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Effects of poling, and implications for metastable phase behavior in barium strontium titanate thin film capacitors

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Barium strontium titanate ($Ba_{0.5}Sr_{0.5}TiO_3$–BST) thin film capacitor structures were made using pulsed laser deposition, and their functional properties were monitored with varying temperature. It was found that poling at low temperature could induce distinct differences in the behavior of the dielectric constant and loss tangent, on heating. In relatively thick BST films ($>\sim 650$ nm), poling the sample at 80 K produced a change from a single broad anomaly to one in which three distinct anomalies could be observed. The temperatures of these anomalies (~ 140, ~ 200, and ~ 260 K) were close to those known to be associated with phase transitions in bulk. Monitoring changes in polarization loops with temperature confirmed the likelihood that the dielectric anomalies observed were indeed the result of phase transitions in the films. Unusually, though, when the films were poled at 150 K, and then cooled to 80 K prior to collection of dielectric data on heating, the dielectric anomaly around 140 K was completely suppressed. The lack of a phase transition was confirmed by monitoring depolarization currents in the sample. It is suggested that poling has therefore allowed the phase state that existed at 150 K to persist metastably down to 80 K. For relatively thin BST films ($<\sim 400$ nm), poling at 80 K only induced two distinct anomalies in the dielectric response (at ~ 200 and ~ 290 K). Nevertheless, poling-related metastability could again be observed: when the samples were poled at 250 K and then cooled to 80 K prior to data collection on heating, the anomaly at ~ 200 K was completely suppressed. These experiments suggest that metastable phase behavior could be commonplace in thin film ferroelectrics. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1827934]

Inherent in the definition of ferroelectricity is the existence of a polarization state, the direction of which can be reversed by an externally applied electric field.[1] This property makes ferroelectric materials obvious candidates for non-volatile binary data storage (NVRAM).[2,3] Integration of ferroelectrics into electronic devices demands their use in the form of thin films. However, while phase diagrams of the various possible polarization states are mapped and well understood for bulk ferroelectrics, the issue of phase behavior within the thin film regime is still a matter of considerable interest and debate. The thermodynamics of thin film systems could certainly be different from bulk,[4–8] and the alterations in kinetics of phase transitions due to thin film geometry are largely unknown. For applications involving the manipulation of polarization (such as NVRAM), such knowledge could, nevertheless, prove to be extremely important.

In this letter, the authors present functional measurements that have been performed on a series of thin film capacitor structures of the form $Au/Ba_{0.5}Sr_{0.5}TiO_3$ (BST)$/(La,Sr)CoO_3$ (LSCO)$/MgO$. Poling (by application of an electric field significantly greater than that of the coercive field at temperatures below the Curie temperature) has induced interesting changes in the low-field dielectric response of the films as a function of temperature. In general, poling at 80 K has revealed a series of dielectric anomalies on heating that look to be related to phase transitions. Poling at temperatures higher than that of the first observed anomaly before cooling to 80 K, results in complete suppression of the first anomaly when data are collected on heating. Such observations are interpreted in terms of phase stability and metastability in the thin film BST system.

Thin film capacitors were produced by pulsed laser deposition (PLD) on commercially available MgO {100} substrates. A KrF excimer laser (Lambda Physik COMPex 205i) with $\lambda = 248$ nm, energy density of ~ 2 J cm^{-2} on the target surface, repetition rate of 10 Hz and a target–substrate distance of 75 mm was used. The pressure in the growth chamber was maintained at 0.15 mbar O_2 and the deposition temperature at 650 °C for both the lower electrode and the dielectric layer. A postdeposition anneal for 30 min in 0.15 mbar O_2 and 20 min at 1 bar O_2 at 550 °C was used. Thermal evaporation of Au top electrodes through a hard mask enabled functional measurements by contacting two gold pads and measuring two capacitors in series. The electrode area was $\sim 1.77 \times 10^{-6}$ m^2. Low-field capacitance and the dielectric loss tangents were measured using an HP 4284A Precision LCR Meter and HP 4263B LCR meter. Polarization measurements were taken using a Radiant Technologies Precision Workstation. Depolarization current was measured using a Keithley 6514 electrometer. For varying temperature, capacitors were mounted in an Oxford Instruments cryostat with temperature regulated using a Lakeshore

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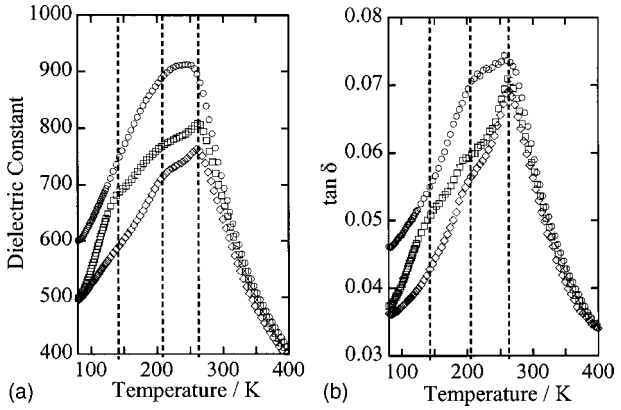

FIG. 1. Dielectric constant (a) and loss tangent (b) of a 975 nm BST thin film at 100 kHz as a function of temperature on heating from 80 K. (○) correspond to the unpoled "virgin"functional measurements, while (□) were obtained after poling the BST at 80 K. Unfilled diamonds correspond to poling at 150 K, then cooling to 80 K and taking functional data on heating.

