

The effect of annealing on the microwave properties of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ thin films

Wontae Chang,^{a)} James S. Horwitz, Adriaan C. Carter, Jeffrey M. Pond, Steven W. Kirchoefer, Charles M. Gilmore, and Douglas B. Chrisey
Naval Research Laboratory, Washington, D.C. 20375

(Received 15 June 1998; accepted for publication 15 December 1998)

Oriented, single phase thin films ($\sim 5000 \text{ \AA}$ thick) of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ (BST) have been deposited onto (100) MgO and (100) LaAlO_3 (LAO) substrates using pulsed laser deposition. The capacitance and dielectric Q ($1/\tan \delta$) of as-deposited and annealed films have been measured from 1 to 20 GHz as a function of electric field (0–80 kV/cm) at room temperature using interdigitated Ag electrodes deposited on top of the film. For films deposited onto MgO, it is observed that, after a postdeposition anneal (1000–1200 °C), the dielectric constant decreases and the dielectric Q increases. For films deposited onto LAO, a postdeposition anneal ($\leq 1000 \text{ °C}$) resulted in a significant increase in the dielectric constant and a decrease in Q . The observed dielectric properties of the BST films are attributed to the changes in film stress, which affects the extent of ionic polarization. © 1999 American Institute of Physics. [S0003-6951(99)03307-0]

Ferroelectrics are a class of nonlinear dielectrics which exhibit an electric field dependent dielectric constant.^{1–3} This property is currently being used to develop a new class of frequency tunable microwave circuits. $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ (BST) is a solid solution ferroelectric material suitable for micro-electronic device applications due to its large electric field dependent dielectric constant and composition dependent Curie temperature. A large electric field effect has already been demonstrated in ferroelectric films deposited by pulsed laser deposition (PLD).^{4,5} The critical properties that need to be optimized for tunable microwave devices are the magnitude of the change in the dielectric constant as a function of the applied electric field and dielectric loss at microwave frequencies.

In this letter, we report an investigation of the effects of a postdeposition anneal on the dielectric properties of BST ($x=0.5$) thin films measured at microwave frequencies (1–20 GHz). $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ thin films ($\sim 5000 \text{ \AA}$) were grown on (100) MgO and (100) LaAlO_3 (LAO) single crystal substrates at 750 °C in an oxygen ambient pressure of 350 mTorr by pulsed laser deposition (PLD). The BST films were postdeposition annealed in flowing O_2 at 900–1000 °C for 24 h. Films were also annealed at 1050–1250 °C for 2 h using an encapsulated-sample annealing technique.⁶ BST films were characterized for structure and morphology using x-ray diffraction (XRD) and scanning electron microscopy (SEM). Film composition was determined by inductively coupled plasma-optical emission spectroscopy (ICP). Interdigitated capacitors with gaps from 6 to 12 μm were deposited on top of the BST films through a polymethylmethacrylate (PMMA) lift off mask by e -beam evaporation of 1 to 2- μm -thick Ag and a protective thin layer of Au. Microwave 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 ($1/\tan \delta$).⁷ Dielectric constants (ϵ) were calculated using the device dimensions.

BST ($x=0.5$) films grown on (100) MgO and (100) LAO substrates were found by XRD to be single phase and exclusively oriented in the (100) direction. Typical full-width at half-maximum (FWHM) of the ω -scan peaks for the (002) reflection of BST films on (100) MgO were 0.7°–0.9°. For films deposited onto LAO, ω (FWHM) was 0.16° (the resolution limit of the diffractometer). From the XRD data, it was determined that the as-deposited films had larger lattice parameters than the bulk BST, presumably due to oxygen deficiencies. Postdeposition annealing of deposited films in O_2 caused the lattice parameter to decrease approaching the bulk value. As the annealing temperature increased, the ω -scan FWHMs for BST film on MgO reached a minimum of $\sim 0.4^\circ$. The BST ($x=0.5$) films were Ba and Sr deficient, (Ba/Ti=0.45 and Sr/Ti=0.49), as determined by ICP. SEM images of as-deposited BST films on MgO and LAO showed that both films were fine grained with an average grain size of $\sim 500 \text{ \AA}$.

