THE STRUCTURE AND ELECTRIC FIELD DEPENDENT DIELECTRIC PROPERTIES OF ANNEALED $Sr_{1-x}Ba_xTiO_3$ FERROELECTRIC THIN FILMS

L.A. KNAUSS[†], J.M. POND, J.S. HORWITZ, C.H. MUELLER*, R.E. TREECE* AND D.B. CHRISEY
Naval Research Laboratory, Code 6670, 4555 Overlook Ave., SW, Washington, DC 20375
[†]NRL/NRC Cooperative Research Associate, *SCT, 720 Corporate Circle, Golden, CO 80401

ABSTRACT

The effect of a post deposition anneal on the structure and dielectric properties of epitaxial $Sr_{1-x}Ba_xTiO_3$ (SBT) thin films with $x = 0.35$, 0.50 and 0.60 has been measured. The films were grown by pulsed laser deposition on $LaAlO_3$ (001) substrates at 750°C in 350 mTorr of oxygen. The as-deposited films were single phase, (00ℓ) oriented with ω-scan widths for the (002) reflection between 0.16° and 0.50°. The dielectric properties of the as-deposited films exhibit a broad temperature dependence and a peak which is as much as 50 K below the peak in bulk SBT. Also, the lattice parameter, as measured by x-ray diffraction, of the as-deposited films was larger than the bulk indicating strain in the films. The as-deposited films were annealed for 8 hours at 900°C in oxygen. The dielectric properties of the annealed films were closer to that of bulk SBT and the lattice parameter was closer to the bulk lattice parameter indicating a reduction of strain. Annealing of as-deposited films also resulted in an increased dielectric tuning without increased dielectric loss.

INTRODUCTION

Ferroelectrics are a class of non-linear dielectrics which exhibit an electric field dependent dielectric constant. These materials are currently being used to develop active microwave electronics such as phase shifters, tunable 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) as compared to the 1-10 kV which must be used for mm-size single crystals [2]. $Sr_{1-x}Ba_xTiO_3$ (SBT) is currently the material of choice for microwave applications due to its low loss and composition dependent Curie temperature. The Curie temperature of bulk SBT ranges from 30 to 400 K for Ba concentrations ranging from $x = 0$ to 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. Also, SBT can be grown on high temperature superconductors, minimizing conductor losses in the devices.

Previously we observed that SBT thin films grown on $LaAlO_3$ substrates exhibit a non-uniform strain as large as 0.1% resulting from the large lattice mismatch of ~3% between the film and substrate and twinning in the substrate [4]. For as-deposited thin films, the temperature dependence of the dielectric constant and its magnitude differed significantly from bulk SBT [2,4]. As-deposited films have been annealed in an effort to reduce the strain. We report here an investigation of the effects of a post-deposition anneal on the structural and dielectric properties of SBT thin films.

EXPERIMENTAL

Thin films of SBT on (001) $LaAlO_3$ were grown by pulsed laser deposition (PLD) for compositions $x = 0$, 0.35, 0.50 and 0.65. The PLD system used to grow these SBT films has been described previously in more detail [5,6]. A KrF excimer laser (~30 nsec pulses, ~300 mJ/pulse and $\lambda = 248$ nm focused with a 50 cm focal length lens to a fluence of ~2 J/cm^2) was used to ablate mixed oxide targets of $SrTiO_3$ and $BaTiO_3$ formed from pressed powders sintered at 900°C in oxygen. The vaporized material was deposited onto a conductivly heated $LaAlO_3$ substrate positioned approximately 3 cm away from the target. The substrate was heated to 750°C in an oxygen ambient pressure of 350 mTorr. The films grew at approximately 2 Å/pulse to a total film thickness of 0.6 μm. The films were then cooled to room temperature in oxygen at ~10°C/min.

