Giant Enhancement of Polarization and Strong Improvement of Retention in Epitaxial Ba$_{0.6}$Sr$_{0.4}$TiO$_3$-Based Nanocomposites

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1. Introduction

A paradigm shift in ferroelectrics toward miniaturization has come about because of the considerable interest in low energy consumption and nonvolatile nanoelectronics. The advances in the fabrication of ferroelectric structures in the nanometer range have brought to life new physical phenomena and encouraged unique combinations of functionalities.$^{[1–3]}$ Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ (BSTO) is a ferroelectric of topical interest, since it exhibits a wide variety of functional properties, including switchable polarization, piezoresponse, electro-optical behavior, tunability, and non-linear dielectric behavior. It is also Pb-free. It could replace conventional microwave tunable devices made from III–V semiconductors, which have drawbacks of slow response to input signal, high loss, and high operating voltage.$^{[4]}$ To date, Pb(Zr,Ti)O$_3$ (PZT) remains the industry standard material in nano- and microdevices for exploiting the aforementioned functional properties.$^{[5]}$

Reducing dimensions to the nanoscale is challenging for standard ferroelectrics. When the lateral and vertical dimensions of (Ba,Sr)TiO$_3$ and BaTiO$_3$ are downscaled to below 26 nm in vertical thickness, or below 20 nm in nanowire lateral dimension, their functional properties are degraded compared to the bulk.$^{[6,7]}$ On the other hand, using vertically aligned nanocomposite films (of BaTiO$_3$-Sm$_2$O$_3$ and Ba$_{0.6}$Sr$_{0.4}$TiO$_3$-Sm$_2$O$_3$ compositions) containing lateral nanoscale features of sizes down to 10 nm, we have shown that size-limited property degradation is eliminated.$^{[8,9]}$ A key reason for this is that the interfaces of the ferroelectric nanostructures in the films are epitaxially coupled to a second scaffold phase in the film. In such films, there is strong vertical strain that causes a strong enhancement of Curie temperature.$^{[8,9]}$ Enhanced dielectric tunability, reduced dielectric loss and leakage current,$^{[10]}$ and finally, enhanced saturation polarization.$^{[2]}$ On the other hand, in these promising nanocomposite ferroelectrics neither the extent of polarization nor the polarization retention has been systematically studied.

In Ba$_{0.6}$Sr$_{0.4}$TiO$_3$ (BSTO)-based epitaxial nanocomposite films increased $P_r$ values are demonstrated by up to a factor of 3 compared to standard BSTO films. A strongly reduced temperature coefficient of polarization retention is also obtained, i.e., 0.07% °C$^{-1}$ compared to 0.24% °C$^{-1}$. Piezopoling with only marginal leakage current is also achieved up to 200 °C, the highest temperature studied. The origin of the improved performance is the incorporation of Sm$_2$O$_3$ nanopillars in the films which acted as stiff vertical nanoscaffolds, inducing a strong tetragonal distortion in the BSTO (up to 1.033(7) in terms of the out-of-plane/in-plane lattice dimensions). The films have comparable performance to industry-standard Pb(Zr,Ti)O$_3$ films, at the same time as being Pb-free.

2. Results and Discussion

First, we present the microstructures and structural information on the BSTO-SmO nanocomposites of most interest. These are for (BSTO)$_{1-x}$(SmO)$_x$ compositions with $x = 0.50$ and 0.75. An example cross-sectional transmission electron microscopy (TEM) image for a $x = 0.75$ sample reveals the nanocolumnar structure obtained (Figure 1a,b). The $x = 0.75$ film was found to be the...
optimum composition for enhanced polarization owing to the greatest induced tetragonal distortion of the BSTO.\[2,9\] Figure 1c shows a similar nanocolumnar matrix for \(x = 0.50\). The lateral length scales for both \(x\) values are similar, i.e., 10–20 nm. The selected area electron diffraction pattern for \(x = 0.50\) (Figure 1d) shows 45° rotated growth of SmO on the (00l) SRO-buffered STO substrate. The distinct spots show high epitaxial quality growth with a low degree of misorientational spread.

