

## THE EFFECT OF (Ba,Sr) AND (Mn,Fe,W) DOPANTS ON THE MICROWAVE PROPERTIES OF $Ba_xSr_{1-x}TiO_3$ THIN FILMS

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### ABSTRACT

Single phase  $Ba_xSr_{1-x}TiO_3$  ( $x=0.5$  and  $0.6$ ) thin films ( $\sim 5000\text{\AA}$  thick) have been deposited onto (100) MgO single crystal substrate with (Ba,Sr) compensated and/or (Mn,Fe,W) doped targets using pulsed laser deposition (PLD). The room temperature capacitance (C) and dielectric Q ( $1/\tan\delta$ ) have been measured at microwave frequencies of 1 to 20 GHz as a function of electric field (0-80kV/cm). Microstructural defects associated with cation and anion vacancies have been observed in  $Ba_xSr_{1-x}TiO_3$  films. Compensation of the ablation target with excess Ba and Sr tends to increase the dielectric constant and the dielectric Q. A film deposited with (Ba,Sr) compensated target has been obtained with 25% tuning, where % tuning is defined as  $\{(C(0)-C(E))/C(0)\} \times 100$ , and dielectric Q of  $\sim 100$  at room temperature (1 - 10 GHz) for DC bias field ( $E=67$  kV/cm). A further increase in the dielectric Q is observed by the addition of donor/acceptor dopants such as Mn, Fe, and W ( $Q \approx 100-240$ ). The effects of (Ba, Sr) compensation and (Mn,Fe,W) doping on the film structure and dielectric properties are discussed.

### INTRODUCTION

Commercially available voltage-variable capacitors, e.g., varactor diodes based on p-n junctions in semiconductor materials, are currently used in most tunable RF voltage controlled oscillators (VCO's). However, the use of these devices is typically limited to frequencies  $\leq 2$  GHz. Pervoskite barium strontium titanate,  $Ba_xSr_{1-x}TiO_3$  (BST) is a ferroelectric material suitable for the development of a new type of high frequency varactors (1-20 GHz) due to its ability to change dielectric constant with applied DC electric field [1]. One of the most critical properties that needs to be optimized in developing tunable microwave devices based on ferroelectric thin films is the dielectric Q ( $1/\tan\delta$ ) at high frequencies. A dielectric Q  $> 200$  will be required for many of these applications. Dielectric Q's of 10 - 70 have been reported for BST ( $x=0.5$ ) thin film and bulk ceramic at room temperature and zero bias [2,3]. To increase the dielectric Q, we have investigated the relationships between microstructural defects in BST thin films and dielectric loss.

### EXPERIMENTAL

BST ( $x=0.5$  and  $0.6$ ) thin films ( $\sim 5000\text{\AA}$ ) were deposited by pulsed laser deposition (PLD) onto (100) MgO single crystal substrates at  $750^\circ\text{C}$  in an oxygen ambient pressure of 350 mTorr. Some films were also deposited using a two-step process. First, a very thin ( $\sim 50\text{\AA}$  thick) amorphous BST buffer layer was deposited at room temperature to relieve stress. Then a second 5000  $\text{\AA}$  BST film was further grown on top of the amorphous BST film at a higher

temperature (e.g., 750° C). Details of the two-step process are reported separately in this proceedings. The deposited BST films were annealed at 900 - 1200° C for 6 - 12 hours in flowing O<sub>2</sub>. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to determine film structure and examine the surface morphology. Compositional analysis was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Interdigitated capacitors were deposited on top of the BST films through a polymethylmethacrylate (PMMA) lift off mask by *e*-beam evaporation of 1 - 2 μm thick Ag and a protective thin layer of Au. Microwave reflection coefficient S<sub>11</sub> measurements were made on an HP 8510C network analyzer at room temperature. The data are fitted to a parallel resistor-capacitor model to determine capacitance and dielectric Q (1/tanδ) [3]. Dielectric constants were calculated from the device dimensions. Temperature dependent measurements were performed at 1 MHz with DC bias changes from 0 to 40 V and at 0 V with frequency changes from 500 Hz to 1 MHz using a HP4284A Precision LCR Meter.

