PULSED LASER DEPOSITION OF $Ba_xSr_{1-x}TiO_3$ THIN FILMS FOR FREQUENCY AGILE MICROWAVE ELECTRONICS

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ABSTRACT

Oriented, single phase thin films (~5000Å thick) of $Ba_xSr_{1-x}TiO_3$ (BST) have been deposited on to (100) MgO and $LaAlO_3$ (LAO) single crystal substrates using pulsed laser deposition (PLD). A strong correlation is observed between the microstructure of the deposited film and the dielectric tuning and loss at microwave frequencies. Microstructural defects observed in as deposited films include strain, due to film substrate lattice mismatch and oxygen and cation vacancies. Compensation of the ablation target with excess Ba and Sr is observed to increase the dielectric constant and to reduce the dielectric loss. Post-deposition, bomb annealing of films at high temperatures (1250°C) is observed to fill oxygen vacancies and increase grain size. The difference in the dielectric behavior for as-deposited and low temperature annealed BST films on MgO and BST films on LAO is observed and may be attributed to the differences in film stress. A further improvement in the dielectric behavior is observed by the addition of donor/acceptor dopants such as Mn. 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.

INTRODUCTION

Ferroelectrics are a class of non-linear dielectrics which exhibit an electric field dependent dielectric constant. This property is currently being used to develop frequency tunable microwave circuits. $Ba_xSr_{1-x}TiO_3$ (BST) is a solid solution ferroelectric material suitable for the microelectronic device due to its large electric field dependent dielectric constant and composition dependent Curie temperature. Thin film ferroelectrics offer the potential for low device operating voltage. A large electric field effect has already been demonstrated in ferroelectric films deposited by pulsed laser deposition (PLD)[1]. One of the most critical issues that needs to be addressed in developing tunable microwave devices is the dielectric loss (tanδ) at high frequencies. A loss tangent $\leq 5\times10^{-3}$ is desirable.

EXPERIMENTAL

BST targets were prepared by a standard solid-state reaction process. Powders of $BaTiO_3$ (BTO) and $SrTiO_3$ (STO) were mixed in a plastic vial using plastic balls for 30 minutes by 8000 SPEX Mixer. The mixture were pressed into 1" diameter targets at 15,000 pounds and calcined at 800°C for 4 hours. The calcined targets were then zirconia ball milled in a zirconia ceramic vial for 2 hours and pressed the targets again. The targets were then sintered at 1350°C for 6 hours. The PLD system used to grow BST films has been described previously[2]. BST films were characterized using x-ray diffraction (XRD) and scanning electron microscopy (SEM).

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Compositional analysis of BST films was determined by inductively coupled plasma-spectroscopy (ICP).

Interdigitated capacitors were deposited on top of the BST films through a PMMA lift off mask by e-beam evaporation of 1-2 μm thick Ag and a protective thin layer of Au. Temperature dependent measurements were performed at 1 MHz with DC bias changes (0-40V) using an HP 4284A. The DC resistance measurements at room temperature were carried out using a 1864 Megaohm at 10-40V. One to twenty GHz microwave measurements were made on an HP 8510C network analyzer at room temperature.

RESULTS AND DISCUSSION

As-deposited and low-temperature (≤ 1000°C) annealed films

BST (x=0.5) films grown on (100)MgO and (100)$LaAlO_3$(LAO) substrates were found to be single phase and exclusively oriented in the (100) direction. Typical FWHM of the ω-scan peaks for the (002) reflection of BST films on (100)MgO were 0.7° to 0.9°, and at or below the 0.16° resolution limit of the diffractometer for BST films grown on (100)LAO. The high frequency (1-20GHz) dielectric properties (capacitance and Q (1/tanδ)) of as-deposited BST films (x=0.5) on MgO and LAO substrates and of the annealed films at 1000° C for 24 hours in flowing O_2 are shown in Fig.1. It is observed that after the annealing process the device Q's increase in BST films on MgO. On the contrary the Q's decrease in BST films grown on LAO. Fig.2 shows SEM images of as- deposited BST films on MgO and LAO. Both films are polycrystalline with grain size is ~500Å. According to the film characterizations by XRD and SEM, no significant difference is seen in the film phase and the surface morphology, even though BST films on LAO, having a narrower rocking curve, show better crystallinity than BST films deposited on MgO. Film stress may be a critical factor in determining the differences of the dielectric properties. Fig.3 shows a possible stress field in each system forming from the lattice mismatch between the film and substrate. For BST films on MgO, the film (a_{bulk}=3.947Å) may be expanded near the interface to match to the larger lattice

