The effect of annealing on the structure and dielectric properties of $Ba_xSr_{1-x}TiO_3$ ferroelectric thin films

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(Received 9 February 1996; accepted for publication 26 April 1996)

The effect of a postdeposition anneal on the structure and dielectric properties of epitaxial $Ba_xSr_{1-x}TiO_3$ (BST) thin films (x=0.35–0.65) have been measured. The films were grown by pulsed laser deposition on $LaAlO_3$ (001) substrates. The films were single phase and (001) oriented with a lattice parameter larger than the bulk. The dielectric properties of the x=0.35 film exhibited a broad temperature dependence and a peak at 168 K, which is 36 K below the peak observed in bulk BST (x=0.35). Annealing films for 8 h in flowing oxygen at 900 °C caused the lattice parameter to decrease and dielectric properties to become more like the bulk. Annealing also resulted in an increased electric field dependent dielectric tuning without increased dielectric loss.
 [S0003-6951(96)00127-1]

Ferroelectrics are a class of nonlinear dielectrics that exhibit an electric field dependent dielectric constant. These materials are currently being used to develop active microwave electronics such as phase shifters, frequency agile filters, and tunable high Q resonators.[1,2] Thin film ferroelectrics offer several advantages over bulk ferroelectrics for these applications. Large electric fields (0–200 kV/cm) can be achieved in thin films (~0.5 μm) using low bias voltages (0–10 V).[2] $Ba_xSr_{1-x}TiO_3$ (BST) is currently the material of choice for microwave applications due to its low loss and composition dependent Curie temperature, T_c. The T_c of bulk BST ranges from 30 to 400 K for $x=0$ to $x=1$, respectively.[3] The ability to control the dielectric properties in a simple way will allow device structures to be easily optimized for maximum tunability and minimum loss at the desired frequency and operating temperature. We report an investigation of the effects of a postdeposition anneal on the structural and dielectric properties of BST thin films.

Thin films of BST on (001) $LaAlO_3$ were grown by pulsed laser deposition (PLD) for compositions x=0.35, 0.50, and 0.65. The PLD system used to grow these BST films has been described previously in more detail.[4,5] The films were grown on $LaAlO_3$ at 750 °C in an oxygen ambient pressure of 350 mTorr to a total film thickness of 0.6 μm.[6] The films were then cooled to room temperature in oxygen at ~10 °C/min.

Films were annealed in flowing oxygen at 900 °C for 8 h in a quartz tube furnace. Structural measurements were made before and after annealing the films by x-ray diffraction using $\theta/2\theta$ scans and ω scans. Measurements of the dielectric properties were made on as-deposited and annealed films using 1500 Å Cr/Au interdigital electrodes on the surface of the BST films. The interdigital electrodes had a gap spacing of 10 μm, a finger width of 7.5 μm, and a finger length of 75 μm. The capacitance and relative dissipation factor were measured as a function of temperature (30–375 K) in vacuum and with dc bias voltages (0–40 V) at 1 MHz using a HP4285A *LCR* meter. In the coplanar geometry, the capacitance measures the dielectric properties of vacuum, the film, and the $LaAlO_3$ substrate. A reference measurement was made on a bare $LaAlO_3$ substrate, which showed a negligible temperature and dc bias field dependence. Thus, changes in the capacitance as a function of temperature were due to changes in the dielectric susceptibility of the film.

BST films were found, by x-ray diffraction, to be single phase and exclusively (001) oriented with a (002) ω-scan full width at half-maximum between 0.16° and 0.50°. The film lattice parameters normal to the substrate were precisely measured by x-ray diffraction before and after annealing for BST (x=0.35, 0.50, and 0.65) using a technique described elsewhere.[6,7] The lattice parameters for the as-deposited and annealed thin films and bulk BST are plotted in Fig. 1 as a function of % Ba composition. The as-deposited films had larger lattice parameters than bulk BST samples of the same composition. After annealing in oxygen, the lattice parameters were smaller and closer to the bulk lattice parameters. The change in the lattice parameter may be caused by an

