PULSED LASER DEPOSITION OF $Ba_xSr_{1-x}TiO_3$ FILMS ON MgO, $LaAlO_3$ AND $SrTiO_3$ FOR TUNABLE MICROWAVE APPLICATIONS

WONTAE CHANG*, JAMES S. HORWITZ**, WON-JEONG KIM***, JEFFREY M. POND**, STEVEN W. KIRCHOEFER**, CHARLES M. GILMORE* **, SYED B. QADRI**, AND DOUGLAS B. CHRISEY**

* *Institute for Materials Science, School of Engineering and Applied Science George Washington University, 725 23rd Street, NW, Washington, D.C. 20052*

** *Naval Research Laboratory, 4555 Overlook Ave., SW, Washington, D.C. 20375*

*** *SFA Inc., 1401 McCormick Dr., Largo, MD 20774*

ABSTRACT

Single phase $Ba_xSr_{1-x}TiO_3$ (BST) films (~0.5–7 μm thick) have been deposited onto single crystal substrates (MgO, $LaAlO_3$, $SrTiO_3$) by pulsed laser deposition. Silver interdigitated electrodes were deposited on top of the ferroelectric film. The room temperature capacitance and dielectric Q (1/tanδ) of the film have been measured as a function of electric field (≤ 80 kV/cm) at 1 – 20 GHz. The dielectric properties of the film are observed to strongly depend on substrate type and post-deposition processing. After annealing (≤1000° C), it was observed that the dielectric constant and % tuning decreased and the dielectric Q increased for films deposited onto MgO, and the opposite effect was observed for films deposited onto $LaAlO_3$. Presumably, this change in dielectric properties is due to the changes in film stress. Very thin (~50 Å) amorphous BST films were successfully used as a stress-relief layer for the subsequently deposited crystalline BST (~5000 Å) films to maximize % tuning and dielectric Q. Films have been deposited from stoichiometric targets and targets that have excess Ba and Sr. The additional Ba and Sr has been added to the target to compensate for deficiencies in Ba and Sr observed in the deposited BST (x=0.5) films. Films deposited from compensated targets have higher dielectric constants than films deposited from stoichiometric targets. Donor/acceptor dopants have also been added to the BST target (Mn, W, Fe ≤ 4 mol.%) to further improve the dielectric properties. The relationship between the dielectric constant, the dielectric Q, the change in dielectric constant with electric field is discussed.

INTRODUCTION

Ferroelectrics are non-linear dielectrics that exhibit an electric field dependent dielectric constant [1]. This property is currently being used to develop a new class of 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. The critical issues that need to be addressed for tunable microwave devices are 1) the magnitude change in the dielectric constant as a function of the applied field and 2) dielectric Q (1/tanδ) at microwave frequencies. Most microwave applications will require a % tuning ≥ 50, where % tuning is defined as $\{(C(0)-C(E))/C(0)\}\times 100$, and a dielectric Q ≥ 200.

In this paper, we report on the effect of substrate type and film structure on the dielectric properties of BST thin films.

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EXPERIMENTAL

BST (x=0.5 and 0.6) thin films (~5000 Å) were grown on (100)MgO, (100)$LaAlO_3$ (LAO) and (100)$SrTiO_3$ (STO) single crystal substrates at 750° C in an oxygen ambient pressure of 350 mTorr by pulsed laser deposition (PLD). BST films were also deposited using 2-step growth techniques. First, a thin (~50 Å) amorphous layer of BST was deposited at room temperature. The substrate temperature was then increased to 750° C and a second BST film (~5000 Å) was deposited. The deposited films were characterized for structure and morphology using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Films were annealed in flowing O_2 at 900 -1250° C for 6-24 hours. Film composition was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES). Interdigitated capacitors with gaps from 5 to 12 μm were deposited on top of the BST films through a polymethylmethaacrylate (PMMA) lift off mask by *e*-beam evaporation of 1-2 μm thick Ag and a protective thin layer of Au. Microwave input reflection coefficient S_{11} 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) [2]. Dielectric constants were calculated from the device dimensions.

