Nanoscale polarisation switching and leakage currents in \((\text{Ba}_{0.955}\text{Ca}_{0.045}\text{Zr}_{0.17}\text{Ti}_{0.83})\text{O}_3\) epitaxial thin films

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Nanoscale polarisation switching and leakage currents in (Ba$_{0.955}$Ca$_{0.045}$) (Zr$_{0.17}$Ti$_{0.83}$)O$_3$ epitaxial thin films

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Abstract

This paper investigates the crystal structure, ferroelectric, temperature-dependent leakage current conduction mechanism and the piezoresponse force microscopy (PFM) behaviours of (Ba$_{0.955}$Ca$_{0.045}$) (Zr$_{0.17}$Ti$_{0.83}$)O$_3$–BZT–BCT ($x = 0.15$) films at the vicinity of the morphotropic phase boundary (MPB) of the $[(1-x)$ BaZr$_{0.20}$Ti$_{0.80}$O$_3$–$x$Ba$_{0.70}$Ca$_{0.30}$TiO$_3]$ ($x = 0.50$) composition. Epitaxial BZT–BCT thin films were grown on conductive La$_{0.5}$Sr$_{0.5}$CoO$_3$ (LSCO) layers coated onto MgO (1 0 0) single-crystal substrates by pulsed laser deposition (PLD). High resolution x-ray diffraction (HR-XRD) reciprocal space maps (RSMs) confirmed the epitaxy with in-plane tetragonal symmetry ($c < a$), and Raman spectra also revealed a tetragonal perovskite crystalline lattice structure. Polarisation studies demonstrate that BZT–BCT films exhibit a high saturation polarisation of 148 $\mu$C cm$^{-2}$ and a high recoverable (discharged) energy-storage density of 39.11 J cm$^{-3}$ at 2.08 MV cm$^{-1}$. Temperature-dependent $P$–$E$ hysteresis loops resulted in a decrease in polarisation. Temperature-dependent leakage current behaviour was obtained and possible conduction mechanism is discussed. PPFM images revealed switchable ferroelectric piezoelectric contrasts after the application of a $\pm 9$ V dc voltage on the conductive tip of the piezoresponse force microscope.

Keywords: ferroelectric, piezoresponse, imprint

(Some figures may appear in colour only in the online journal)
and health concerns due to ~60 weight percent lead toxicity during the manufacture, use, and recycling of these devices [3]. Both worker safety and waste disposal are areas of growing legislation. Therefore, it is highly desirable to search for lead-free alternative materials for these applications and to reduce the impact of Pb-containing materials on the environment. Recently there have been tremendous efforts to develop lead-free ferroelectric ceramics with excellent piezoelectric properties, which include BaTiO3—BTO, BiFeO3 (BFO) Na0.5Bi0.5TiO3 (NBT), K0.5Bi0.5TiO3 (KBT), Na0.5K0.5NbO3 (NBN), Bi2Ti2O7 (BIT) and their solid solutions. These are priorities for specific applications of piezoelectric ceramics, especially with regards to energy harvesting [4]. However the main drawback of these (BFO, NBT, KBT, BIT and NBN) materials is the presence of highly volatile elements like Bi, Na and K [4].

BTO is one of the most widely studied lead-free ferroelectric piezoelectric materials; however, the ferroelectricity or piezoelectricity of BTO is low when compared with PZT. Previous research reveals that by suitable site engineering both at Ba2+ and Ti4+ sites in BaTiO3 solid solutions (Ba0.7Ca0.30TiO3, BaZr0.20Ti0.80O3) (1 − x) BaZr0.2Ti0.8O3−xBaCa0.7Ti0.3O3, etc), it is possible to observe an improvement in the dielectric, ferroelectric and piezoelectric properties. Recently Ren et al [5], developed a lead-free pseudobinary ferroelectric system (1 − x) BaZr0.20Ti0.80O3−xBaCa0.70Ti0.30O3 with a MPB bulk ceramics composition: 0.5BaZr0.20Ti0.80O3−xBaCa0.70Ti0.30O3, etc, which shows an outstanding piezoelectric effect (d33 = 620 pC N−1) with the potential for replacing lead-based ferroelectric materials. This strong piezoelectric effect is attributed to a phase coexisting (rhombohedral and tetragonal) MPB composition starting from a triple point (tetragonal—cubic—rhombohedral), which causes a very low energy barrier for polarisation rotation and lattice distortion [5]. This research led to worldwide attention on lead-free (1 − x) BZT−xBCT ceramics over a wide range of compositions (x = 0.10 to 0.90) with optimised parameters for improved ferroelectric piezoelectric materials properties and the potential for replacing lead-based materials for various multifunctional applications [5–32].