## RESULTS AND DISCUSSION

### Ba, Sr, and O deficiencies as loss sources in BST films

Ba and Sr deficiencies have been reported in BST films and BST single crystals [4,5]. BST films deposited from stoichiometric BST ( $x=0.5$ ) targets showed Ba and Sr deficiencies, (Ba/Ti = 0.45, and Sr/Ti=0.49). These cation deficiencies may be caused by anion (oxygen) deficiencies formed during the deposition process in a relatively low partial pressure of oxygen (350 mTorr). The idea is supported by the observation that the calculated lattice parameter for the BST film is ~ 0.1 - 0.5% larger than the bulk BST ( $x=0.5$ ) lattice parameter (3.947 Å). [6,7]. These defects may serve as a significant source of dielectric loss although a clear understanding on the loss mechanisms in ferroelectric thin films has not been established. These defects affect the conductivity of the film by generating free carriers, e.g., electrons, and oxygen vacancies, and the increase in the conductivity must cause more conduction loss of the films.

Another significant loss mechanism due to (Ba,Sr,O) deficiencies is the dielectric relaxation loss. The dielectric relaxation loss of the BST films can be caused by relaxation of weakly bound ions associated with (Ba,Sr,O) vacancies and the defect dipoles, e.g., dipole of (Ba,Sr) vacancy and oxygen vacancy [8,9]. Fig. 1 shows capacitance and relative dissipation factor for BST ( $x=0.5$ ) films as a function of frequency (10KHz-1MHz) and temperature

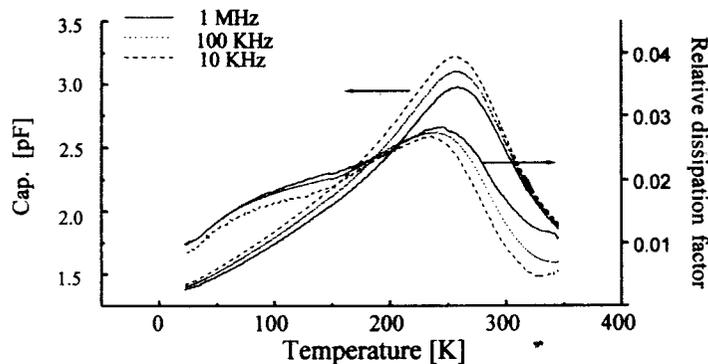


Fig. 1 Temperature dependence measurements of BST ( $x=0.5$ ) films as function of frequency change at 0 DC V ( $|E_{AC}|_{MAX}=200$  mV and finger gap=12 μm).

(20–350K). The paraelectric–ferroelectric phase transition peak is shifted to a lower temperature with decreasing frequency, which is known as a dielectric relaxation behavior. Generally, the dielectric relaxation can be accompanied with any polarization mechanism whose relaxation frequency is comparable to the probing frequencies. The relaxation behavior at the frequencies (10KHz–1MHz) may be due to domain wall motion and defect dipole motion. Possibly, the defect dipole relaxation can be a source of dielectric loss at low microwave frequencies because the relaxation frequencies of dipole polarization are known to be about 0.1–1 GHz. As (Ba,Sr,O) vacancies are formed in the lattice, the space for cations, e.g., Ba, Sr and Ti, is expected to expand so that the amplitude of localized movement or vibration of the cations in the alternating electric field will increase. Similarly, the Ba, Sr, and O vacancies themselves can be excessively vibrated in the electric field, e.g., field energy absorption, because they may be thought of as charged particles like other ions. The amplitude of the cation and vacancy motions in the presence of (Ba,Sr,O) vacancies may serve as a significant source of dielectric loss at microwave frequencies.

#### Efforts to remove Ba, Sr, and O deficiencies in BST film

To correct for deficiencies in Ba, Sr and oxygen, BST films were grown using targets prepared with excess Ba and Sr and then post deposition annealed in flowing oxygen. Table I. summarizes the dielectric properties (1–20 GHz) of BST films as a function of target type. Compensation of the ablation target with excess Ba and Sr tends to increase the dielectric constant, % tuning, where % tuning is defined as  $\{(C(0)-C(E))/C(0)\} \times 100$ , and dielectric Q. A maximum dielectric constant of ~3000 (10 GHz) was observed by the compensation with 2–4% excess Ba and Sr composition. A film deposited with 2% Ba and 2% Sr compensated target has been obtained with 25% tuning and dielectric Q of ~100 at room temperature (1–10 GHz) for DC bias field ( $E=67\text{kV/cm}$ ). The chemical composition of the deposited films was determined using ICP. All BST ( $x=0.5$ ) films showed (Ba,Sr) deficiencies, (Ba/Ti=0.44–0.45, and Sr/Ti=0.46–0.49), regardless of how much (Ba,Sr) was added to the target. As mentioned above, these cation deficiencies may be caused by anion (oxygen) deficiencies formed during the deposition process. If the (Ba,Sr) deficiency is caused by oxygen deficiencies during the deposition, it will be hard to correct for it.