Mat. Res. Soc. Symp. Proc. Vol. 401

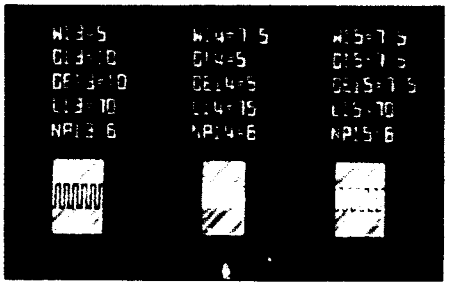

Figure 1. Optical photograph of the gold interdigital electrodes for measurement of the capacitance and loss tangent.

The films were removed from the deposition chamber for structural analysis and then annealed in flowing oxygen at 900°C for 8 hours in a quartz tube furnace. Structural measurements were made before and after annealing the films by x-ray diffraction using a Rigaku Rotaflex diffractometer with Cu K_{α} radiation from a rotating anode source. Measurements of the dielectric properties were made using gold interdigital electrodes on the surface of the SBT films. A matrix of Au electrodes with varying dimensions were patterned by a standard lithography technique. An optical photograph of a subset of these electrodes is shown in Figure 1. The dielectric measurements reported here where made on electrodes with a gap spacing of 10 μm, a finger width of 7.5 μm and a finger length of 75 μm. The electrodes were ~1500 Å thick, and electrical contact was made by wire bonding four gold wires to the large contact pads. Two wires were attached to each pad next to the fingers providing a four point measurement at the device. The capacitance and relative dissipation factor were measured as a function of temperature (30 - 375 K) and with dc bias voltages (0 - 40 V) at 1 MHz using an HP4285A LCR meter. The temperature control was achieved with an APD Cryogenics closed-cycle refrigerator with a Lakeshore 330 temperature controller. A reference measurement was made on a $LaAlO_3$ substrate without an SBT film which showed a negligible temperature and dc bias field dependence. Thus changes in the capacitance as a function of temperature are due to changes in the dielectric susceptibility of the film.

RESULTS AND DISCUSSION

Structural Measurements

SBT films of all compositions were found, by x-ray diffraction, to be single phase and well-oriented. Figure 2 shows a $\theta/2\theta$ scan for $x = 0.35$ which is typical of all the compositions investigated. The film is exclusively (00ℓ) oriented with a (002) ω-scan FWHM of only 0.19°. The ω-scan FWHM for the (002) line of all the compositions was less than 0.5°.

The lattice parameters were measured by x-ray diffraction out of the plane of the substrate-film interface before and after annealing for SBT (x = 0, 0.35, 0.50 and 0.65). By using four (00ℓ) reflections, corrections can be made for mounting errors in the diffractometer to obtain precise lattice parameters [7]. The lattice parameters for the as-deposited and annealed thin films and bulk SBT are plotted in Figure 3 as a function of %Ba composition. The as-deposited films have a large lattice parameter compared to bulk SBT. After annealing in oxygen, the lattice parameter is smaller and closer to the bulk lattice parameter. The room temperature lattice parameter for $SrTiO_3$ is ~3% larger than the $LaAlO_3$ substrate. This results in a compressional strain in the plane of the substrate-film interface. The lattice parameter out of the plane is therefore larger than the bulk value. The decrease in the out of plane lattice parameter after annealing indicates a reduction of strain in the films.