A number of deposition methods have also been employed to prepare the (1 − x)BZT−xBCT based thin films [18–25]. By metalorganic decomposition method, dielectric tunable properties of (Ba0.95Ca0.05) (Zr0.16Ti0.84)O3 thin films on Pt/Ti/SiO2/Si substrate are reported for microelectronic device applications [18, 19]. There are only a few studies reporting on the piezoresponse force microscopy (PFM) studies on this system of ceramics and thin films [25, 28–32], which has been proven to be a powerful technique for nanoscale characterisation of the static and dynamic polarisation behaviour in ferroelectrics.

In this work we have grown epitaxial (Ba0.95Ca0.05) (Zr0.16Ti0.84)O3−BZT—BCT thin films (~360 nm), in the proximity of the morphotrophic-phase-boundary (MPB) on conductive L40S30R30CoO3 (LSCO)-coated MgO (100) single-crystal substrates using pulsed laser deposition (PLD) at 700 °C. Polycrystalline ceramic targets were prepared by conventional powder processing techniques, starting from high purity raw materials - the detailed experimental procedure is reported in [26, 27]. The crystal structure with its reciprocal space maps (RSM), room-temperature capacitance−voltage (C−V) measurements, temperature-dependent leakage current behaviour, nonlinear ferroelectric hysteresis (P−E) loops and PFM were studied as well as the energy storage characteristics of these films.

**Experimental procedure**

The BZT–BCT thin films (360 nm) were grown via PLD at ~100 mTorr oxygen pressure, ~700 °C substrate temperature and ~350 mJ pulse energy at the target with an excimer laser (Coherent Inc.) (KrF; λ = 248 nm) operating at a pulse repetition rate of 10 Hz. After deposition, the as-grown films were annealed at 700 °C in high-purity oxygen (~99.99%) at 300 Torr for 30 min and then cooled down to room temperature slowly. Similar deposition parameters were used to grow highly epitaxial LSCO layers (acting as the bottom electrode) on the MgO substrate. Structural characterisation of these films was carried out using four-circle high resolution x-ray diffraction (HR-XRD) (a Bruker AXS D8 Discover x-ray powder diffractometer equipped with monochromatic Cu Kα radiation (κα = 1.5406 Å)). For electrical measurements, test capacitors with a metal–insulator–metal (MIM) structure were fabricated on (100) MgO substrates, circular Au top electrodes (100 nm thick) were deposited with a shadow mask ~200 μm in diameter and conductive LSCO- coated MgO substrates acted as the bottom electrode. Electric field dependent dielectric and ferroelectric properties were obtained at 4 kHz with an HP4294A impedance analyser and a Radiant Precision Multiferroic Materials Analyzer (Radiant Technologies Inc., NM, USA). The leakage current measurements of these BZBCT films were done under a vacuum (10−4 Torr) at different temperatures (273−450 K) and measured in a top−bottom electrode sandwich configuration using the Radiant Precision Multiferroic Materials Analyzer and the K-20 (MRM Technologies) temperature programmable controller.

PFM measurements were carried out with a multimode Nanoscope V (Veeco Instruments, now Bruker) in ambient conditions. The conductive tips used were from Bruker and were coated with Pt/Ir. They had a resonant frequency of 140 kHz and a force constant of 4.5 N m−1. The driving voltage was applied on the surface of the thin film. The resonance frequency of the material was found to be 225 kHz. Single frequency excitation PFM measurements were done to observe the polarisation switching, hysteresis and the amplitude of the material.