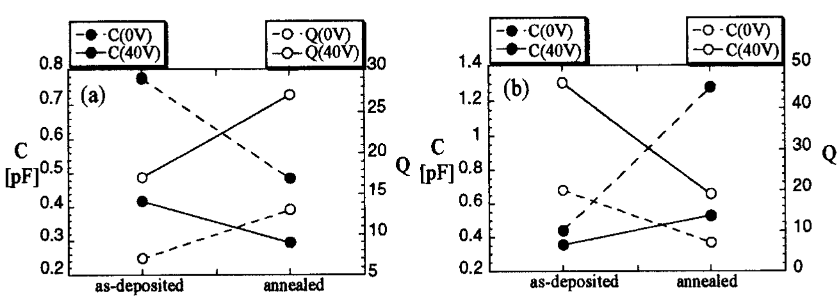

Figure 1 High frequency (1-20GHz) dielectric properties of as-deposited and low-temperature annealed BST (x=0.5) films (a) on MgO and (b) on LAO.

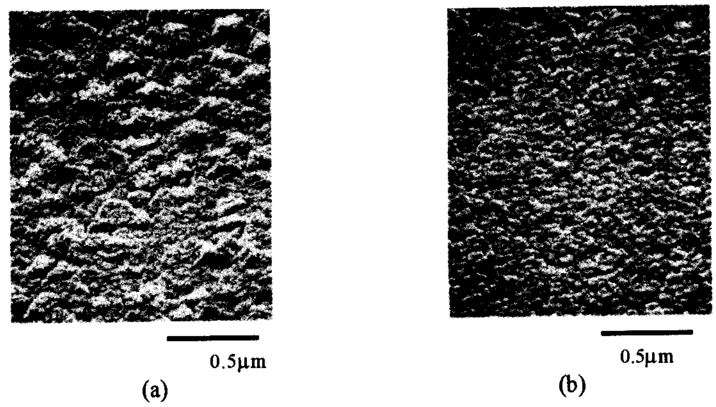

Figure 2 Scanning electron micrographs of as-deposited BST (x=0.5) films (a) on MgO and (b) on LAO .

of the substrate (4.213Å) and then contract further from the interface due to the interionic attractive forces within the film. Therefore, there are two competing force factors affecting the stress field of the film: tension by the MgO substrate and compression by the BST film. Two forces may be expected to compete with each other all the time within an elastic strain limit unless the film deform plastically. The change in the dielectric property before and after the low-temperature annealing process may be affected by this competition between two forces.

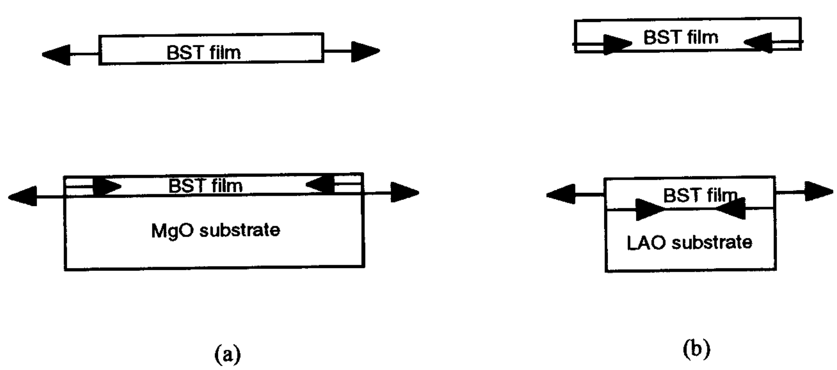

Figure 3 Schematic diagrams of a possible force factors affecting the stress field of BST (x=0.5) films (a) on MgO and (b) on LAO

