality were analyzed and correlated to the films dielectric and insulating properties. Dielectric properties of unpatterned films were measured at 10 GHz with a coupled/split dielectric resonator system and at 100 kHz using metal-insulator-metal capacitors. The Mg-doped BST films exhibited improved dielectric loss and insulating characteristics compared to the undoped $Ba_{0.6}Sr_{0.4}TiO_3$ thin films. The improved dielectric properties, low leakage current, and good tunability of the low level Mg-doped BST thin films merit strong potential for utilization in microwave tunable devices.

INTRODUCTION

Thin films of $Ba_{1-x}Sr_xTiO_3$ (BST) have recently received considerable attention as promising candidates for applications in tunable electronically controllable microwave devices. For the realization of such tunable devices at microwave frequency it is important to develop a paraelectric thin film material with low microwave loss, high tunability, and good insulating properties. To date, thin film BST which simultaneously possesses both low loss at microwave frequency 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 properties, i.e., lower dielectric loss, of ferroelectric materials such as BST [1-3]. Recently, 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 Mg doped BST thin films [1,4]. In this paper we evaluate the process-structure-property relationships and report the microwave dielectric properties for pure and 1 mol% Mg doped BST thin films prepared via the metalorganic solution deposition technique.

EXPERIMENTAL

Undoped and 1 mol% Mg doped $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ thin films were fabricated by the metalorganic solution deposition (MOSD) technique. Ba acetate, Sr acetate, and Ti isopropoxide were used as precursors to form BST. Acetic acid and 2-methoxyethanol were used as solvents and magnesium acetate was employed as the dopant precursor. The precursor films were spin coated onto Pt-coated silicon and (100) single crystal MgO substrates. Crystalline films were achieved via post-deposition annealing in an oxygen ambient 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 were characterized utilizing both microwave and low frequency measurement techniques. The microwave dielectric properties of unpatterned undoped and Mg-doped BST thin films grown on MgO substrates were measured at 10 GHz with a coupled/split dielectric resonator system [5]. Figure 1 displays a schematic diagram of the split dielectric resonator system. This measurement technique is noncontacting and non-destructive. The measurement process is two-phase: First, the permittivity and dielectric loss of the MgO substrate is determined. Second, 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. The film capacitance (C_p) and dissipation factor ($\tan \delta$) were measured with an HP 4194A impedance/gain analyzer^a. The insulating properties of the films were evaluated via I-V measurements using a HP 4140B semiconductor test system. The film crystallinity was assessed via glancing angle x-ray diffraction (GAXRD) using a Rigaku diffractometer with CuK α 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.

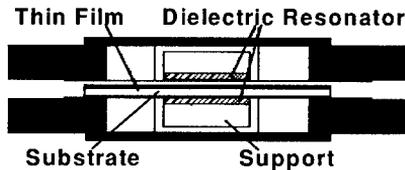


Figure 1. Schematic diagram of the split dielectric resonator system.

^aCertain commercial equipment is identified in order to adequately specify the experimental procedure; recommendation or endorsement by NIST or U.S. Army Research Laboratory is not therein implied.

RESULTS AND DISCUSSION

The microwave dielectric measurements in this investigation were achieved in the unpatterned state, that is, without the use of any contact metallization. This measurement configuration has the advantage of eliminating the influence of conductor losses from the microwave dielectric loss measurement. However, without a contact metallization the tunability and leakage current measurements cannot be obtained. Thus, we have also characterized these thin films at low frequency (100 kHz) in the MIM configuration in order to acquire film tunability and leakage current/film resistivity values. The low frequency data is useful only as a composition-tunability trend indicator since the correlation between 100 kHz and 10 GHz data is not absolute [4]. The insulating (leakage current/film resistivity) thin film data is an electrical measure of the quality and reliability of a dielectric film, and the low frequency data is valid for this assessment. 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 than that of the undoped BST thin film at both low and microwave frequencies. The dielectric constant of the 1 mol% Mg-doped BST thin film was lower than that of the undoped BST at 100 kHz and 10 GHz. The dielectric constant for both the undoped and 1 mol% Mg-doped thin films, at both frequencies, is reasonable for device impedance matching purposes, 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 which has been converted to resistivity in Table I. The Mg-doped BST thin film possessed an enhanced film resistivity (low leakage current) value with respect to that of the undoped BST thin film. 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 tunability, measured at 200 kV/cm was found to decrease with the addition of the Mg dopant. Considering the tradeoffs between tunability and the values of $\tan \delta$, dielectric constant and film resistivity, the 1 mol% Mg-doped BST film possessed better overall material properties with respect to that of undoped BST for tunable device applications. 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. Therefore, in order to fully evaluate the properties discussed above the influence of the Mg dopant on the structural, microstructural, interfacial, and surface morphological properties must be evaluated and correlated with the films dielectric and insulating properties.