**Results and discussion**

BZT–BCT ceramics have been shown to have a polycrystalline perovskite crystal structure and exhibit a rhombohedral and tetragonal phase coexistence that is characterised by a splitting of the (002)/(200) peaks at approximately 20−45° and as well as a splitting of the (202)/(220) peaks at approximately 20−65°−66°, as reported in [26, 27]. The HR-XRD measurements
confirm the epitaxial growth of the BZT–BCT films on MgO (001) substrates, as shown in figure 1 which demonstrates a representative BZT–BCT film grown at 100 mTorr oxygen pressure. The 20–θ graph in figure 1(a) shows strong (00l) reflection peaks from the BZT–BCT, LSCO, and MgO substrates without any identifiable peaks from secondary phases, indicating that the BZT–BCT thin films have a single perovskite phase and are highly oriented along the c-axis. The inset is the HR-XRD RSMs around the BZT–BCT peaks from the BZT–BCT (113) reflections for the same film. The film peak for the BZT–BCT has shifted from the MgO (113) along the horizontal axis, suggesting that the film is strain-relaxed. From the horizontal and vertical positions of the BZT–BCT (113), the in-plane (a = 4.072 Å) and the out-of-plane (c = 4.043 Å) lattice constants exhibit a slight tetragonal distortion (c < a) (a/c ~1.007). Lattice parameters for the bulk BZT–BCT were a ~4.026 Å, c ~4.028 Å, tetragonal distortion (a/c ~0.99), and volume (~65.33 Å³). The use of an oxygen pressure of 100 mTorr in our films has led to structural distortion where c < a, which is similar to the result found by Allredge et al [33] and Sondes Bauer et al [34]. The rocking curves of (002) BZT–BCT and (001) LSCO peak in figures 1(b) and (c) showing full-width at half-maximum (FWHM) of 0.6° and 0.7° respectively. The broad rocking curves indicate a large mosaic spread of the BZT–BCT and LSCO films on the MgO substrate. The epitaxial growth of BZT–BCT/LSCO/MgO (001) is verified by the θ-scans of the BZT–BCT (2 0 2), LSCO (2 0 2), MgO (2 0 2) in figures 1(e)–(g), respectively. The θ-scans confirm the epitaxial relationship: BZT [0 0 1] || LSCO [0 0 1] || MgO [0 0 1] and BZT–BCT [1 1 0] || LSCO [1 1 0] || MgO [1 1 0]. The structural analysis from x-ray diffraction (XRD) suggests that the epitaxial BZT–BCT films on the MgO (001) substrate grew in single-phase perovskite structures with no detectable impurity or any other secondary phases. Similar phenomena were observed in pure BaTiO3 (BTO) and as well as BZT–BCT thin films deposited on single-crystalline STO substrates, which in turn suggest a similar nucleation and growth pattern in the thin films of BTO and its solid solutions [25, 35, 36].

A four-peak structure indicates an in-plane ‘cube-on-cube’ epitaxy of the BZT–BCT on the MgO (100) substrate. Epitaxial BZT–BCT films were obtained at a 700°–750 °C annealing temperature. The oxygen pressure was an important factor to be considered for the film growth and the optimized 100 mTorr oxygen pressure resulted in epitaxial film. A higher annealing temperature (700 °C and above) is needed to completely transform the metastable pyrochlore phase into the perovskite phase with random orientation [10]. High-quality epitaxial BZT–BCT films can be only achieved in the relatively narrow temperature range of 700–750 °C by PLD. However such an annealing temperature is dramatically lower than the calcination/sintering temperature of 1250–1600 °C required for forming the perovskite phase in the counterpart BZT–BCT bulk ceramics [2, 5, 25]. The particle size of the BZT–BCT thin films were estimated to be in the range of 0.27 nm, using the (100) peak of XRD patterns using the Scherer formula \[ D = \frac{(K \times \lambda)}{(\beta \times \cos(\theta))} \]. Thin film growth on a substrate induces a structural stain due to lattice mismatch between the thin film and the substrate. The lattice mismatch between the substrate and the film leads to the lattice strain, which can be calculated using the formula \[ \xi = \frac{(\delta_{\text{substrate}} - \delta_{\text{film}})}{\delta_{\text{film}}} \times 100 \], where \( \delta_{\text{substrate}} = 4.043 \) Å and \( \delta_{\text{film}} = 4.213 \) Å (cubic MgO has a lattice constant of 4.213 Å). The lattice constant of the BZT–BCT film (4.043 Å) is less than the lattice constant (4.213 Å) of the MgO substrate. In general the positive lattice mismatch (\( \xi \)) indicates a tensile strain and the negative lattice mismatch (\( \xi \)) indicates a compressive strain in the films respectively. The lattice mismatch between the film and the substrate was found to be ~4%. From the lattice mismatch calculations, the tensile strain in the BZT–BCT film on the MgO is observed.