While no significant differences were seen in the microstructure of BST films deposited onto MgO and LAO, i.e., deposited films on both substrates are single phase, oriented and have similar grain size, we observed significant differences in the microwave properties for as-deposited films and films which have been annealed at low temperature ($\leq 1000 \text{ °C}$) as shown in Table I. The data used in this analysis was observed to be a representative of several samples measured under similar conditions. The reported values for capacitance and Q are nominally at 10 GHz although most of the samples were very stable over the frequency range of 1–20 GHz. For the same capacitor geometry, the as-deposited BST film on MgO shows a higher capacitance ($\epsilon = 1540 \pm 382$) and a lower dielectric Q than the as-deposited BST film on LAO ($\epsilon = 874 \pm 54$). After annealing, the capacitance (C) ($\epsilon = 770 \pm 70$) and % tuning, defined as $\{[C(0) - C(E)]/C(0)\} \times 100$ where E is an applied electric

^{a)}Institute for Materials Science, School of Engineering and Applied Science, George Washington University, Washington, D.C. 20052. Electronic mail: chang@ccf.nrl.navy.mil

TABLE I. 1–20 GHz dielectric properties as a function of electric field (0–67 kV/cm) of as-deposited and low-temperature ($\leq 1000^\circ\text{C}$) annealed BST ($x=0.5$) films on MgO and on LAO. The number of device measurements is 12 and 21 for BST on MgO and LAO, respectively. (The interdigitated capacitor has eight fingers with 6 μm gap, 80 μm length, and 10 μm width.)

	Electric field [kV/cm]	BST on MgO		BST on LAO	
		as-deposited	annealed	as-deposited	annealed
C [pF]	0	0.775 ± 0.193	0.387 ± 0.035	0.440 ± 0.028	1.281 ± 0.161
	67	0.418 ± 0.121	0.253 ± 0.031	0.354 ± 0.039	0.594 ± 0.098
$Q (= 1/\tan \delta)$	0	7 ± 1	15 ± 6	20 ± 1	6 ± 1
	67	17 ± 4	31 ± 15	46 ± 13	19 ± 3

field, decrease and the dielectric Q increases in BST films on MgO. The opposite effect is observed for films deposited onto LAO. The capacitance ($\epsilon = 2545 \pm 319$) and % tuning increase and the dielectric Q decreases in postdeposition annealed BST films grown on LAO.

The temperature dependence of the dielectric properties for BST films is significantly different from the corresponding bulk material. The variation in dielectric constant of BST system have been reported as a function of sample composition,^{1,8} crystallinity,^{9,10} grain size,^{11–13} and stress.¹⁴ Of these factors, the large difference in the dielectric behavior for the BST films deposited onto MgO and LAO may be only attributed to the differences in film stress because no other microstructural differences are observed. The induced film stress arises from several contributions (e.g., a lattice mismatch and a difference in the thermal expansion coefficients between the film and substrate). The relevant data for the single crystalline substrates and bulk BST ($x=0.5$) are summarized in Table II.

Figure 1 shows a possible stress field in each system caused by the lattice mismatch and the thermal expansion mismatch. For BST films on MgO, the lattice of the film may be expanded near the interface to match to the larger lattice of the substrate and compressed on cooling by the thermal expansion mismatch ($\alpha_{\text{BST}} < \alpha_{\text{MgO}}$). As the film is annealed, the lattice constant of the film contracts due to the film relaxation. Therefore, there are two competing force factors affecting the stress field of the film, which generate film strain. The dielectric properties of the film are affected by this force competition and the lattice contraction. As mentioned above, the observed lattice parameter indicates that the as-deposited BST films contain significant oxygen vacancies.^{15,16} These oxygen vacancies can be filled by annealing in flowing O_2 . This process cause a lattice contraction in the BST films. It is worthwhile to note that the study of film stress due to the film-substrate mismatch and difference in thermal expansion coefficients is complicated because additional change in the film lattice parameter. These vacancies may increase, decrease, or screen the overall film stress. In the interdigitated capacitor geometry, the compres-