TABLE I. Dielectric and insulating properties of the undoped and 1 mol% Mg-doped BST thin films.

Sample	Frequency	ϵ_r (Zero bias)	$\tan \delta$ (Zero bias)	Tunability (%) (200kV/cm)	ρ (Ω -cm) (200kV/cm)
MgO subst.	10 GHz	9.71	2.88×10^{-5}	----	----
BST/MgO	10 GHz	406	2.50×10^{-2}	----	----
1 mol% Mg-BST/MgO	10 GHz	348	2.40×10^{-2}	----	----
BST/PtSi.	100 kHz	450	1.3×10^{-2}	28.1	0.40×10^{12}
1 mol% Mg-BST/PtSi	100 kHz	423	1.0×10^{-2}	23.0	0.55×10^{12}

The as-pyrolysed undoped and 1 mol% Mg-doped BST thin films were amorphous and 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 stoichiometric deficiencies, which create vacancies, film strain, and the presence of a large grain boundary to grain ratio [4]. 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 2 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. 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 and indicating a smaller grain size for the Mg doped BST films with respect to that of the undoped films.

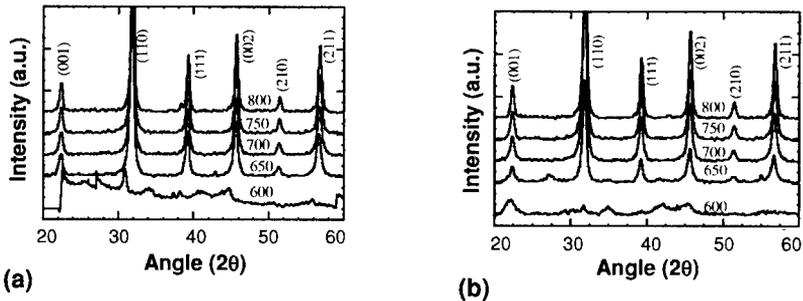


Figure 2. X-ray diffraction patterns of the (a) undoped and (b) 1 mol% Mg doped $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ films deposited on MgO substrates annealed at temperatures from 600 to 800 °C for 60 min.

The surface morphology of the films was assessed via tapping mode AFM over a $1 \times 1 \mu\text{m}^2$ scan area. The AFM images of the films annealed at 800 °C are displayed in Fig. 3 and show that both the undoped and Mg-doped films exhibited a 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 parameter 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 the electrode (required for microwave devices)-film interface. It has been reported that surface roughness has a strong influence on the value of

leakage current or film resistivity [6], thus, the fact that the undoped and Mg doped MOSD films are extremely smooth is consistent with the excellent film resistivity values reported in Table I. 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. Figure 3c 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 for the fully crystallized films was 75 nm and 67 nm for the undoped and Mg doped films respectively.

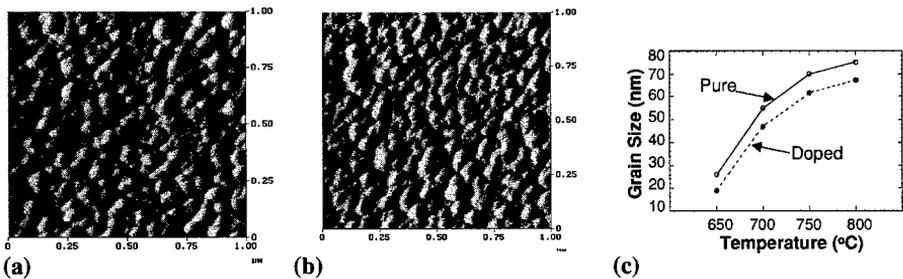


Figure 3. AFM micrographs of the (a) undoped BST and (b) 1 mol % Mg doped BST film surfaces postdeposition annealed at 800 °C. Grain size as a function of annealing temperature for the undoped and 1 mol% Mg doped BST thin films on MgO substrates is plotted in (c).

The films microstructure, in the direction perpendicular to the film surface was analyzed via cross-sectional FESEM. The cross-sectional FESEM micrographs of the 800 °C annealed films, not shown, demonstrated that both films possessed a dense well-crystallized microstructure with a uniform cross-sectional thickness of 165 nm. The films were polycrystalline and were composed of granular multigrains randomly distributed through out the film thickness. The FESEM micrographs show a distinct structural delineation between the film and the MgO substrate. No amorphous layer or voiding/defects was observed at the film-MgO interface. This defect free and structurally abrupt interface bodes well for the excellent mechanical integrity and good adhesion characteristics of the undoped and Mg doped BST film-MgO substrate.

The AES depth profiles of the undoped and 1 mol% Mg doped BST films 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 [7, 8]. Acceptor type dopants can prevent the reduction of Ti^{4+} to Ti^{3+} , 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 Mg^{2+} , should, in theory, help to lower the loss tangent. We further speculate that the Mg dopant served to enhance the insulation resistance (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.

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 dielectric constant 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.

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