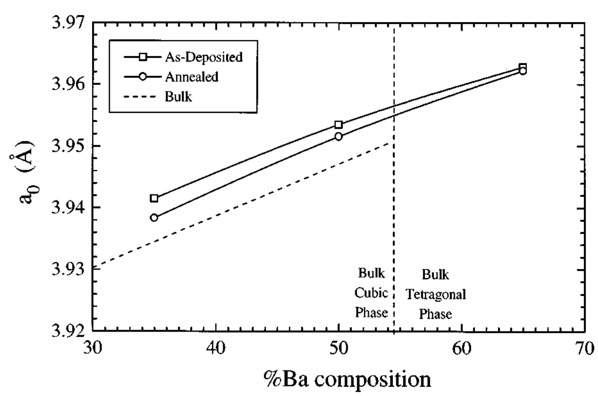

FIG. 1. Lattice parameters normal to the film surface vs % Ba composition, determined by x-ray diffraction, for as-deposited and annealed thin films on (001) $LaAlO_3$. The composition dependence of the bulk BST lattice parameter has been determined by Vegard's law using Slater-type orbitals and BST (x=0.5) as references. Lattice parameter error is ±0.0001 Å.

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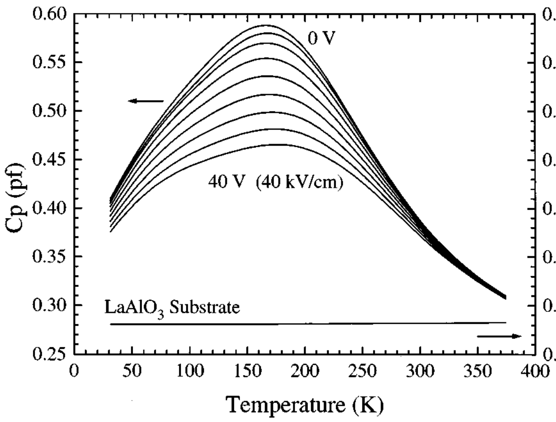

FIG. 2. Capacitance vs temperature measured at 1 MHz for dc bias electric fields from 0 to 40 kV/cm (0–40 V) in 5 kV/cm steps for as-deposited BST (x=0.35).

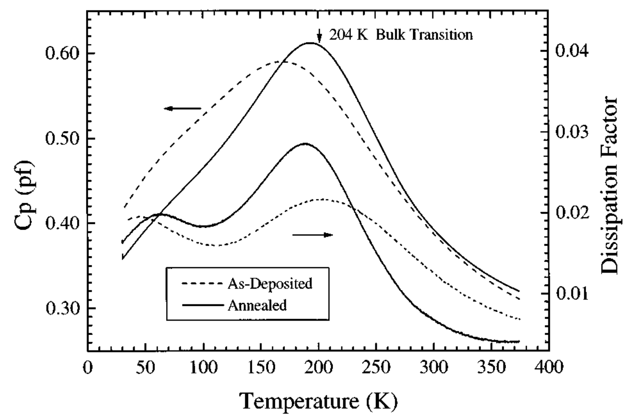

FIG. 4. Capacitance and dissipation factor vs temperature for BST (x=0.35) as-deposited and annealed films. Measurements were made at 1 MHz without a dc bias field.

increase in oxygen stoichiometry for the film or by a reduction in strain, which is caused by the 3% lattice mismatch between the film and substrate.

Capacitance and dissipation factor measurements at 1 MHz were made as a function of temperature for several dc bias electric fields for a BST thin film of composition x=0.35 (Fig. 2). Field biases were applied from 0 to 40 kV/cm (40 V applied for a gap spacing of 10 μm). The capacitance is suppressed by as much as 20% with increasing dc bias, and the peak in the capacitance as a function of temperature shifts to higher temperatures with increasing dc bias. This behavior is typical of a ferroelectric, but the temperature dependence is significantly different from that of the bulk material. The capacitance vs temperature curve for the film is much broader than that of the bulk with a peak at 168 K. This is about 36 K lower than observed in the bulk. A similar peak shift has been observed previously in thin films of x=0.35 and 0.50 composition.[2,8] The dissipation factor (tan δ) is presented in Fig. 3 for the as-deposited x=0.35 composition. The lowest value of the measured dissipation factor is 7×10^{-3} at 375 K and increases to 2×10^{-2} at the peak. By applying a 40 kV/cm dc bias electric field, the dissipation factor can be reduced by 29% at the peak. There is a second peak in the dissipation factor between 50 and 60 K that is coincident with a shoulder in the capacitance. This is attributed to a second phase transition from tetragonal to orthorhombic with decreasing temperature.[3]