RESULTS AND DISCUSSION

Substrate type

Table I shows a general trends and maximum data of dielectric properties for the BST (x=0.5) films (1 – 20 GHz) as a function of substrate type, e.g., MgO and LAO. The related data is presented in Table II. The reported values for the dielectric properties are nominally at 10 GHz although most of the samples were very stable over the whole frequency range (1–20 GHz), except for the films deposited onto STO, which was relatively stable at around 5 GHz only. STO may not be a suitable substrate for microwave device and thin film applications in the interdigitated capacitor geometry because of its high dielectric constant (ε~300 at room temperature). As shown in Table I, the dielectric constant and % tuning are strongly correlated, for example, as dielectric constant increases, % tuning also increases. However, it was also observed that as % tuning increases, the dielectric Q is decreased, an inverse relationship, e.g., Kramers-Krönig relations. BST films deposited onto MgO have higher dielectric Q than those onto LAO, and BST films onto LAO have higher % tuning than the films onto MgO. These observations raise two questions; 1) how do we optimize the film properties to achieve both high % tuning and high Q at the same time and 2) why does the substrates affect the dielectric

Table I. The trends and maximum data of dielectric properties for the BST (x=0.5) films (1 – 20 GHz) as a function of substrate type.

	trends		maximum data	
substrate	MgO	LAO	MgO	LAO
film dielectric constant	1000	1500	2973	3328
tuning [%] @67kV/cm	30	50	62	75
Q (1/tanδ)	45	25	100-250	50-70

properties of the BST (x=0.5) films. Films deposited onto both substrates were found by XRD to be single phase and exclusively oriented in the (100) direction. Typical full width half maximum (FWHM) of the ω-scan peaks for the (002) reflection of BST films on (100) MgO were 0.7° to 0.9°. For films deposited onto LAO, ω(FWHM) was below the resolution limit of the diffractometer (0.16°). Although the lattice mismatch between the BST film and substrate (~7% for BST on MgO and ~4% for BST on LAO) are relatively large, deposited films on all substrates were oriented both in-plane and with respect to the surface normal. The origin of the differences in the dielectric properties as a function of substrate type may be caused by the difference in the film stress due to the lattice and thermal expansion mismatch between film and substrate (Table II).

Table II. Lattice parameters (a), thermal expansion coefficients (α), and dielectric constant (ε) of MgO and LAO substrates.

substrate	MgO	LAO	Bulk BST (x=0.5)
a [Å]	4.213	3.787 (pseudocubic)	3.947
α [10^{-6}/°C]	13.8	10.0	10.5
ε (at RT)	9.5	25	~10^3

Post-deposition processing

Previously, we reported on the effect of stress on the dielectric properties of BST films deposited onto MgO and LAO substrates [3,4]. It was observed that for BST films deposited onto MgO, the dielectric constant decreased and dielectric Q increased after a post-deposition anneal (≤ 1000° C). However, for films deposited onto LAO, the post-deposition anneal resulted in a significant increase in the dielectric constant and a decrease in Q [4]. The observed dielectric properties of the BST films as a function of substrate type and post deposition annealing temperature are attributed to the changes in film stress, which affects the extent of ionic polarization [4].

Fig. 1 shows XRD patterns of (004) and (024) reflections for (001) oriented BST films deposited onto LAO at 750° C. From these reflections we can calculate the normal lattice

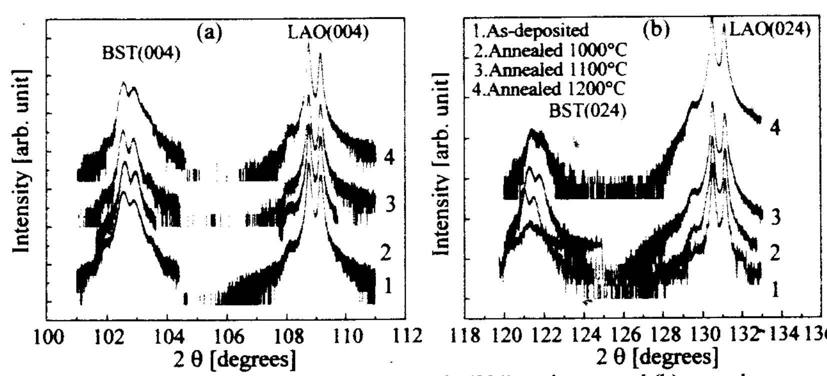


Fig. 1 X-ray diffraction patterns of (a) normal symmetric (004) peak scan and (b) normal asymmetric (024) peak scan for highly oriented BST film deposited onto LAO at 750° C.