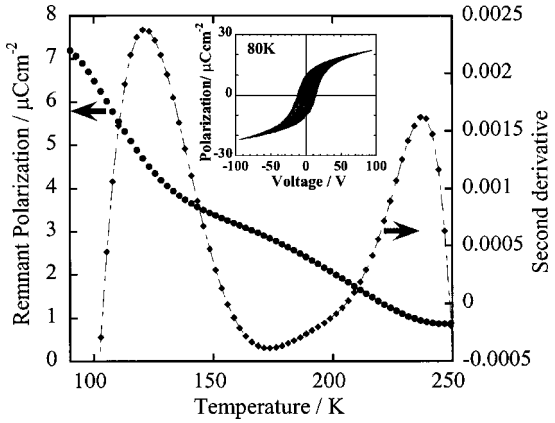

FIG. 2. Remnant polarization as a function of temperature on heating for a BST thin film. Also shown is the rate of change of gradient of remnant polarization with temperature, to illustrate the points at which sudden changes in gradient occur. Inset: Nested set of polarization loops for the BST capacitor at 80 K.

330 temperature controller. All instrument control was achieved using HPVEE software. A Tecnai F20 field-emission transmission electron microscope (FEGTEM) was used for microstructural characterization including film-thickness information, with cross-sectional specimens made in a focused ion beam microscope (FEI FIB200TEM). The successful deposition of BST and LSCO were confirmed crystallographically using a Brüker-AXS D8 x-ray diffractometer, and found to be almost entirely ⟨001⟩-out-of-plane-oriented, as is typical of such deposition onto {100} MgO.[9–11]

The behavior of the low-field dielectric constant and loss tangent as a function of temperature, for a relatively thick BST film (975 nm), is illustrated in Fig. 1. Initial data collection was performed by cooling the capacitor to 80 K and then taking data, on heating, to 400 K. Under these circumstances, the dielectric constant showed a single broad anomaly, consistent with most observations made in literature,[12] with the temperature of maximum dielectric constant (T_m) at ~250 K. Slightly more structure was evident in the dielectric loss, with hints of two anomalies at ~200 and ~260 K. However, poling the capacitor at 80 K prior to data collection on heating, revealed dramatic changes in behavior: the dielectric constant and loss tangent both displayed three distinct peaks at ~140, ~200, and ~260 K. Above 260 K, both the dielectric constant and loss mapped reasonably well onto the initial unpoled "virgin" behavior. The temperatures of the anomalies are close to those at which anomalies are observed in bulk and single crystal $Ba_{0.5}Sr_{0.5}TiO_3$, associated with phase transitions at ~155, ~195, and ~235 K.[13–16] The existence of the anomalies in thin film, and their proximity to the temperatures expected for the same composition in bulk, suggest their association with phase transitions in the thin film BST. In this context, the similarity between dielectric responses of "virgin" and poled data runs in the implied paraelectric state is reassuring.

In an attempt to confirm the phase transition interpretation given above, a series of saturated polarization loops was taken on heating from 80 to 260 K. The remnant polarization $\{[+P_r-(-P_r)]/2\}$ as a function of temperature is illustrated in Fig. 2, along with an example of a $P-V$ nested loop. As can be seen, the remnant polarization decreases with increasing temperature, with two distinct changes in gradient apparent. The positions of these gradient changes have been highlighted by plotting the rate of change of gradient showing peaks at ~120 and ~240 K. Such sudden changes in polarization represent clear evidence of phase transitions. Since these temperatures correspond reasonably to the lowest and highest temperature anomalies seen in the dielectric response (with a systematic 20 K downward shift), there is confirmation that the dielectric anomalies are indeed related to phase transitions in the films. A strong polarization change relating to the dielectric anomaly at ~200 K, which would have been expected at ~180 K (with the apparent 20 K temperature shift) was not evident in Fig. 2, although slight disturbance to the rate of change of gradient function can be seen. Overall, then, it appears that poling the capacitor at low temperature has revealed phase transitions similar to those expected in bulk.

A key question is why distinct anomalies in dielectric behaviour are not evident in the virgin unpoled data runs. Some insight may be given by the third series of dielectric data with temperature shown in Fig. 1. Here the capacitor has been cooled to 150 K (between the anomaly at 140 K and that at 200 K), and then poled, before further cooling to 80 K and collecting functional data on heating. What is immediately apparent is that the anomalies in both dielectric constant and loss tangent previously seen at 140 K have been totally suppressed, with the associated implication that no phase transition has occurred at this temperature. The anomalies at ~200 K and ~260 K are still clearly evident.