Figure 1(a) shows the HR-XRD RSMs around the BZT–BCT (113) and the MgO (113) reflections. The in-plane lattice parameter of the grown BZT–BCT thin film was derived by recording the RSM of the asymmetric 113 reflection. The lattice parameters of the film along the c-axis ~4.043 Å and along the a-axis ~4.072 Å were calculated from the RSM images. The films showed an in-plane (c < a) (a/c ~1.007) tetragonal distortion. The in-plane and out-of-plane lattice constants of the film can be calculated from the horizontal and vertical peak positions. The position of the film peak indicates an in-plane tetragonal symmetry due to the coherent epitaxial tensile strain from the substrate.

A Raman spectrum reveals a close relationship between ferroelectricity and lattice dynamics and is a valuable non-destructive technique for the study of ferroelectric materials. Room-temperature Raman spectra are used to confirm the crystallite structure. In BaTiO3-based perovskite materials above the cubic→tetragonal phase transition there are fifteen degrees of freedom, which are divisible into 4F1u+ 1F2u [2]. One of the F1u symmetry modes corresponds to the acoustic branch. The remaining 3F1u and 1F2u belong to the optical branches in the cubic phase with O_h or Pm3m point group symmetry [2]. Due to the presence of long-range ordering electrostatic forces, the high temperature cubic–phase Raman optical modes \( A_1 \) and \( E \) are further split into longitudinal optical (LO) and transverse optical (TO) branches [37]. Raman-active optical lattice vibrations for BaTiO3 in the tetragonal phase are \( A_1(TO) + 3 A_1(LO) + E(TE) + 3 E(TE) + 3 E(LO) + 1E(LO+TO) + 1 B_1[38] \).

Figure 1(e) illustrates the Raman spectra for BZT–BCT ceramics and epitaxial thin films. The peaks corresponding to tetragonal symmetry were indexed as \( A_1(TO)\), \( A_1(TO)\), \( B_1(TE)\), \( A_1(LO)\), \( A_1(LO)\), \( A_1g\) modes respectively. Another interesting feature of these bulk and thin-film Raman spectra is the presence of the \( A_1g\) octahedral breathing mode at around 800 cm\(^{-1}\) [2, 26, 27]. The presence of this breathing mode demonstrates that Ca\(^{2+}\) resides partially on the Ti-site in the BaTiO3 lattice. Shifts in \( A_1(TO)\) and \( A_1g(TO)\) modes either to a lower or higher frequency are attributed to the asymmetric Ti–O–phonon vibrations, while the presence of the \( A_1(TO)\) mode at around 516 cm\(^{-1}\) is due to O–Ti–O symmetric stretching vibrations. On the other hand, the peak positions of some of the Raman modes such as \( B_1(TE)\) and \( A_1(LO)\) in the bulk BZT–BCT and the epitaxial films shifted down and some shifted up, compared with barium titanate. This may be due to strain; our BZT–BCT epitaxial
films are almost fully constrained by the substrate, resulting in large in-plane tensile strain as explained above.

**Ferroelectric and energy storage properties of BZT–BCT thin films**

Due to their unique set of physical and electrical properties, ferroelectric thin films are promising materials in electronic applications. Ferroelectric materials with domain walls as thin as possible are favoured for high-density data storage. High dielectric constant ($\varepsilon > 10^3$) ferroelectric and antiferroelectric (AFE) materials are essential to attain high energy densities in compact storage capacitors. In contrast, low dielectric constant materials ($\varepsilon > 10^2$) are used in conventional capacitors. When compared to linear dielectrics and nonlinear ferroelectrics, field induced AFE materials have become the most attractive candidate materials for charge-storage devices, micro-actuators, and electro-optic devices, due to their enhanced double hysteresis