X-ray diffraction (XRD) patterns in Figure S1 (Supporting Information) show the strong epitaxial growth of (00l) perovskite BSTO, cubic SmO, and pseudocubic SRO on (00l) perovskite STO substrates. The BSTO (002) peaks shift to lower angles (indicating out-of-plane lattice parameter expansion) with increasing SmO fraction, \(x\). Hence, a systematic coherent tensile strain tuning in the vertical direction is achieved.\[2\] Based on Landau–Devonshire phenomenological theory, strain induced tetragonality is a crucial parameter influencing the polarization, tunability, Curie temperature, \(T_c\), and dielectric properties of a ferroelectric.\[13\] Herein, the tetragonality, \(c/a\) is defined as the ratio of out-of-plane lattice parameter, \(c\), and in-plane lattice parameter, \(a\).

We now study the ferroelectric properties of the nanocomposite films. Figure 2a shows remnant polarization, \(P_r\), obtained from pulsed polarization measurements, also known as positive up negative down (PUND) measurements, versus tetragonality for the different films (more discussion and data on PUND measurements is shown later). In Table S1 (Supporting Information), we show \(c\) and \(a\) parameters, as well as \(c/a\), and
$P_r$ for all the films of different $x$ values and film thicknesses. We note in the middle region of Figure 2a, an unusual auxetic-like behavior (increase in both $c$ and $a$, as shown in Table S1 of the Supporting Information) is observed. This behavior is related to how, upon cooling, the stiff SmO shrinks and, in doing so, expands the BSTO matrix in-plane, as explained and modeled previously.[2]

Across the entire thickness range, a trend of increasing $P_r$ with tetragonality is observed with a much more marked increase in $P_r$ for the $x = 0.75$ samples. The highest $P_r$ values are for the 1000 nm thickness films. $P_r$ is 5.1 $\mu$C cm$^{-2}$, 5.8 $\mu$C cm$^{-2}$, and 12.1 $\mu$C cm$^{-2}$ for the $x = 0.25$, 0.50, and 0.75 films, consistent with the high $c/a$ values of 1.006(6), 1.012(9), and 1.033(7), respectively. The $P_r$ values for the $x = 0.75$ sample are 3 times higher than that for plain BSTO ($x = 0$) of similar thickness ($P_r = 3.9 \mu$C cm$^{-2}$) and is approaching state-of-the-art, similar thickness epitaxial PZT films grown by PLD on Si (001) with SRO and yttria-stabilized zirconia (YSZ) buffer layers, where $P_r = 18.6 \mu$C cm$^{-2}$ from $P–E$ loops measured at ±200 kV cm$^{-1}$.[14]

The $c/a$ values obtained for the composite films are significantly larger than the plain BSTO ($x = 0$) films studied here and compared to literature BSTO films.[15] The highest value achieved was 1.033(7) for the $x = 0.75$ film of thickness 1000 nm. It is noted that in plain films a high level of tetragonality is maintained only up to a critical layer thickness of a few nanometres.[2,9] On the other hand, in the nanocomposite films the different strain control mechanism means that there is no theoretical limit to strain control.[18] Indeed, $c/a$ for our films increases with film thickness. For a given composition (or $x$ value), the trend of increased tetragonality with film thickness is related to the fact that substrate control of the BSTO lattice parameters diminishes as the film thickness increases.[9,16] allowing the stiff second phase to have a full effect on the film strain state.

The highest $c/a$ value of 1.033(7) ($x = 0.75$, 1000 nm film) obtained is significantly higher than $c/a$ value reported for standard ferroelectric films previously, e.g., 1.019(9) for BTO.[17] Furthermore, the leakage is lower in the thicker films (see Figure S2, Supporting Information), consistent with earlier studies of BTO nanocomposite films.[18] The two factors of increased tetragonality and reduced leakage with film thickness explain why, for a given $x$ value, $P_r$ increases markedly with film thickness, e.g., for $x = 0.75$, $P_r = 5.8 \mu$C cm$^{-2}$ for a film thickness of 300 nm, whereas it is 12.1 $\mu$C cm$^{-2}$ for a film thickness of 1000 nm.

Figure 2b shows a schematic of the BSTO-SmO vertical interface heteroepitaxial matching depicting the strong tetragonal distortion induced in vertical nanocomposite films (thickness $> 50$ nm) compared to plain, unstrained films which are cubic at room temperature. The enhanced $c$-axis in the BSTO in the nanocomposite films originates from vertical lattice heteroepitaxy with the stiff nanoscaffold SmO phase. As already mentioned, the $a$ lattice parameter is controlled by how the in-plane thermal contraction of the stiff SmO phase upon cooling the film acts on the film matrix.[2] In short, since the SmO is much stiffer than the BSTO and it is epitaxially coupled to the BSTO, this leads either to in-plane contraction or expansion of the BSTO when the SmO either forms the nanocolumns (for $x < 0.5$) or matrix ($x > 0.5$), respectively.[2,18] This is very different to conventional epitaxial films.