parameter ($a_\perp$) and in-plane lattice parameter ($a_\parallel$) for a pervoskite structure (cubic) of BST (x=0.5) or, possibly, a distorted pervoskite structure (tetragonal). As shown in Fig. 1, almost no change is observed in the peak position for the (004) reflections of (001) oriented BST films, but significant changes are observed in that for the (024) reflections compared to the corresponding reflection peaks of the LAO substrate, indicating almost no change in normal lattice parameter but significant changes in in-plane lattice parameter.

Fig. 2 shows how the lattice parameters and dielectric constant changes for BST films as a function of annealing temperatures. The dielectric constant changes are strongly correlated with the in-plane parameter changes. These observations are very important to our understanding of how to control the dielectric properties of the film. The dielectric properties observed in Fig. 2 can also be explained by lattice size effect without any stress effect [5]. The polarization, related to dielectric constant, can be expressed as a function of two competing factors, the number of dipoles per volume and the magnitude of each dipole, which are directly related to the lattice size. It has been reported that the latter factor dominates the overall effect of the lattice size on the dielectric properties [5]. At this point, it is not clear which effect, stress or lattice size, dominates the dielectric properties of the film. A possible contribution from the lattice size effect can not be ruled out completely.

Two important characteristics on the dielectric properties of the highly oriented BST films are observed. One is that both films on MgO and LAO showed a strong correlation of the dielectric constant, which is directly proportional to % tuning, and the dielectric Q. The other is that the effect of low temperature (≤ 1000° C) annealing is significantly different in the BST films on MgO and the films on LAO. Therefore, it may be hard to get a high % tuning from the annealed BST films deposited onto MgO because of the decrease in the dielectric constant.

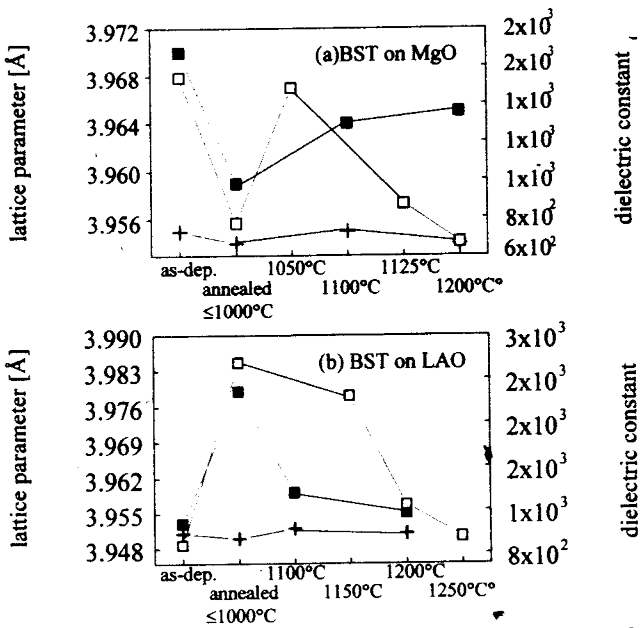
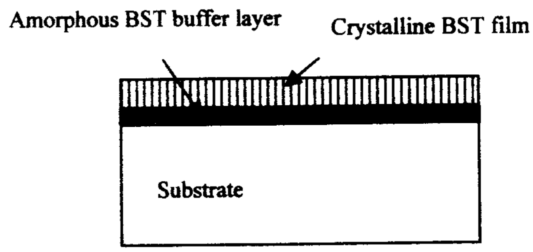


Fig. 2 Lattice parameter and dielectric constant changes with annealing temperature for ~0.2 μm thick BST (x=0.5) films deposited (a) on MgO and (b) on LAO (+ = normal lattice parameter, ■ = in-plane lattice parameter, □ = dielectric constant).