sion, which is parallel to the applied electric field (Fig. 1) 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). As shown in Table I the as-deposited BST film on MgO exhibits a higher capacitance and a lower Q than both the as-deposited BST film on LAO and the annealed BST film on MgO. It may be inferred from this observation 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 are reversed. This is because the lattice parameter and the thermal expansion coefficient for LAO are smaller than for BST. This interpretation of the strain induced modification of the dielectric properties of the BST film is consistent with several reports on the study of stress on the dielectric constants for bulk ferroelectric and incipient ferroelectric materials.^{14,17,18} For bulk BaTiO_3 ,¹⁴ SrTiO_3 ,¹⁷ and KTaO_3 ,¹⁸ pressure induced changes were observed in the dielectric constant, which was shown to decrease under compression and increase in extension. At the present time we can only discuss the effect in thin films qualitatively as we do not know exactly the zero stress state for the thin films. We have identified forces that are both compressive and tensile however, we do not have well defined equilibrium position with which to reference the tran-

TABLE II. Lattice parameters (a) and thermal expansion coefficients (α) of MgO and LAO substrates and bulk BST ($x=0.5$).

	MgO	LaO	Bulk BST ($x=0.5$)
a [\AA]	4.213	3.787 (Pseudocubic)	3.947
α [$10^{-6}/^\circ\text{C}$]	13.8	10.0	10.5

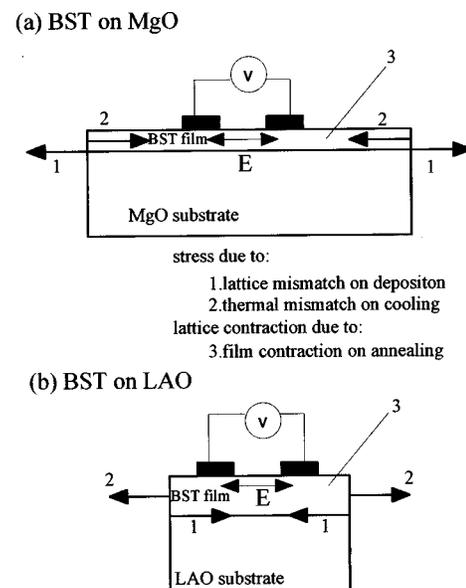


FIG. 1. Schematic diagrams of a possible force factors affecting the stress field of BST ($x=0.5$) films (a) on MgO and (b) on LAO.

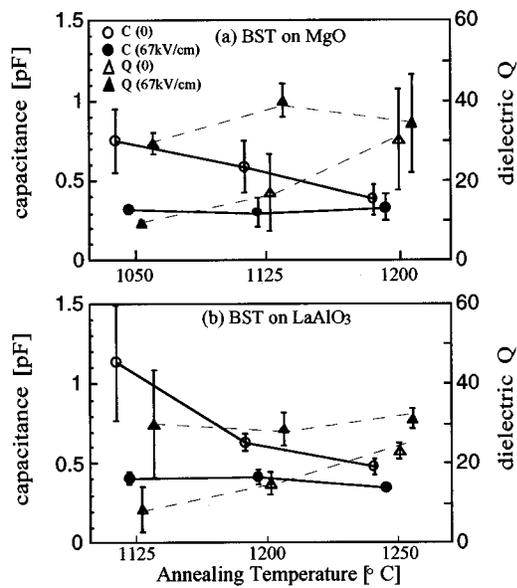


FIG. 2. 1–20 GHz dielectric properties as a function of electric field (0–67 kV/cm) of high-temperature annealed BST ($x=0.5$) films (a) on MgO and (b) on LAO. The error bar indicates standard deviation.

sition between a film under tension to a film under compression.

BST films were annealed in a BST ceramic vessel for 2 h in flowing O₂ at temperatures up to 1200 °C for MgO substrates and up to 1250 °C for LAO substrates. The high-temperature annealed films did not show any surface degradation but showed smaller lattice parameters, narrower x-ray rocking curves, smoother surfaces, and larger grain sizes (~ 2000 Å) as characterized by XRD and SEM. The dielectric properties of BST films ($x=0.5$) deposited on MgO and LAO which have been postannealed at $T \leq 1250$ °C are shown in Fig. 2. As the annealing temperature increases, the capacitance and the % tuning decrease and the dielectric Q increases. Since the film is more contracted as the lattice parameter decreases, the ionic displacement is reduced which results in lower net polarization. This decrease in polarization lowers the dielectric constant which results in lower dielectric loss as expected from the Kramer–Krönig relations. The change in dielectric properties with lattice parameter is in agreement with literature reports on the cell volume effect in BST system. In that study, the authors observed that a decrease in lattice parameter leads to decrease in T_C and dielectric loss.^{19,20} The decrease in T_C means lower dielectric

constant, lower tuning, and lower dielectric loss for our BST system (e.g., $x=0.5$). Our results are consistent with this as we observe that the increase in the % tuning is related to the increase in the dielectric constant.