Table I. Trends of 1–20 GHz dielectric properties of BST ( $x=0.5$ ) film as a function of target type.

target type	stoichiometric	(Ba,Sr) compensated	(Fe,Mn,W) doped with/without (Ba,Sr) compensation
dielectric constant	970	1200	780
Tuning [%]	30	40	15
Dielectric Q	25	45	60

We observed some structural differences between the film deposited with stoichiometric target and those with (Ba,Sr) compensated target [Fig. 2 and 3]. Films deposited from compensated targets have a rougher surface morphology compared to films deposited from stoichiometric targets. There have been several investigations on the increase in the surface roughness of BST films with an increase in Ba deficiency [10,11], which is consistent with the result of our chemical analysis. The films deposited with a compensated target also show a larger grain size ( $d \approx 1000 \text{ \AA}$ ) than those deposited with stoichiometric target do ( $d \approx 250\text{--}500 \text{ \AA}$ ). The XRD patterns show exclusively (100) oriented films deposited with stoichiometric target while most of the films deposited with compensated targets exhibited diffraction from other

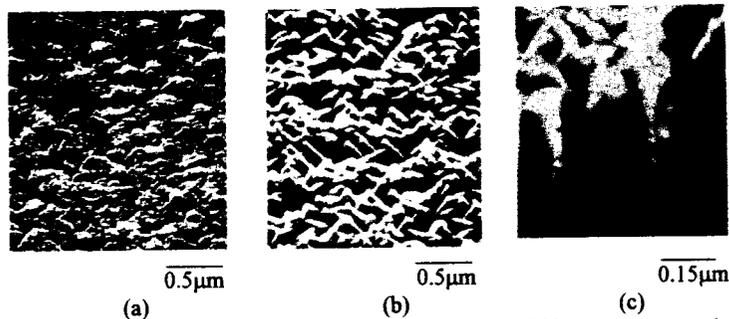


Fig. 2 SEM images on BST ( $x=0.5$ ) films as deposited with (a) stoichiometric target and (b) and (c) 12% Ba and 6% Sr compensated target.

orientation, such as (110) and/or (111) with (100) diffraction. In addition to the changes in grain growth, the microstructural change, e.g., other orientation(s) formation, in the film may play a role in improving the dielectric properties. It was observed that films with other orientation(s), such as (110) and (111) had a higher dielectric Q, presumably due to the film stress relief.

To correct for deficiencies in Ba and Sr in the BST films the oxygen vacancies also should be corrected at the same time. We also tried to decrease the effects of the compositional deficiencies by acceptor/donor doping.

#### Efforts to decrease the effects of the compositional deficiencies

In bulk perovskite ferroelectrics, it has been reported that doping with Fe, Mn, and W into the bulk ceramics showed a significant reduction in the loss tangent and the dopants ( $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ ) were believed to act as acceptors and  $\text{W}^{6+}$  as donors [12,13]. Acceptor ions provide electron traps, but they may also cause oxygen vacancies and holes to compensate their effective negative charge. Donor ions reduce the oxygen vacancies, but they may generate (Ba,Sr) vacancies and free electrons to compensate their effective positive charge [14]. The defect chemistry can be very complex depending on the nature of the charged defects, e.g., Ba, Sr, and O deficiencies. Generally, if the film has oxygen vacancies before doping, the acceptor

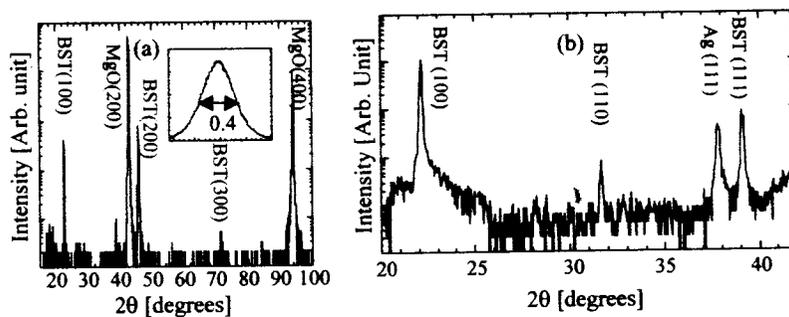


Fig. 3 XRD patterns for BST ( $x=0.5$ ) films deposited with (a) stoichiometric target and (b) 2%Ba and 2% Sr compensated target

ions reduce the free electrons. Similarly, if the film contains (Ba,Sr) vacancies before doping, the donor ions reduce the oxygen vacancies [14]. Therefore, acceptor/donor doping can be used to decrease the effects of the compositional deficiencies.