Figure 2c shows the $P–E$ loops for the optimum composition, $x = 0.75$, films of different thickness. The $P_r$ values of 6.0, 7.9, and 13.2 $\mu$C cm$^{-2}$ for the 300, 600, and 1000 nm thicknesses, respectively (marginally higher than the values obtained from the PUND measurements because PUND eliminates leakage and other spurious effects) correlate with the increasing $c/a$ values of 1.023(9), 1.030(1), and 1.033(7), in the same way as the PUND-determined $P_r$ values do. Comparing the $P–E$ loop for the $x = 0.75$ sample to the pure BSTO film, $\approx 3 \times$ higher nominal polarization values were achieved.

We now study the ferroelectric retention. High thermal and temporal retentions are critical for achieving unlimited switching without degradation of polarization but they are limited in many ferroelectric systems, e.g., in BSTO, BaTiO$_3$, BiFeO$_3$, and PZT because of depolarization, inhomogenous field distributions, and defects.

In terms of thermal retention, thermal depolarization or back-switching of the poled state in the ferroelectric element occurs. The retention as a function of temperature is defined as

$$R(T) = \left[1 - \frac{\Delta P_r(T)}{P_r(T_0)}\right] \times 100 \quad (1)$$

where $R(T)$ is the retention determined via PUND measurements. The change of remnant polarization, $P_r$, can be described as $\Delta P_r(T) = P_r(T_0) - P_r(T)$, whereas $P_r(T_0)$ and $P_r(T)$ are the remnant polarizations measured at the initial temperature and elevated temperature, respectively.

In terms of temporal retention, $R(t)$ is defined as

$$R(t) = \left[1 - \frac{\Delta P_r}{P_r(0)}\right] \times 100 \quad (2)$$

where $\Delta P_r$ is the change in remnant polarization during time, $t$.[19] With this definition, 100% retention in the ferroelectric element at any $t$ will be observed if $\Delta P_r = P_r(0) - P_r(t)$, meaning that the state of polarization for the ferroelectric element has not changed. On the other hand, 0% retention will be obtained if $\Delta P_r = P_r(0)$ and $P_r(t) = 0$, i.e., the ferroelectric element is depoled entirely.

Figure 3 shows remnant polarization as a function of temperature for the nanocomposite films for $x = 0.25$ to $x = 0.75$, in comparison to plain BSTO films with 300 nm thickness obtained from both conventional $P–E$ loops (Figure 3a) and PUND measurements (Figure 3b) as a function of temperature. The conventional hysteresis loops and PUND measurements complement each other. The former allows the charge or polarization developed from intrinsic polarization, parasitic capacitance, and leakage contributions, to be determined when the electric field is applied to the ferroelectric film. The contribution of parasitic capacitance and leakage is inevitable if the measurement is carried out at an elevated temperature. The complementary PUND measurements, on the other hand, mitigate this problem since the remnant polarization is obtained through subtracting the nonswitching polarization from the switching polarization, thus allowing intrinsic polarization to be determined.[20,21] Figure 3d shows a series of PUND pulses.
of 300 kV cm\(^{-1}\), 1 ms pulse width and 1000 ms pulse delays for capturing both switching and nonswitching polarizations.

\( P_r \) as a function of temperature (from \( P-E \) plots, Figure 3a) shows negative gradients at lower temperature and positive gradients at higher temperature (except for \( x = 0.75 \)). The temperature at which there is transition of the gradient increases strongly with \( x \). The positive gradients arise from thermally activated loss and the leakage build-up of free electric charges.\(^{[19,22]}\)

For \( x = 0 \), we find only a positive gradient component to the plot. This is consistent with previously reported PLD grown BSTO films on MgO which were measured at much lower temperatures, from 80 to 220 K.\(^{[23]}\) in order to avoid the influence of parasitic interfacial capacitance. Such substrate-strained, very thin (50 nm) epitaxial films grown by RF-magnetron sputtering exhibited ferroelectric hysteresis up to 200 °C.\(^{[24]}\) The substrate strain effect increases the \( T_c \) from the bulk, unstrained value of \( \approx 250 \) K (\( -23^\circ \)C).\(^{[23]}\) but only in very thin films where strain relaxation is limited.