Step 1: Deposit Stress Relief Film using ~50 Å thick amorphous BST buffer layer.
Step 2: Obtain High Dielectric Constant using ~5000 Å thick crystalline BST layer, annealing, and (Ba,Sr) compensation.
Step 3: Obtain High Dielectric Q using annealing, (Ba,Sr) compensation and (Fe,Mn,W) doping.

Fig. 3 A possible way to get both high Q and high tuning in the BST film at the same time.

To remove the stress in the deposited BST films, a thin (~50 Å) amorphous layer of BST was first deposited onto the dielectric substrate at room temperature (Fig. 3). The substrate was then heated to 750° C in O_2 where the remainder of the 5000 Å thick film was deposited. An analysis of the X-ray diffraction pattern indicates that the deposited film is single phase but not a single crystallographic orientation. Without a compressive stress with respect to the electric field, the film ions are more free to be polarized. We expect that the stress relieved film should have a high dielectric constant and therefore a larger tuning range. Several methods to increase the dielectric constant are presented in Fig. 3.

Fig. 4 shows how changes in the stress in an oriented BST film deposited at 750° C influences the dielectric properties. This dielectric behavior is dramatically different in BST films in which the stress has been reduced.

CONCLUSIONS

BST films deposited onto (100) MgO and (100) LAO substrates at 750° C in 350 mTorr of O_2 are highly oriented. The film properties are significantly different from the corresponding bulk material, e.g., the dielectric constant of the film is lower and its temperature dependence is much broader, and also show to depend on the substrate type. Presumably, this is due to stress in the films as a consequence of the lattice mismatch between film and substrate and differences in the thermal expansion coefficients. The desirable dielectric properties for microwave application, (e.g., a high % tuning and a high dielectric Q), can be achieved by relieving the film stress, which results in an increase in the dielectric constant. A very thin amorphous BST buffer layer can be used to relieve the film stress. The dielectric constant of the stress relieved film can be increased by a post deposition anneal. At the same time, the annealing is observed to increase the dielectric Q of the film.

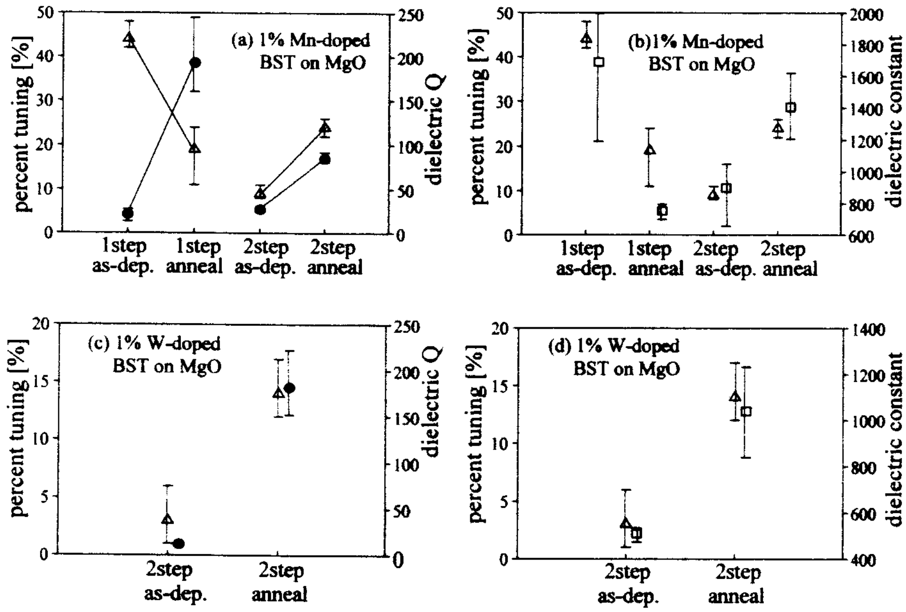


Fig. 4 Dielectric properties (1 – 20 GHz) for (a) and (b) 1% Mn doped BST films and (c) and (d) 1% W doped BST films (1 step and 2 step indicate film deposition without and with a BST buffer layer, respectively. Δ = percent tuning, ● =dielectric Q, □ =dielectric constant).

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