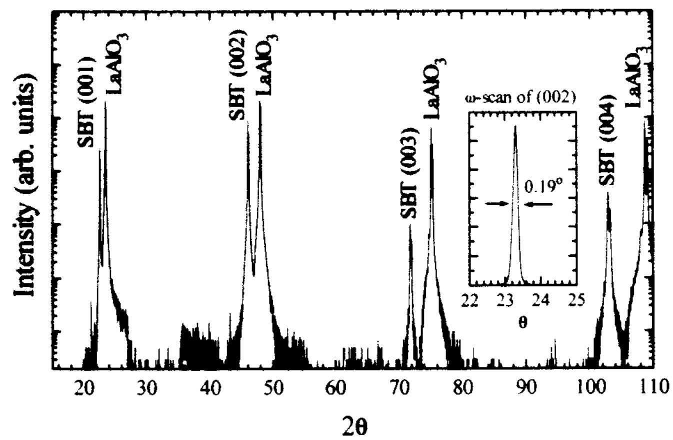

Figure 2. X-ray diffraction from a thin film of SBT ($x = 0.35$) on (001) oriented $LaAlO_3$ (LAO). The ω-scan for the (002) line is plotted in the inset and has a FWHM of 0.19°.

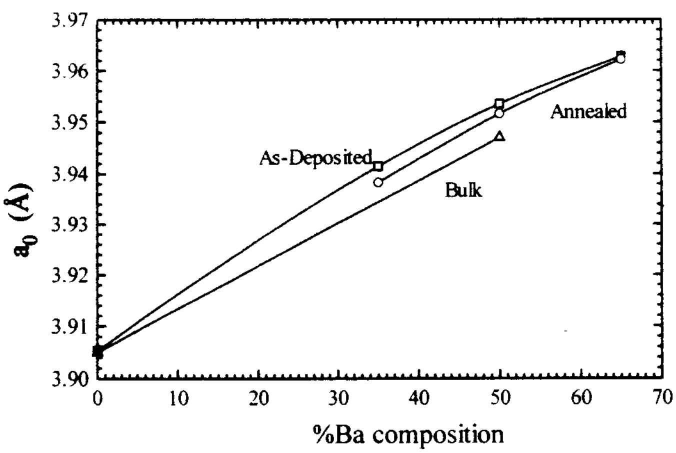

Figure 3. Lattice parameters versus %Ba composition, determined by x-ray diffraction, for bulk SBT and as-deposited and annealed thin films on (001) $LaAlO_3$.

Capacitance Measurements

Capacitance and dissipation factor measurements at 1 MHz were made as a function of temperature for several dc bias electric fields for an SBT thin film of composition $x = 0.35$. The data were collected while cooling and warming to detect any thermal hysteresis. In Figure 4 the capacitance is presented for the as-deposited $x = 0.35$ composition. Several dc electric 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 shifts to higher temperatures with increasing dc bias. This behavior is typical of a ferroelectric under the influence of a dc bias, but the temperature dependence is significantly different from that of the bulk material. The capacitance versus temperature curve is much broader than that of the bulk with a maximum 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 [2,4]. The dissipation factor (tan δ) is presented in Figure 5 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 K and 60 K which is coincident with a shoulder in the capacitance. This is most likely due to a second phase transition from tetragonal to orthorhombic with decreasing temperature.

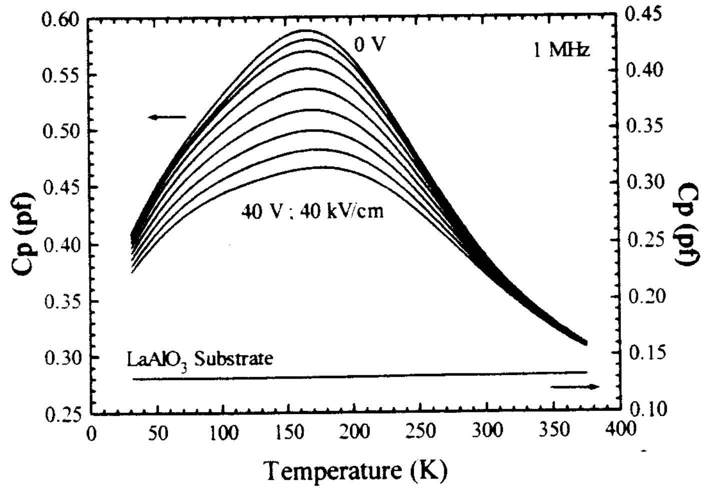

Figure 4. Capacitance versus temperature for dc bias electric fields from 0 to 40 kV/cm (0 - 40 V) in 5 kV/cm steps for SBT ($x = 0.35$).