The reduction of the positive gradient component of the graph for increasing \( x \) indicates that the reduced leakage scales inversely with tetragonality. The tetragonal distortion leads to an increase in the ferroelectric–paraelectric transition, \( T_c \) to well above room temperature (to \( \approx 500 \) °C).\(^{[9]}\) without thickness limitation since the strain is not controlled by the substrate. Owing to the lower \( T_c \) of standard plain unstrained BSTO films, the \( P-E \) loops in the literature were measured at low temperatures (typically \(<300 \) K), where thermally activated leakage is not large. Here, leakage is low at much higher temperatures, i.e., above 250 K. The \( P_r \) as a function of temperature from PUND measurements (Figure 3b) shows the intrinsic polarization of the BSTO-SmO films without the contribution of parasitic leakage. This is the reason that the positive gradient part is eliminated. Figure 3a,b shows that the polarization is larger with increased \( x \), while Figure 3b shows that \( P_r \) decays less rapidly with temperature with increasing \( x \), indicating again the strong role of vertical strain on improving the ferroelectric behavior.

Figure 3c shows a reduced decay of the thermal retention, \( R(T) \), as \( x \) is increased. At 125 °C, \( R(T) \) values as high as 89% and 93% were obtained for the \( x = 0.50 \) and \( x = 0.75 \) films. These values are comparable to 89% measured in epitaxial Pb(Zr\(_{0.52}\)Ti\(_{0.48}\))O\(_3\) films at the same temperature.\(^{[25]}\) Both the \( x = 0.50 \) and \( x = 0.75 \) films maintain their retentions with 74% and 58% values measured at 375 °C. The \( x = 0.75 \) sample demonstrates a very low temperature coefficient of polarization retention of 0.07% °C\(^{-1}\) (up to 375 °C) which compares to 0.24% °C\(^{-1}\) for the \( x = 0 \) (plain BSTO) film. This temperature coefficient of polarization retention for the \( x = 0.75 \) sample is similar to the 0.09% °C\(^{-1}\) value for Pb(Zr,Ti)O\(_3\) films.\(^{[25]}\)

Normally, as the structural dimensions of ferroelectrics are scaled down, polarization (depolarization), dielectric permittivity, and Curie temperature are all reduced compared to bulk.\(^{[1]}\) Indeed, depolarization effects are normally severe for nanoscale ferroelectrics.\(^{[26–28]}\)

The enhanced thermal retention of polarization observed in the nanocomposites is consistent with the presence of a very
high density (Tb In.) of vertical interfaces which can compensate the surface polarization charge between the electrodes and BSTO lattice. Hence, the depolarization field, which influences the domain motion and degrades the polarization retention, is strongly reduced. Also, the high density of vertical interfaces in the nanocomposites likely act as ferroelectric domain nucleation centers to produce vertical growth of “needle-like” domains through the film, giving lateral expansion of domains within the BSTO with applied field. Furthermore, the lateral domain growth of BSTO is constrained by the vertical interfaces. Thus, these needle domains are pinned in a stable state when they are confined by the ~10 nm lateral dimensions in the nanostructured films (Figure 1). Our results are consistent with BSTO needle domains being stable, retaining ferroelectric polarization and giving rise to a strong improvement in thermal retention. They are unlike the needle domains in the compositionally graded PbZr0.25Ti0.75O3 heterostructures which are labile under electrical excitation.[29]

The excellent retention shown in the nanocomposites is very beneficial for miniaturized devices incorporating ferroelectrics where retention after many switching cycles at elevated temperature presents a serious challenge. The x = 0.75 composition which has a low temperature coefficient of polarization, high retention, and good depolarization stability. This contrasts to ferroelectrics nanostructures which do not involve having a supportive, strain-controlling scaffold phase as we do here, e.g., individual BaTiO3 nanowires, PbTiO3 nanotubes, BaTiO3 and BiFeO3 ultrathin films.[30–33]

Figure 4 demonstrates piezo phase contrast and effective piezodisplacement, d33, of the x = 0.75 film of a 300 nm thickness measured by piezoresponse force microscopy (PFM) at room temperature (Figure 4a) and at 200 °C (Figure 4b). The sequential polarization switching with 10 kHz excitation frequency and ±5 V AC modulating voltage superimposed on a ±10 V DC bias was performed over various scan areas.[31] A clear contrast was observed indicating reversal of domain polarization at room temperature. The irreversibile piezoresponse with complete out-of-plane switching confirms the ferroelectric nature even up to 200 °C even though the contrast is slightly lower than at room temperature owing to the thermally activated leakage current. We recall that plain BSTO films of thicknesses above a few 10 nm are relaxed and exhibit a bulk Tc of only ~250 K (~23 °C).[23]