Figure 3 shows the depolarization current measured for the BST capacitor on heating at 5 K min^{-1}. When poled at 80 K, current associated with depolarization on heating was apparent between 80 and ~170 K decreasing gradually in this temperature window, before increasing dramatically towards the Curie temperature. In contrast, when poled at 150 K and cooled to 80 K prior to data collection, no measurable current was observed until ~170 K, when a double peak in depolarization current developed (at ~200 K and ~235 K). The implication is that the poling at 150 K has suppressed all polarization reorientation/change between 80 and ~170 K, and therefore that the polarization state that existed at 150 K was maintained down to 80 K, even though, thermodynamically, a phase transition should have been expected to occur around 140 K. In other words, the symmetry

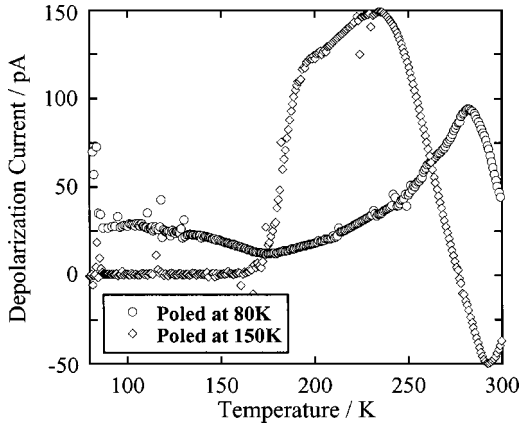

FIG. 3. Depolarization current measured on the BST film on heating from 80 K at 5 K min^{-1} (○) were obtained when the capacitor was poled at 80 K prior to collection of data. (◇) were obtained by poling at 150 K before cooling to 80 K and taking data on heating.

state at 150 K has been maintained to 80 K metastably as a result of poling.

While discussion so far has concentrated on data from a 975 nm BST film, similar data were obtained for films 1200, 775, and 650 nm in thickness. For films at 350 and 260 nm the behavior was slightly different; unusual metastable behavior was nevertheless again implied: Fig. 4 illustrates the sequence of results in dielectric constant and loss tangent on heating from 80 K for the virgin sample, for the sample after poling at 80, 150, and 250 K. In this 260 nm film, the unpoled response shows a single broad anomaly as before, but with a reduced T_m. This reduction of T_m on decreasing BST thickness is entirely consistent with previous literature.[11,12] Poling at both 80 and 150 K prior to data collection on heating reveals two distinct anomalies at ~200 and ~300 K, in

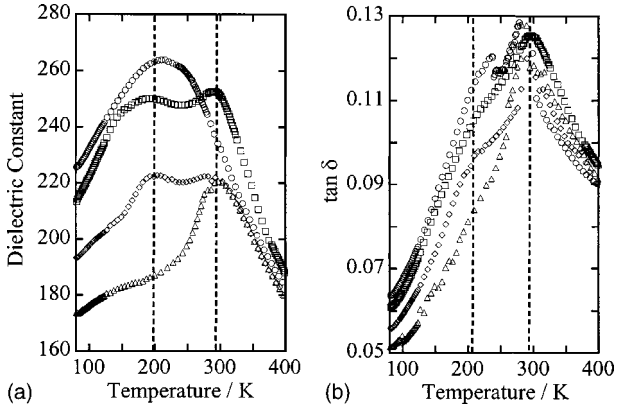

FIG. 4. Dielectric constant (a) and loss tangent (b) as a function of temperature for a 260 nm BST film, at 100 kHz. (○) correspond to the unpoled "virgin" response; (□) were obtained after poling at 80 K; (◇) were obtained after poling at 150 K prior to cooling to 80 K and taking data on heating; (△) were obtained after poling at 250 K, then cooling to 80 K and taking data on heating.

both dielectric constant and in the loss tangents. Two, rather than three, anomalies might imply that the thermodynamics of these thinner films differs from that of the thicker films, and different symmetries may be implied.[4–6] Nevertheless, similar suppression of the dielectric anomalies due to poling as those outlined above can be seen: poling at 250 K (between the anomalies at 200 and 300 K), before cooling to 80 K and collecting data on heating, suppresses both the anomaly in dielectric constant and loss tangent at ~200 K. The implication is that poling has maintained the symmetry state present at 250 K metastably down to 80 K, so that no transition is needed at 200 K on reheating.

Overall, it has been observed that low temperature poling (at 80 K) induces a sequence of phase transitions to occur on heating in thin film BST. Moreover that if the films are poled within a particular phase state, then that state can be maintained metastably down to 80 K. This has been found in both relatively thick (>~650 nm) and relatively thin (350 and 260 nm) BST thin film capacitor structures. Exactly how poling the ferroelectric thin films suppresses phase transitions on cooling is not yet known, but further experiments are underway to characterize the kinetics of the system more quantitatively. Since metastability appears to have been established as an important feature in poled thin film BST behavior, it seems likely that unpoled virgin films will also display functional properties that are a reflection of the kinetics rather than the thermodynamics in the system.

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