Characterization of doped BST thin films deposited by sol-gel for tunable microwave devices

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***Abstract*— BST thin films with various dopants are growth by sol-gel method on Platonized silicon and MgO substrates. Thiers dielectric properties are investigated at low frequency(less than 1MHz) on silicon with plate capacitor and high frequency (up to 15GHz) by interdigital capacitor on MgO substrate. These results are discussed with the nature of dopant and show, Mg as very good candidate to reduce grain size and dielectric losses. In opposite K is good candidate as dopant of BST thin film to increase the drastically the tunability**

I. INTRODUCTION

Thin films of barium strontium titanate $Ba_{1-x}Sr_xTiO_3$ have been very attractive to the microelectronic industry as good candidates for application in microwave devices such as phase shifters [1]. Thus the fabrication of high-quality $Ba_{1-x}Sr_xTiO_3$ thin films possessing high dielectric tunability and low loss tangent values have become very important technical issues for developing these materials for practical application [2]. Many researches have improved the dielectric characteristics by doping with foreign ions on the A or B sites of ABO_3 perovskite system [3]. Some dopants including Mg, Ni, Fe, Mn, Mn, Co, Al, Cr, and Bi, which can occupy the B sites of ABO_3 [4]. However, La, Er and K can occupy the A sites of ABO_3 [5]. The BST thin films usually have been deposited by radio frequency (RF) sputtering [6], metal organic chemical vapour deposition (MOCVD)[7], pulsed laser deposition (PLD) [8] and sol-gel methods [9]. Compared with the conventional methods, sol-gel technique offers a homogeneous distribution of elements on a molecular level, ease of composition control, high purity, the possibility of low temperature processing, and the ability to coat large and complex area substrates [10]. In the present study, BST thin films were prepared by sol-gel method on Pt/Si or MgO in order to investigate the influence of Bi, Mg, K and Fe on the microstructure, surface morphology, and dielectric properties of BST thin films.

II. EXPERIMENTAL PROCEDURE

Sol-gel technique was employed in this study to produce BST doped Bi, Mg, K and Fe thin films. Barium acetate, Strontium acetate, Bismuth acetate, Magnesium acetate, kalium acetate and Iron acetate were used as precursor materials. Acetic acid and isopropanol were used as the solvent. Initially barium acetate, strontium acetate in the ration 50:50 and once of dopants (the dopants precursor, in concentrations ranging from 2.5 to 10 mol %) were dissolved in acetic acid. After getting a clear solution, titanium isopropoxide was added to obtain the precursor solution. After total dissolution ethylene glycol was added to improve the high stability [11]. The precursor solution was spin coated on platinum coated silicon (100) substrates by a spinner of 3000 rpm for about 30 sec. the samples were annealed during 1min into hot plate at 350°C in order to evaporate solvents. After in order to crystallizing the films in the perovskite phase [12], thermal annealing at temperature 750°C was employed. Finally gold have been evaporated through a shadow mask to realize the top electrode with circular ranging from 150µm to 2mm in diameter. The Pt\Ti layers act as the bottom electrode to form a plate capacitor. Interdigital top electrodes were patterned in the gold film using S1818 photoresist. The morphology of surface was observed by a scanning electron microscopy (SEM). Electrical proprieties were determined at room temperature in the frequency range 100Hz-1MHz as function of DC bias with HP 4284A impedance analyser and high frequency (1GHz-15GHz) with a vectrial network analyser

III. RESULTS AND DISCUSSION

A. Morphology

The surface morphology and cross-section of undoped and doped $Ba_{0.5}Sr_{0.5}TiO_3$ thin films are shown figure1.These micrographs clearly show the grain size range at 45 to 55 nm (undoped), 45 to 65 nm (Bi doped BST), 30 to 50 nm (Mg doped BST), 50 to 70 nm (K doped) and 40 to 60 nm (Fe doped BST). Via surface analysis the average grain size is 50

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nm, 55 nm, 40 nm, 60 nm and 50 nm respectively. The grain size increase with Bi and K doped BST while it reduced with Mg doped BST. This is in relation with the size of the corresponding ions: Mg^{2+} is smaller than K^{+} and Bi^{3+}. The thickness of the film is about 350nm. Observation of the films surface morphologies showed a small dependence of grain size on composition. The films were dense, smooth and crack free.