![HR-XRD patterns with $2\theta$-$\theta$ scans of: (a) (00l) orientation of BZT–BCT films with LSCO coated on an MgO (100) single crystal substrate by PLD. The inset shows HR-XRD RSMs showing BZT–BCT (113) and MgO (113) reflections of the BZT–BCT films on MgO (100); (b) the rocking curve for the BZT–BCT (002) reflection of the film; (c) the rocking curve for the LSCO (002) reflection of the buffer layer; (d) $\phi$ scans of the BZT–BCT (202), LSCO(202), MgO(202) reflections, respectively from the BZT–BCT film with LSCO coated on MgO (100) single crystal substrate; (e) room temperature Raman spectra for the bulk BZT–BCT and the BZT–BCT thin films.](image-url)
loops with small coercive voltages and high saturation polarization [39, 40]. AFE materials exhibit higher energy densities than nonlinear ferroelectrics and linear dielectrics, due to the absence of remnant polarization in their AFE double hysteresis loops, where the total storage charge can be released. Even though AFE materials exhibit higher energy densities, their charge-discharge cycles cannot be sustained for more than several hundred cycles because of cracking in the films due to the repeated strain during the field-induced phase transitions [41].

There is a greater demand for dielectric capacitors for the next generation of hybrid capacitor applications which can accumulate a huge amount of energy and then discharge instantaneously (in nanoseconds (ns)). Such materials play a vital role in "pulse power" applications, i.e. power electronics, mobile electronic devices, high-power microwave systems and hybrid electrical vehicles, and are required to work at higher voltages and release large discharge current rapidly (in ns) [42].

The ferroelectric nature of prepared BZT–BCT thin films was confirmed by a hysteresis loop of polarization ($P$) as a function of an applied electric field ($E$) obtained at different voltages (20 to 75 V at 4000 Hz), as shown in figure 2(a). Careful examination of different Pt top dot electrodes on shadow masks with the LSCO bottom electrode on the MgO substrate at room temperature revealed saturated ferroelectric hysteresis loops. The hysteresis loops reveal that as the voltage increases, the $P$–$E$ loop becomes slanted. As the electric field increased from 0.55 MV cm$^{-1}$ to 2.08 MV cm$^{-1}$, both saturation polarization ($P_s$) and the remnant polarization ($P_r$) were increased. Ferroelectric loops showed a maximum of 148 $\mu$C cm$^{-2}$ saturation polarization with 95.80 $\mu$C cm$^{-2}$ remnant polarization in the BZT–BCT thin films, much higher than their bulk BZT–BCT ceramic counterparts [26, 27]. The coercive field of 0.56 MV cm$^{-1}$ was dramatically higher than the value of 1.75 kV cm$^{-1}$ for the bulk ceramic [26, 27]. The hysteresis curves exhibited a discontinuity along the polarization axis at the zero applied field in all room temperature $P$–$E$ loop measurements of the BZT–BCT films. The reason for this phenomenon is due to the way measurement is performed by the Radiant Ferroelectric Test system (Radiant Technologies Inc. NM, USA) in the virtual ground mode. The gap is real and is caused by temporary memory that decays away in a few seconds. So the origin of the discontinuity in the $P$–$E$ ferroelectric hysteresis loops observed here may be due to the polarization relaxation.

The much higher coercive field might be due to much smaller grains in the BZT–BCT films in comparison with the bulk ceramic hence there being many more grain boundaries. It might also be due to substrate clamping effects [27]. However, when the BZT–BCT films are grown on LSCO coated MgO substrates, the hysteresis loops are strongly asymmetric in terms of the polarity of the applied voltage. In addition, the centers of the hysteresis loops were not located at zero bias fields, but shifted horizontally towards the negative bias field. This type of horizontal shift in polarisation loops is termed ‘imprint’[43, 44]. Such behaviour is usually observed in PLZT and PZT/LSCO hetero-epitaxial ferroelectric films, due to oxygen vacancies or an alignment of defect dipoles, and is also due to built-in internal electric fields inside the ferroelectric material [43–45]. The built-in internal electric field is also related to the semiconducting dielectric and its interface with the metal bottom electrode [46]. Built-in internal electric
fields exist at the film/electrode interface and have an independent polarisation, always pointing in one direction [47].