In summary, the microwave (1–20 GHz) dielectric properties (ϵ) $\tan \delta$ of pulsed laser deposited BST ($x=0.5$) films were analyzed as a function of substrate type and postdeposition annealing temperature. After a high-temperature (1050–1250 °C) anneal, it was observed that the dielectric constant and the dielectric loss decreased for BST films on both MgO and LAO. A different trend in the annealing effect was observed for BST films grown on LAO with low-temperature (≤ 1000 °C) annealing. The change in dielectric properties before and after annealing is attributed to the change in film stress and the contraction in film lattice.

Support of this research has been provided by Office of Naval Research and SPAWAR. This work was performed when A.C.C. was an NRL/NRC Cooperative research associate.

- ¹L. Davis, Jr. and L. G. Rubin, *J. Appl. Phys.* **24**, 1194 (1953).
- ²K. M. Johnson, *J. Appl. Phys.* **33**, 2826 (1962).
- ³K. Bethe and F. Welz, *Mater. Res. Bull.* **6**, 209 (1971).
- ⁴K. R. Carroll, J. M. Pond, D. B. Chrisey, J. S. Horwitz, R. E. Leuchtner, and K. S. Grabowski, *Appl. Phys. Lett.* **62**, 1845 (1993).
- ⁵J. S. Horwitz, D. B. Chrisey, J. M. Pond, R. C. Y. Auyeung, C. M. Cotell, K. S. Grabowski, P. C. Dorsey and M. S. Kluskens, *Integr. Ferroelectr.* **8**, 53 (1995).
- ⁶A. C. Carter, J. S. Horwitz, D. B. Chrisey, J. M. Pond, S. W. Kirchoefer, and W. Chang, *Integr. Ferroelectr.* **17**, 273 (1997).
- ⁷S. W. Kirchoefer, J. M. Pond, A. C. Carter, W. Chang, K. K. Agarwal, J. S. Horwitz, and D. B. Chrisey, *Microwave Opt. Technol. Lett.* **18**, 168 (1998).
- ⁸T. Nakamura, Y. Yamanaka, A. Morimoto, and T. Shimizu, *Jpn. J. Appl. Phys., Part 1* **34**, 5150 (1995).
- ⁹A. Nazeri and M. Kahn, *J. Mater. Sci. Lett.* **14**, 1085 (1995).
- ¹⁰M. S. Tsai, S. C. Sun, and T. Y. Tseng, *J. Appl. Phys.* **82**, 3482 (1997).
- ¹¹W. R. Buessem, L. E. Cross, and A. K. Goswami, *J. Am. Ceram. Soc.* **49**, 33 (1966).
- ¹²K. Kinoshita and A. Yamaji, *J. Appl. Phys.* **47**, 371 (1976).
- ¹³M. P. McNeal, S. J. Jang, and R. E. Newnham, *J. Appl. Phys.* **83**, 3288 (1998).
- ¹⁴W. R. Buessem, L. E. Cross, and A. K. Goswami, *J. Am. Ceram. Soc.* **49**, 36 (1966).
- ¹⁵S. Shin, *Mater. Res. Bull.* **16**, 299 (1981).
- ¹⁶J. Ye and K. Nakamura, *Phys. Rev. B* **48**, 7554 (1993).
- ¹⁷T. Shimizu, *Solid State Commun.* **102**, 523 (1997).
- ¹⁸W. R. Abel, *Phys. Rev. B* **4**, 2696 (1971).
- ¹⁹L. Zhang, W. L. Zhong, Y. G. Wang, and P. L. Zhang, *Solid State Commun.* **104**, 263 (1997).
- ²⁰I. V. Barskii, O. G. Vendik, A. D. Smirnov, and G. S. Khizha, *Sov. Phys. Tech. Phys.* **34**, 1065 (1990).