In the interdigitated capacitor geometry, the compression, which is parallel to the applied electric field and subsequently to the polarization field for the oriented BST (x=0.5) film, is expected to decrease the net polarization, (i.e. a reduced ionic displacement). In Fig.1 the as-deposited BST film on MgO shows a higher capacitance than the as-deposited BST film on LAO even though

LAO substrate has higher dielectric constant (ε~25) than MgO substrate (ε~9), indicating a smaller substrate effect on the dielectric property of the film. After annealing, the trend is reversed. It may be inferred that the as-deposited BST film on MgO is under tension, which promotes the polarization of electric dipoles, and the annealed film is under compression, which constrains the polarization. For BST films deposited onto LAO the dielectric properties can be explained with the same argument, but reversed since the lattice parameter for LAO is smaller (3.787Å) than BST.

High-temperature (1050°C~1250°C)annealed films

We observed that annealing at a high temperature (≥1100°C) degraded the film surface. BST films deposited on MgO and LAO were annealed in a BST ceramic bomb at up to 1200°C and 1250°C for 2 hrs in flowing O_2, respectively. The annealed films did not show any surface degradation. Fig.4 shows X-ray rocking curve widths for BST films deposited onto (100)MgO as a function of the annealing temperature. Increasing the annealing temperature leads to a decrease in ω indicating a more highly oriented film. The dielectric properties of BST films (x=0.5) on MgO and LAO is shown in Fig.5. A similar trend is observed in both systems unlike

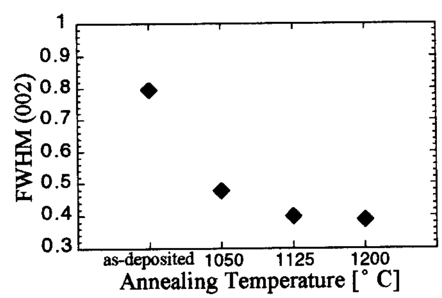

Figure 4 X-ray rocking curve widths for BST films deposited onto (100)MgO as a function of the annealing temperature.

the low temperature annealing case. As the annealing temperature increases, the dielectric constant and the % tuning decrease and the loss decreases (higher Q). Both the XRD and SEM indicate that the high-temperature annealed films had better crystallinity, smaller lattice parameter, more smooth surface and larger grain size (~2000Å). As lattice size decreases, the film is under increased compression. However, a smaller polarization is observed for less energy consuming and the film has a lower dielectric loss.

Films with compensated BST targets with excess Ba and Sr

Ba and Sr deficiency has been reported in the BST film and BST single crystal[3,4]. To keep the electroneutrality the cation deficiency may cause an oxygen deficiency. This can be an

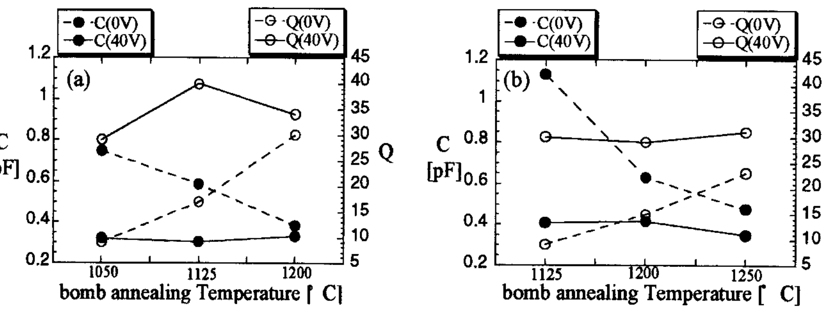

Figure 5 High frequency (1-20GHz) dielectric properties of high-temperature annealed BST (x=0.5) films (a) on MgO and (b) on LAO.