The so-called ‘imprint effect’ is a voltage shift attributed to an asymmetric distribution of trapped electrons at the interfacial sites. This voltage shift reduces one (+P or −P) of the remnant polarisations, and the coercive voltage becomes too large in one direction for switching to occur (this is due to memory failure). Tahakashi et al. reported that donor doping decreased the voltage shift in bulk PZT [48].

To achieve large energy densities, it is necessary for nonlinear ferroelectrics to exhibit a very large spontaneous polarisation and low remnant polarisation with low energy loss from hysteresis. Leaky behaviour leads to the overheating of devices, and more power is consumed, which is an undesirable effect for device applications; hence leakage measurements are a crucial part of any electrical characterisation of a ferroelectric device [49]. Current flow through the material should be as low as possible from an application point of view, and it is vital to know the conduction mechanism in the material [50].

A dielectric capacitor with very high dielectric field strength plays a key role in achieving high energy densities. Hence leakage current behaviour was measured to determine the breakdown field and physical origin of the conduction [51]. The temperature-dependent leakage current mechanism is discussed in the next section. Enhanced polarisation of the ferroelectrics when compared to the bulk value might be due to the in-plane strain caused by the mismatch between the lattice parameters of the ferroelectric films and the substrate [49].

In general for nonlinear ferroelectric capacitors, the energy density (E_d) of a capacitor is evaluated from the P–E hysteresis loop. The energy density is the integral area of the P–E loop (charging the lower branch of the P–E curve or discharging the curve—upper branch of the P–E curve); the y-axis is given by E_d = ∫E.dP, where E is the applied electric field and P is the polarisation [52, 53] if the capacitor is a perfect insulator. That is, the vertical axis of the hysteresis loops is actually a measure of charge, integrating dP/dt + J, where the first term is the displacement current and the second term is the real conduction current; only if J = 0 does measure the hysteresis of P. The energy efficiency (η) of the capacitor is evaluated using the ratio of discharging energy density (J_d) to that of the charging energy density (J_c) [27]. Charge and discharge energy densities calculated from the ferroelectric hysteresis loops were ~117.5 and ~39.1 J cm⁻³ with an energy storage efficiency of 33% at the dielectric breakdown field (~2.08 MV cm⁻¹) before the ultimate dielectric breakdown field occurs, as shown in figures 2(b) and (c). BZT–BCT thin films have shown higher charge and discharge energy densities when compared to the bulk values (E_d of ceramics ~0.94, 0.68 J cm⁻³) [27]. When compared to present lead-free BZT–BCT thin films, lead based (Pb0.97La0.02)(Zr0.95Sn0.05)O3 sol–gel synthesised AFE thin films have shown recoverable energy density ~56 J cm⁻³ [53]. In addition, the Hf0.5Zr0.5O2 AFE double hysteresis loops have also shown higher energy density ~45 J cm⁻³ [54]. However, AFE poly(ethyl methacrylate) (PEMA) grafted poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) thick films have shown a lower recoverable energy density ~14 J cm⁻³ than the present BZT–BCT thin films [55]. The field-dependent charge/discharge energy densities of the films are shown in figure 2(b). As the electric field increased, the charge and discharge energy densities of the thin films increased. These films also followed the expected trend, that the charge curve energy densities are higher than the discharge curve energy densities. Reducing dielectric and ferroelectric loses in these ceramic thin films can further enhance energy storage densities.

Figures 2(c) and (d) show the temperature dependence on the ferroelectric properties of the BZT–BCT thin films. The P–E loops are saturated and non-linear in nature, and they become slimmer with increasing temperature, accompanied by the gradual decrease in P_r and E_c as indicated in figures 2(c) and (d). The non-linear ferroelectric hysteresis nature, which is significantly above the Curie temperature, is mainly attributed to the presence of residual polar micro-regions or ferroelectric clusters [56].