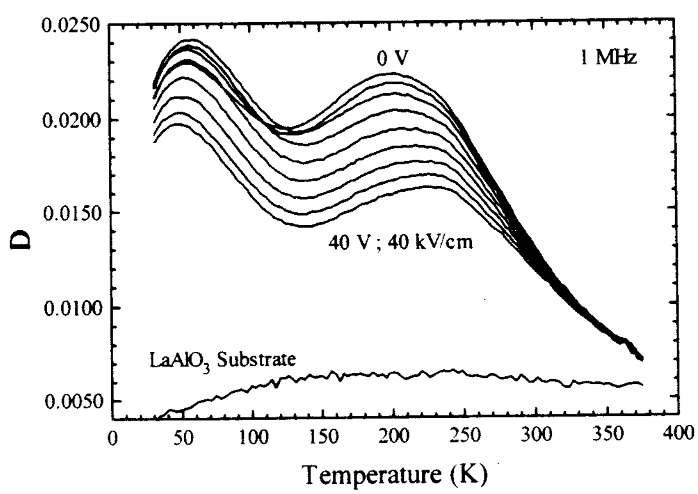

Figure 5. Dissipation factor (D) as a function of temperature for dc bias electric fields from 0 to 40 kV/cm (0 - 40 V) in 5 kV/cm steps for SBT ($x = 0.35$).

After annealing the as-deposited films in oxygen at 900°C for 8 hours, significant changes were observed in the dielectric and structural properties. Figure 6 shows the capacitance and dissipation factor as a function of temperature for the as-deposited and annealed films of SBT ($x = 0.35$). The measurements were made at 1 MHz without a dc bias electric field. The peak of the annealed film has moved up in temperature by 26 K which is only 10 K below the bulk transition temperature. Also, the breadth of the temperature dependence is narrower in the annealed film. When cooling the film from 375 K to 30 K, the dissipation factor in the as-deposited film starts to increase immediately with decreasing temperature, but the annealed film has a lower dissipation factor at high temperatures which does not increase until the temperature is closer to the transition temperature. The peak in the dissipation factor also shifts closer to the peak in the capacitance after annealing.

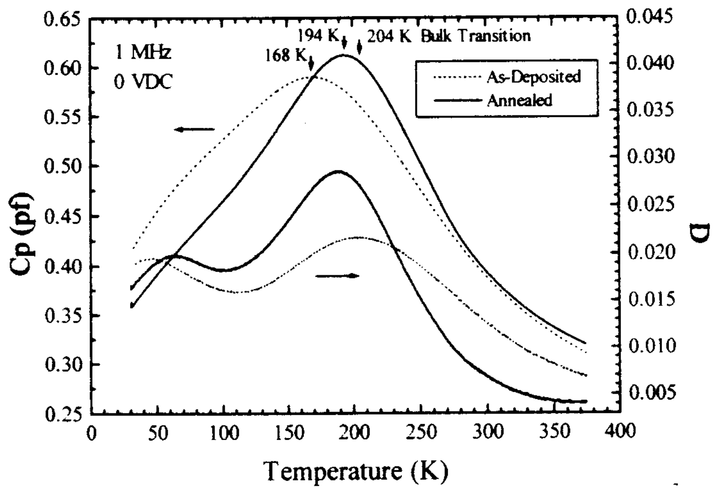

Figure 6. Capacitance and dissipation factor versus temperature for SBT ($x = 0.35$) as-deposited and annealed films.