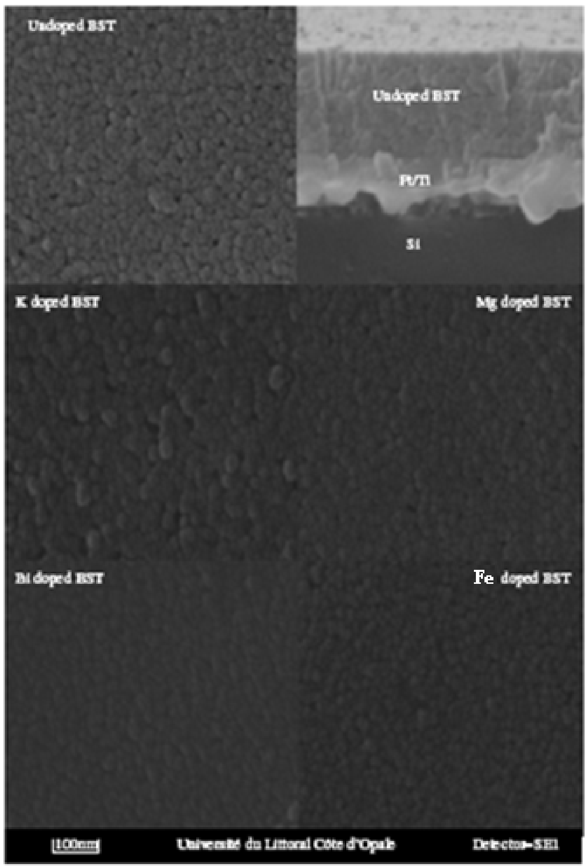

Figure 1. Morphology of thin films undoped and doped BST

B. *Dielectric properties*

1) *BST into Silicon at low frequency*

The room temperature dielectric permittivity and loss tangent of $Ba_{0.5}Sr_{0.5}TiO_3$ undoped and doped Bi, Mg, K and Fe as function of frequency are given in figures2. These results were obtained using on AC measurement voltage of 100 mV and frequency range of 100Hz-1MHz. The dielectric constants are calculated from the capacitance values using the paralleled plate capacitor formula and the film thickness assuming that the dielectric properties of the film are homogeneous throughout the film thickness [13]. The dielectric constants of the undoped, Bi, Mg, K and Fe doped BST thin films are slowly decreases with frequency up to 1MHz. the phenomenon of dispersion of dielectric constant may be attributed to extrinsic contributions to polarization of the materials such as impurities, oxygen vacancies, grain boundaries, domain wall motions[14]. In comparison with doped BST thin films, the dielectric constant of undoped BST thin film is largest one. It is well known that the value of the dielectric constant of dielectric film is strongly affected by microstructure, grain structure, grain size [3] [5]. We think also, that in our case, the effect of the dopants is to reduce the polarization associated with the oxygen vacancies. The formation of non ferroelectric phases such as oxides can also largely reduce dielectric constant. This is probably the case with the doping with Mg giving MgO as dielectric constant at 1MHz is only 110 which is 2.5 times less than the undoped film value. However this smaller value of dielectric constant is favourable in perspective of our applications in microwaves as tunable phase shifter [1]. The dielectric constant values measured at 100MHz for undoped, Bi, Mg, K and Fe doped BST thin films were shown in table1. On the other had the loss tangent of the undoped BST film shown strong dispersion at low frequency [1KHz-100KHz]. The phenomenon of dispersion of loss tangent may be explained by the presence of interfacial layers, such as surface pyrochlore phases or electrode/film interface in the thin film [15] [16]. The losses, they are smaller for all the doped films than for the undoped ones (see figure 2-b). This confirms our hypothesis of the decrease of the oxygen vacancies number in the doped films.