The d33 values for the x = 0.75 film (as shown in Figure 4c) display a characteristic “butterfly” shape for the ferroelectric hysteresis, as expected, but with a reduced curve at 120 °C because of thermally activated leakage. Similar temperature dependent piezoresponse has been observed previously in (001) oriented PbZr0.5Ti0.5O3 (PZT) and epitaxial tetragonal BiFeO3 films up to 400 and 180 °C, respectively.[34,35] The d33 values measured for the x = 0.75 film were 88.1 and 81.4 pm V⁻¹ at room temperature and 120 °C, respectively. These d33 values are significantly higher than the room temperature d33 values for epitaxial BaTiO3 films (54.0 pm V⁻¹)[36] and BaTiO3 nanowires (45.0 pm V⁻¹). They are also close to PZT films (~100 pm V⁻¹) measured at 300 °C.[37] Thus, the PFM measurements confirm that the vertical strain effect in the composites retains the tetragonality in the BSTO up to at least 200 °C, the highest temperature studied here.

3. Conclusion

In summary, the structural and ferroelectric properties of 300, 600, and 1000 nm thickness epitaxial (Ba0.75Sr0.25TiO3)1−x•(Sm2O3)x nanocomposite films grown on SrTiO3 were studied. The most beneficial ferroelectric properties were obtained for x = 0.75. Here, the film structure consisted of ~10 nm vertical nanocolumnar BSTO pillars in stiff Sm2O3 matrix. The simply made, self-assembled films give rise to very high tetragonality in the BSTO (c/a up to 1.033(7), compared to 0.995(3) in plain 1000 nm BSTO films). Consequently, very strongly improved thermal retention of polarization up to 375 °C was obtained. Piezopoling with only marginal leakage current was also achieved up to 200 °C. In addition, depolarization from nanoscale size effects was overcome. Indeed, a threefold increase in remnant polarization was obtained. Nanoscaffold vertical strain control in epitaxial nanocomposite thin films offers a novel and practical route to strongly improve nanoscale ferroelectric films.
4. Experimental Section

Deposition of (BSTO)$_{1-x}$(SmO)$_x$, Vertically Aligned Nanocomposites: (BSTO)$_{1-x}$(SmO)$_x$ were grown by PLD using a KrF excimer laser 248 nm. Five different composition (BSTO)$_{1-x}$(SmO)$_x$ (x = 0.00, 0.25, 0.50, 0.75, and 1.00) composite targets were synthesized via conventional mixing and solid state sintering. The substrate temperature, oxygen pressure, and laser fluence were 800 °C, 20 Pa, and ~2 J cm$^-2$, respectively. The films were made into metal–insulator–metallic oxide test devices with sputtered coated Pt top circular electrodes (with a radius of 50 µm) and with SRO bottom electrodes. The 30 nm thick SRO bottom electrodes were deposited at 700 °C before the nanocomposite layers were grown.

Characterization: Crystallographic and microstructural investigations were carried out by high resolution XRD, TEM, and scanning electron microscopy (SEM). Polarization–electric field hysteresis loops and remnant polarization, $P_r$, as a function of temperature were performed using a radian ferroelectric tester for both conventional polarization–electric field (P–E) loop and PUND measurements. In the PUND measurements a series of 5 pulses were applied at 300 kV cm$^-1$ with pulse sequence of 0.1 ms to capture both switching and nonswitching remnant polarization, $P_{r}$. The switching electric field of 300 kV cm$^-1$ pulse sequence of 0.1 ms to capture both switching and nonswitching remnant polarization, $P_{r}$ was relatively low (e.g., 9 V applied on the BSTO-SmO nanocomposite films of 300 nm thickness. A delay of 1000 ms was set between the pulses. The initial pulse (Pulse 1) was applied to preset the film to the polarization stage and no measurement was made at this point. A second pulse (Pulse 2) was applied to switch the sign of polarization. After a 1000 ms pulse elapsed, the film was left to relax, allowing the nonremnant polarization to be dissipated. A third pulse (Pulse 3) was then applied and the polarization measured without preswitching. Fourth and fifth pulses (Pulses 4 and 5) were again applied, similar to Pulses 2 and 3 but with the opposite polarity. PFM measurements were performed using an Agilent 5500 scanning probe microscope in PFM mode together with 3 lock-in amplifiers. The electrically biased conductive atomic force microscopy tip was used to detect the piezoresponse of the films through tip deflection.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

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