**PFM of the BZT–BCT thin films**

The surface morphology of the PFM image (indicated by the height) of the film is shown in figure 3(a). The surface morphology of the films did not present any evidence of cracking or defects, indicating a fairly uniform deposition. From PFM surface morphology observation, it can be inferred that BZT–BCT films exhibit a uniform and dense microstructure. The measured root-mean-square (RMS) roughness is approximately 3.5 nm. Higher values of surface RMS roughness over the area of 6 µm x 6 µm might be due to a larger substrate target distance. In general by varying the substrate target distance, the grain size of the films also changes. It can be seen that these films have developed a dense granular microstructure (figures 3(a) and (d)) and they are closely packed. Even though the grains are not completely uniform throughout the film, all the regions are completely filled with ablated material. Intermediate island growth is also observed in some parts of the image shown. Ferroelectricity in the BZT–BCT films at the nanoscale level was confirmed using PFM. Piezoresponse images were obtained using a conducting AFM probe and by applying a local electric field bias with the conductive AFM/PFM tip as the top electrode and with the LSCO bottom electrode grounded. A conductive Pt/Ir cantilever tip was used both for the domain visualisation and for the polarisation reversal. From figures 3(c) and (d) it is observed that the ferroelectric switching contrasts in the BZT–BCT film. It is also clear from the phase and amplitude images that there exists a strong domain switching response for both negative (revealed by the outer square) and positive bias (revealed by the inner square). The square patterns clearly show the oppositely written regions; this establishes that the BZT–BCT films show nanoscale switching behaviour which confirms their ferroelectric piezoelectric nature [57]. Further, the polarisation switching was observed by writing square patterns on the BZT–BCT films' surface on
a 6 µm × 6 µm area by applying a poling (writing) dc bias voltage of ±9 V. The domains with opposite polarisation are distinguished with dark and bright contrast in the image. The colour contrast both in the phase and amplitude images demonstrates the switchable ferroelectric response of the films at the nanoscale. Piezoelectric contrast (shown by the bright and dark shades) appears after scanning with a dc voltage to the tip, giving spontaneous polarisation; it can be

Figure 3. (a) Surface topography height (AFM) image; (b) surface topography deflection image; (c) PFM phase image; (d) PFM amplitude image; these confirm the switchability of ferroelectric polarisation under a ±9 V bias voltage; (e) local piezoelectric phase hysteresis loop; (f) local piezoelectric amplitude loop for the (BZT–BCT) films.
switched by applying the external voltage. The out-of-plane (OP) piezoresponse amplitude and phase images are shown in figures 3(c) and (d). In addition, regular square patterns were observed in the center region of the PFM amplitude and phase images, which may be caused by the effect of the grain boundaries on the domain switching. The SS-PFM amplitude and phase hysteresis loops are shown in figures 3(e) and (f); the local piezoelectric amplitude and phase hysteresis loops of the BZT–BCT film in the graphs correspond to the dc tip bias sweep from a positive to a negative voltage cycle. The PFM hysteresis loops were obtained using the AFM tip itself as the top electrode as a function of switching the pulse amplitude. The phase change in the PFM loops indicates complete domain switching in the BZT–BCT films. Local PFM measurements (figures 3(e) and (f)) exhibit bipolar piezoelectric amplitude and phase hysteresis loops. Local PFM phase and amplitude versus voltage hysteresis were observed through the top electrode, indicating that the film is ferroelectric in nature. The local coercive voltages are approximately −2.50 and 0.26 V, as indicated by the minima of the amplitude loop. It has been found that the films also show imprint behaviour at the nanoscale level, i.e. the switching is quite asymmetric with a disparity between the positive and negative coercive voltages. The observed horizontal shift in nanoscale ferroelectric hysteresis loops along the voltage axis is called a ‘local imprint effect’, due to abnormal polarisation regions [47]. Ferroelectric imprint behaviour in these films might be due to abnormal polarisation contrast regions opposite to the applied electric field, which in turn results in spontaneous backswitching to a preferred polarisation state after the electrical poling field is turned off [58]. The asymmetry in our films might also be due to the absence of a separate top electrode (the AFM tip itself is the top electrode in our measurements); in piezoresponse studies, the tip/film/electrode configuration brings about its own asymmetry at the nanoscale [47].

**DC electronic transport of the BZT–BCT thin films**

In order to determine the conduction mechanism of the BZT–BCT thin film, measurements of its current–voltage (I–V) characteristics above room temperature (300 to 450 K) were performed. In order to measure the conduction current, the sample had a MIM structure. The main parameter of this type of measurement is the barrier height of the metal–dielectric interface. There are large numbers of possible leakage current limiting mechanisms for ferroelectric perovskite oxides, and these mechanisms fall into two categories, bulk limited and interface-limited conduction.