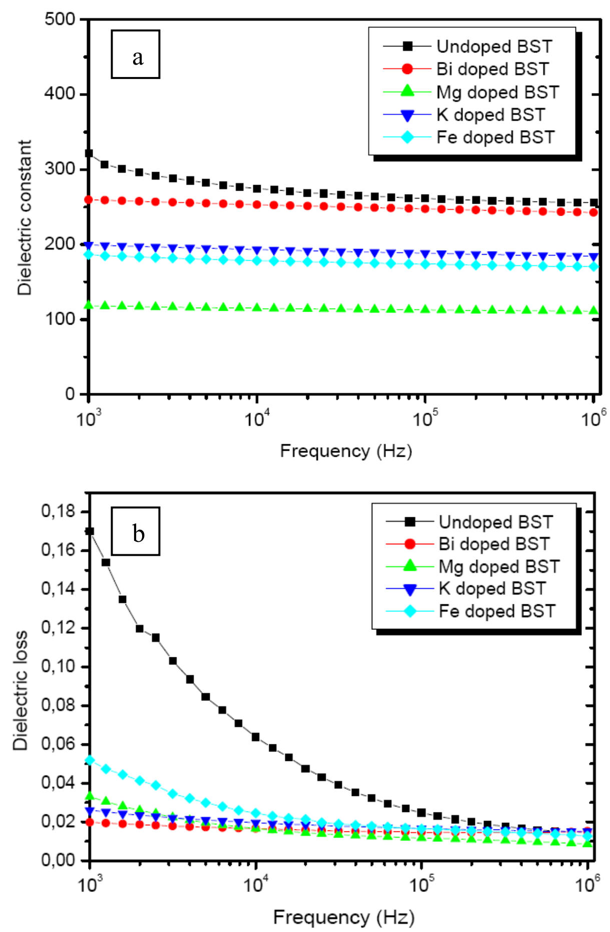

Figure 2. Dielectric constant (a) and loss tangent (b) of undoped and doped $Ba_{0.5}Sr_{0.5}TiO_3$ as function of frequency

The smallest loss tangent is obtained with the Mg doped film: for example tgδ = 0.008 at 1MHz. This value is very encouraging for RF and microwaves applications as it is known either from a theoretical point of view [17] and from an experimental one [18] that the losses increase as a function of frequency from the MHz frequencies up to the THz frequencies.

Figure3-a show the capacitance as function of bias voltage up to ±10V for five samples undoped and doped BST thin films at 1MHz. The measurements have been made at room temperature at 1MHz with an AC voltage of 100mV. It is found that the capacitance of five samples of thin films nonlinearly decrease with increasing voltage such nonlinearity had been explained in the literature [19].

TABLE I. SUMMARY DIELECTRIC PROPERTIES

	Undoped	Doped BST			
	BST	Bi	Mg	K	Fe
ε'	255	242	111	185	170
tanδ(%)	1.4	1.5	0.8	1.5	1.2
Tunability(%)	23.5	31.5	19	36	21
FOM[a]	16.8	21	20	24	17.5

a:FOM=Tunabiliy/tanδ

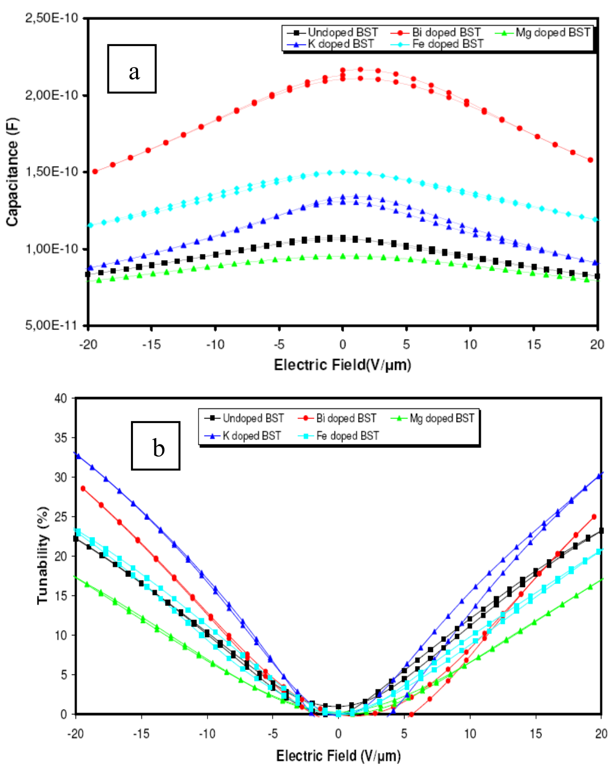

Figure 3. C(E) curves (a) and tenability (b) at 1MHz of undoped and doped $Ba_{0.5}Sr_{0.5}TiO_3$ films