The dopant site in the lattice can be inferred by considering the film defect structure and the dopant size and charge under the condition of electroneutrality. The dopants ( $\text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$ ) are believed to substitute into Ti sites in BST ceramics [12]. Also, the segregation of both acceptor (Fe and Mn) dopants to the grain boundaries was reported even though the evidence for Fe segregation was not as convincing as that of Mn [15]. According to XRD data, the lattice parameter for as-deposited 1 mol.% Fe-doped film was  $\sim 0.9\%$  smaller than that (3.947 Å) for the undoped bulk BST ( $x=0.5$ ), indicating that  $\text{Fe}^{3+}$  ( $r=0.49$  Å) ions substitute into  $\text{Ti}^{4+}$  ( $r=0.61$  Å) sites. However, the lattice parameter for Mn-doped film, which was  $\sim 0.2\%$  larger than the bulk BST, is almost the same as those for an undoped film. The observation for Mn-doped films may indicate that Mn ions ( $r=0.67$  Å for  $\text{Mn}^{2+}$  and  $r=0.54$  Å for  $\text{Mn}^{3+}$ ) can locate either at Ti sites or at grain boundaries. Fig. 4 shows temperature dependent capacitance measurements at 1 MHz on BST ( $x=0.5$ ) films deposited with Fe, Mn, and W doped targets. It is observed that the Curie temperature ( $T_C \approx 40\text{K}$ ) for Fe-doped film appears to be a very low temperature compared to that ( $T_C \approx 240\text{K}$ ) for undoped bulk BST with  $x=0.5$ . It can be inferred that the Fe doping in BST makes it harder to form a spontaneous polarization or undergo a phase transition, due to the lattice contraction of the iron doped BST film (e.g., less ionic displacement). The phase transition peak for Mn-doped film shows a broader width than for Fe and W-doped films although all films shown in Fig. 4 exhibit broader peaks compared to the bulk [12]. The reason for the broader transition peak of Mn-doped film may be due to more broadly distributed chemical inhomogeneities because the large numbers of possible sites are available for Mn ions, e.g.,  $\text{Ti}^{4+}$  site substitution and grain boundary segregation. A further understanding on the dopant sites and defect status of the film is needed to decrease the effects of the Ba, Sr, and O deficiencies on the dielectric properties of BST film. BST films deposited with Mn, Fe, and W doped targets have been obtained with 25% tuning and dielectric Q of  $\sim 100 - 240$  at room temperature for 1 - 20 GHz and DC bias field of 67kV/cm.

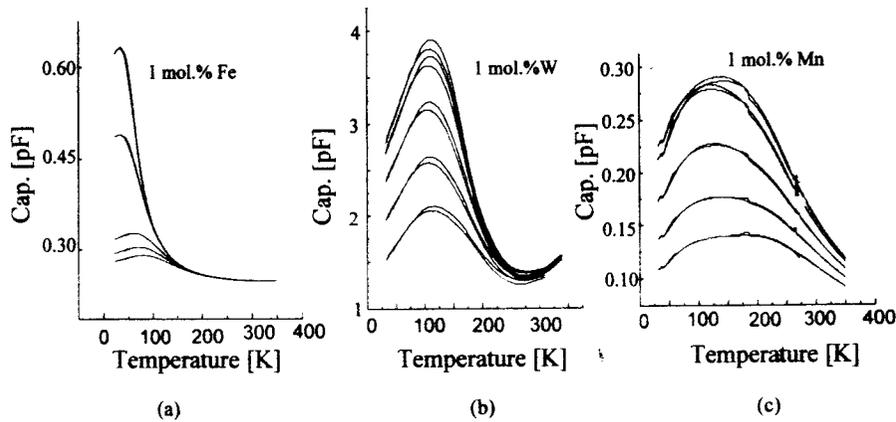


Fig. 4 Temperature dependent capacitance measurements at 1 MHz on BST ( $x=0.5$ ) films deposited with (a) 1mol.% Fe (b) 1mol.% W and (c) 1mol.%Mn-doped targets ( $E = 0$  to 67 kV/cm).

## CONCLUSIONS

The microwave dielectric properties measured at 1 – 20 GHz in BST films were analyzed as a function of target compensation and doping. Ba, Sr, and O deficiencies were observed in BST films using ICP and XRD. Films deposited with (Ba,Sr) compensated targets exhibited a high dielectric Q up to ~100 at room temperature. A strong correlation was observed between the film orientation and the dielectric loss. A further increase in the dielectric Q was observed by the addition of extrinsic dopants such as Mn, Fe and W ( $Q \approx 100-240$ ). The data shows that ferroelectric thin films can be used to build tunable microwave circuits that offer significant performance advantages over devices made from conventional semiconducting materials.

## ACKNOWLEDGMENTS

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