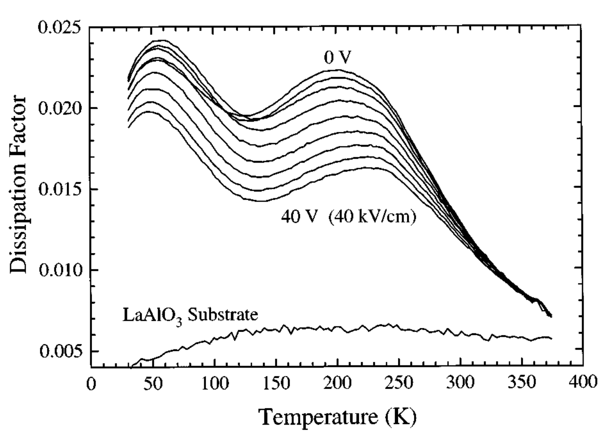

FIG. 3. Dissipation factor (tan δ) as a function of temperature measured at 1 MHz for dc bias electric fields from 0 to 40 kV/cm (0–40 V) in 5 kV/cm steps for as-deposited BST (x=0.35).

After annealing the films for 8 h at 900 °C in oxygen, significant changes were observed in the dielectric properties. Figure 4 shows the capacitance and dissipation factor as a function of temperature for the as-deposited and annealed films of BST (x=0.35). The measurements were made at 1 MHz without a dc bias electric field. The peak in the temperature dependence of the annealed film capacitance increased in temperature by 26 K, which is only 10 K below the bulk transition temperature. Also, the breadth of the temperature dependence of the capacitance and dissipation factor is narrower in the annealed film. When cooling the film from 375 to 30 K, the annealed film had a lower dissipation factor at high temperature that did not increase until the temperature was closer to the transition temperature. This is in contrast to the as-deposited film for which the dissipation factor increased immediately with decreasing temperature. The temperature at which the dissipation factor was maximized also shifted closer to the capacitance peak after annealing.

The postdeposition anneal also provided greater tunability with reduced dielectric losses. Figure 5 shows the tunability as a function of dc bias. From these results, the maximum tunability, for a 40 kV/cm field, is found to be 20% for the as-deposited films and 32% for the annealed films. The maximum tunability occurs at the capacitance peak, which is also the temperature at which the dissipation factor is largest. A better comparison for device applications would be in a region where the losses are minimal. The lowest loss for the as-deposited film is $\tan\delta = 7\times10^{-3}$ where the tunability is only 1%, but for the same loss tangent value in the annealed film there is 8% tuning. Furthermore, at the highest temperature, 374 K, the annealed film has a loss tangent as low as 4×10^{-3} where a tuning of 2.4% is still available. By changing the film composition, the temperature of the most desirable film properties could be shifted to the operating temperature of a particular device.

In summary, we have shown that high quality thin films of BST (x=0.35–0.65) suitable for use in active microwave

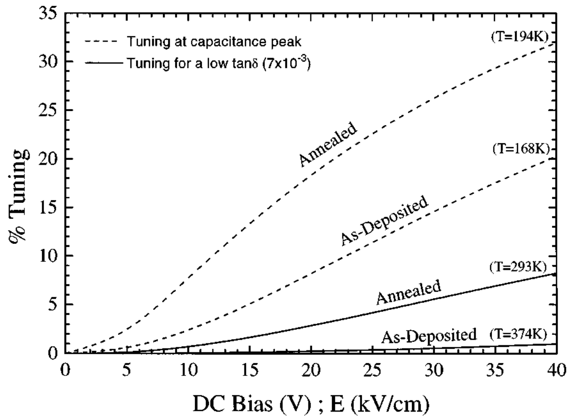

FIG. 5. Capacitance tuning ($[C(0)-C(v)]/C(0)\times 100$) vs dc bias for BST ($x$=0.35) at 1 MHz.

circuits have been grown by PLD on (001) $LaAlO_3$ substrates. Deposited films were annealed at 900 °C for 8 h. The lattice parameter for all compositions of the annealed films are closer to the bulk lattice parameters. The capacitance of the as-deposited film as a function of temperature is broad with a maximum at a lower temperature than the bulk. The capacitance and dissipation factor of the annealed films exhibit a narrower temperature dependence and peaks that are closer to the bulk transition temperature. Also, the dielectric losses in the annealed films are lower than the as-deposited films in the high temperature range. The annealed film had greater tunability with reduced loss. In particular, for a loss of 7×10^{-3}, the as-deposited film had a tunability of 1%, while the annealed film had a tunability of 8%. The change in dielectric properties as a function of oxygen annealing may be due to filling of oxygen vacancies or a reduction in film strain.

Support of this research has been provided by the Office of Naval Research and by Superconducting Core Technologies NCRADA-NRL-94-027.

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