We note the strong dependence of the capacity as function of voltage and the absence of butterfly-shaped C-V curves indicated that the films have paraelectric nature. The asymmetry of the capacitance curves reflected the influence of interfacial structure of different top and bottom electrodes, which should affect the film polarization [20]. Figure3-b represents the tunability DC voltage applied curves of undoped and doped BST thin films at 1MHz. The tunability is determinate as $(C_{max}-C_{min})/C_{max}$ were C_{max} and C_{min} are the values of capacitance at zero and maximum bias voltage, respectively. The tunability of BST thin film was increased with the doping K and Bi, while the dopants Mg was decreased the tunability of the BST thin films. The values of tunability in undoped BST, Bi, Mg, K and Fe doped BST thin films are shown in table1 at 1MHz. The decrease of tunability of BST may be attributed to the internal stress among grains affects the dielectric properties [4]. We think also the small grain size need a high voltage. Therefore, K and Bi doped BST thin films had the maximum tunability as its largest grains. Larger grains size could be a positive factor to dielectric tunability [21]. This will be confirmed in the following paragraph. On the other hand, the lower tunability with Mg doping could be linked to the existence of non ferroelectric phases, for example oxides phases such as MgO (with Mg doping). In general, the low frequency dielectric properties of undoped, Mg doped BST and K doped BST thin films appear desirable for tunable device application.

2) BST into MgO at Microwave frequency

The microwave proprieties of undoped BST, Mg doped BST and K doped BST films grown on MgO substrate were measured using interdigital capacitors IDC structure with five-finger-pair. Using an Anritsu 37369A vector network analyzer (VNA), the one port S_{11} parameter of interdigital structures were measured from 1GHz to 15GHz. One port OSL calibration performed using 150µm pitch SG probe and calibration substrate from GGB Industries. Figure 4 shows the capacitance of IDCs for undoped and doped BST thin films as function of frequency, obtained from measurements by means of: $C = \mathrm{Im}\left[\frac{(1-S_{11})}{2\pi f Z_C (1+S_{11})}\right]$

The capacitance is almost constant up to 15GHz for 3 samples this fact confirms that no relaxation effect occurs in the undoped and doped BST material. The conformal mapping technique was used to extract the values of dielectric constant. The mean values are 275, 245 and 260 for undoped BST, Mg doped BST and K doped BST respectively. The values of dielectric constant are almost same as in low frequency except for Mg doped BST we can explain this effect by the crystallization of the films depends of the nature of the substrate.

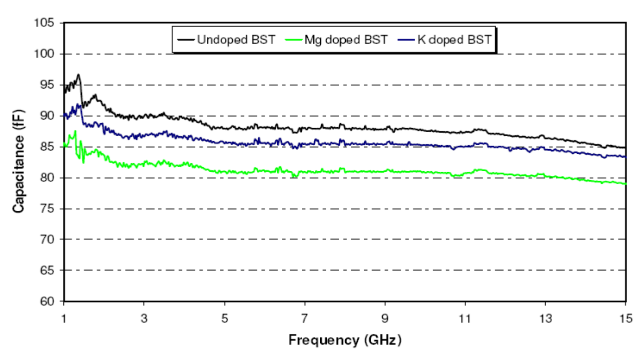

Figure 4. Capacitance as function of frequency up to 15GHz

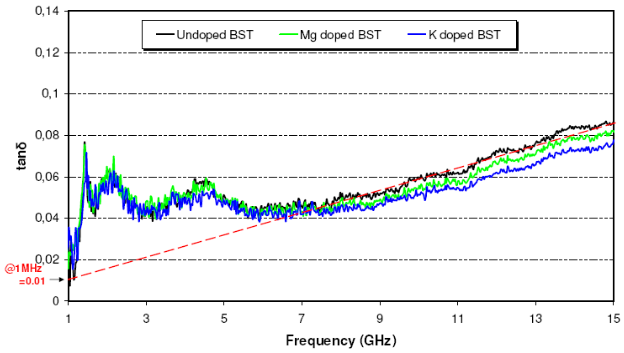

Figure 5. Loss tangent for undoped and doped BST up to 15GHz

Figure 5 displays the loss tangent as function of frequency for undoped and doped BST. The losses start to increase rapidly with frequency. The frequency dependence of the losses in thin films can be rationalized in terms of the existing knowledge on the loss mechanisms in ferroelectrics. For all of the loss mechanisms (intrinsic and extrinsic) the dielectric loss tangent is almost a linear function of the frequency, except the so-called universal-relaxation-law mechanism [22]. The value of loss tangent at 15GHz is 0.082 for undoped BST this value is better by contribution to the work previously done [23] so we can see a reduction in losses for the two films doped Mg and K the values is 0.08 and 0.078 respectively at 15GHz.

IV. Conclusion

The BST thin films deposited by the versatile sol-gel method are studied here with various dopants as Bi, Mg, K and Fe. Their dielectric properties are studied as function of frequency up to 15GHz on platinised silicon and MgO substrates. This study shows Mg as good candidate for BST thin film doping to reduce losses. The lowest value obtained is 0.8% at 1MHz moreover K dopant is also attractive to increase the tunability.

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