There are some real benefits for devices having the dielectric properties of the annealed films. Figure 7 shows the capacitance as a function of dc bias. From these results the maximum tunability is found to be 20% for the as-deposited films and 32% for the annealed films. The maximum tunability occurs at the peak where the dissipation factor is largest. A better comparison for device applications would be in a region where the losses are lowest. The lowest loss for the as-deposited film is 7×10^{-3} where the tunability is only 1%, but for the same loss tangent in the annealed film there is 8% tuning. Furthermore, the annealed film has a loss tangent as low as 4×10^{-3} where a tuning of 2.4% is still available.

CONCLUSIONS

High quality thin films of SBT ($x = 0$ to 0.65) suitable for use in active microwave circuits have been grown by PLD on (001) $LaAlO_3$ substrates. We have investigated the effect that post-deposition annealing of these films at 900°C for 8 hours has on the structural and dielectric properties. The lattice parameters of the annealed films are closer to the bulk lattice parameters indicating a reduction in strain. The dielectric properties of the as-deposited films indicate a broad temperature dependence with a peak in the capacitance that is lower in temperature than the bulk. The annealed films exhibit a narrower temperature dependence and a peak that is closer to the bulk transition temperature. Also, the dielectric loss of the annealed film is lower than the as-deposited film in the high temperature range. By applying a dc bias, we investigated the tunability of the capacitance. 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%, but the annealed film had a tunability of 8%.

The structural and dielectric changes resulting from the oxygen anneal are most likely due to filled oxygen vacancies and a decrease in strain through a slow re-twinning of the substrate. The annealing profile for SBT films has not been fully optimized. A detailed investigation of annealing and its effects on dielectric properties is currently in progress.

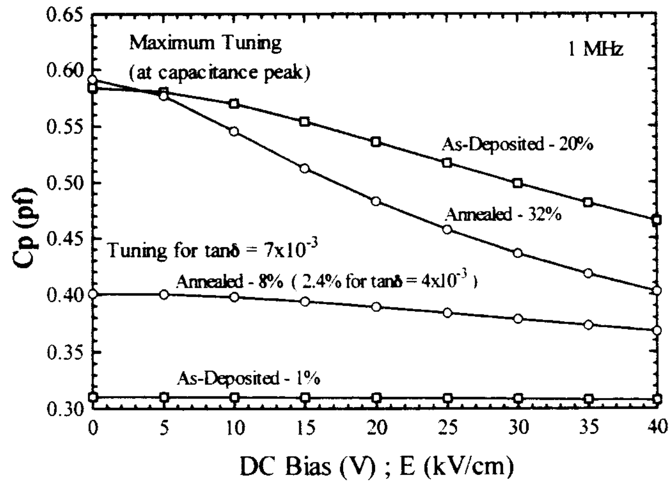

Figure 7. Capacitance tuning versus dc bias for SBT (x = 0.35).

ACKNOWLEDGMENTS

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

REFERENCES

1. V.K.Varadan, D.K. Gohdgaonkar, V.V. Varadan, J.F. Kelly and P. Glikerdas, Microwave Journal Jan, 116 (1992).
2. J.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, Integrated Ferroelectrics **8**, 53 (1995).
3. G.A. Smolenskii and K.I. Rozgachev, Zh. Tekh. Fiz. **24**, 1751 (1954).
4. L.A. Knauss, J.S. Horwitz, D.B. Chrisey, J.M. Pond, K.S. Grabowski, S.B. Qadri, E.P. Donovan and C.H. Mueller in Film Synthesis and Growth Using Energetic Beams, edited by H.A. Atwater, J.J. Dickinson, D.H. Lowndes, and A. Polman (Mater. Res. Soc. Proc. 388, Pittsburgh, PA 1995).
5. K.S. Grabowski, J.S. Horwitz and D.B. Chrisey, Ferroelectrics **116**, 19 (1991).
6. J.S. Horwitz, D.B. Chrisey, K.S. Grabowski and R.E. Leuchtner, Surface and Coatings Technology **51**, 290 (1992).
7. B.B. Cullity, Elements of X-ray Diffraction, Addison-Wesley, 1978, pp. 359-360.