additional loss source of dielectric loss. To correct for deficiencies in Ba and Sr, BST films were grown using targets with excess Ba and Sr. The films deposited with a compensated target show a higher capacitance (i.e. larger dielectric constant) and a lower dielectric loss than those deposited with an uncompensated target. The chemical composition of the films deposited with compensated and uncompensated targets was determined using ICP. All samples show (Ba,Sr) deficiencies (~12% Ba, ~4% Sr) without any trend regardless of how much (Ba,Sr) was added. According to the XRD patterns and the chemical analysis, no significant chemical difference was observed for all the BST films analyzed. However, some structural differences are observed. The films deposited with a compensated target show a large grain size (~1000Å). The X-ray diffraction pattern show <110> and/or <111> peaks together with <100> peak in most of these films. Table 1 shows the dielectric properties of BST films grown on MgO with (Ba,Sr) compensated targets. Films deposited from compensated targets also show a rougher surface morphology. There have been several investigation on increase in the surface roughness with an increase in Ba deficiency[5]. This observation is consistent with the results of our chemical analysis.

Films with (Fe, Mn) doped targets

It has been reported that doping with Mn and Fe into the bulk BST showed a significant reduction in the loss tangent[6]. BST films were deposited with Fe and Mn doped targets. Data is presented in Table 1. These films exhibit a lower capacitance, a lower % tuning and a higher Q than those deposited with an undoped and uncompensated target. According to the XRD data, the lattice parameter for Fe-doped film decreases, indicating that Fe^{3+} ions substitute into Ti^{4+} sites. However, the lattice parameter for Mn-doped film is almost the same as those for an undoped film. Fe^{3+} ion acts as an acceptors while Mn ions can act as either a donors or an acceptors. This analysis is consistent with the resistivity measurements and the temperature dependent capacitance measurements. The resistivities for our undoped films, Fe-doped films and Mn-doped films were on the order of $>10^9$, $>10^{10}$, and 10^7~10^9 Ω-cm, respectively. The Curie temperature (~40K) for Fe doped film appears at very low temperature and the phase transition peak (~150K) for Mn doped film has a broad width. The former case may be due to the strong bondings between Fe ion and oxygen ion, making hard to polarize or undergo a phase transition, and the latter case may be due to the chemical inhomogeneities because of the large number of possibe sites for Mn.

Table 1 High frequency (1-20GHz) dielectric properties at RT (0-40V DC bias) for BST films

dopant [at.%]	excess [at.%]		averaged dielectric properties			highest Q data		
	Ba	Sr	C_{0V}-C_{40V} [pF]	Tuning [%]	Q_{low}-Q_{high}	C_{0V}-C_{40V} [pF]	Tuning [%]	Q_{low}-Q_{high}
-	-	-	0.485-0.295	39	13-27	0.374-0.222	41	18-45
-	2	2	0.860-0.581	32	29-45	1.411-1.058	25	80-107 (1-10GHz)
-	4	4	0.587-0.508	14	50-56	0.462-0.404	13	75-82 (1-15GHz)
Fe 1.0	-	-	0.183-0.181	1	79-86	0.172-0.170	1	105-114 (1-15GHz)
Mn 3.4	-	-	0.223-0.249	10	47-53	0.347-0.270	22	92-125 (1-10GHz)
Mn 3.4	10.44	2.32	0.348-0.299	14	51-56	0.285-0.251	12	81-88
Mn 1.0 Fe 0.5	6	3	0.171-0.157	8	85-125	0.177-0.162	8	105-173

CONCLUSIONS

High quality BST films were grown by PLD for applications in tunable microwave circuits. The film morphology and structure were characterized by SEM and XRD. Film composition analysis was made by ICP. The microwave (1-20GHz) dielectric properties of BST films were analyzed as a function of substrate type, post deposition annealing temperature, taget compensation and donor/acceptor doping. A different trend in the annealing effect was observed for BST films grown on LAO at a low-temperature (≤1000°C) annealing.

After a high-temperature (1050°C~1250°C) annealing process, it was observed for both BST films on MgO and BST films on LAO that the dielectric constant and the dielectric loss decrease (a higher Q). The films deposited with (Ba,Sr) compensated and/or (Mn,Fe) doped targets showed a lower dielectric loss than films grown with uncompensated and undoped tanget.

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