It was seen that the conduction through the dielectric BZT–BCT film is noticeable when a relatively large bias voltage is applied. Of all the possible mechanisms, this conduction current shows a non-Ohmic behaviour as is illustrated in figure 4(a) and is probably an electrode-limited conduction mechanism. Despite an asymmetric structural configuration of the electrodes, a symmetric behaviour of the leakage current was observed on reversing the bias. We can see that the leakage current of the film is affected by heating; we found a steady increase of the leakage current when the temperature was increased (i.e. 780 A at 300 K to 1700 μA at 450 K for 100V). Variable temperature measurements help validate the tunnelling transport mechanism across the metal–dielectric junction. The tunnelling can be described by the modified Simmons model, which is widely used to explain the conduction mechanism in oxide tunnel barriers.

The relation describing the tunnelling current (I) as a function of the applied bias (V) defined by Simmons include four barrier characteristics, namely [59–61]:

\[ G_0 = \text{equilibrium conductance (}\Omega^{-1}\text{)}; \]
\[ \phi_0 = \text{barrier height (V)}; \]
\[ \rho = \text{shape factor (V}^{-1}\text{)}; \]
\[ \alpha = (L/l) = \text{width ratio [59].} \]

The equilibrium conductance \(G_0\) is the first derivative of the current with respect to the voltage near the zero bias and includes information on the current magnitude. The shape factor \(\rho\) is a parameter indicating the ratio between the width and the height of the barrier and describes the shape of the I–V curves. The equilibrium barrier height (\(\phi_0\)) is the difference between the potential at the surface and the bulk of the dielectric sample, generally equal to the average of the difference in work function at the two interfaces. The width ratio (\(\alpha \equiv (L/l)\)) is a dimensionless parameter interpreted as the ratio between the junction width \(L\) and the tunnel barrier width \(l\) and it is introduced to provide a way of applying the tunnelling model of a rectangular barrier to tunnelling through a non-rectangular barrier [59].

Thus the Simmons model is:

\[
I = \frac{2G_0\phi_0}{\alpha^2(\rho\phi_0 - 2)} \left[ 1 - \frac{V}{2\phi_0} \exp \left( \frac{\rho\phi_0}{1 - \alpha} \sqrt{\frac{1 - V}{2\phi_0}} \right) \right]
- \left( 1 + \frac{V}{2\phi_0} \right) \exp \left( \rho\phi_0 \left( 1 - \alpha \frac{1 + \sqrt{1 - V/2\phi_0}}{2\phi_0} \right) \right)
\]  

(1)

By fitting I–V curves using the Simmons model, the four parameters \(G_0, \phi_0, \rho, \alpha\) can be obtained. Our measurements were carried out at the highest bias; therefore the first term in the equation is dominant and the current can be approximated as [62–64]:

\[
I = \frac{2G_0\phi_0}{\alpha^2(\rho\phi_0 - 2)} \left[ 1 - \frac{V}{2\phi_0} \exp \left( \rho\phi_0 \left( 1 - \alpha \sqrt{\frac{1 - V}{2\phi_0}} \right) \right) \right]
\]  

(2)

In order to discuss the leakage current mechanism at different temperatures, we fitted the leakage current curves under the positive applied field using equation (2).

The modified Simmons equation at the highest bias voltage provides a good fit to the experimental data, as represented by the solid lines in figure 4(b) at selected temperatures, and provides the values of the physical parameters \(G_0, \phi_0, \rho, \alpha\). The best-fitting parameters over all the temperature range are shown in table 1. The parameters seem reasonable, in spite of the simplified assumptions of the model.
Figures 4(c) and (d) display the temperature dependence of $G_0$ and $\phi_0$. As expected the conductance ($G_0$) and the barrier height ($\phi_0$) of the BZT–BCT thin film sample increase as the temperature increases. $G_0$ was found to be in the range of $\sim$6 to $\sim$27 $\mu\Omega^{-1}$. These values are typical of metal–dielectric interfaces [65]. On the other hand, the values of $\phi_0$ were found to be in the range of $\sim$300 to $\sim$485 mV.

Increasing temperature shows that the barrier height has a linear decrease. Such a trend has been observed in the negative temperature coefficient (NTC) of semiconductor materials, which is consistent with doped BaTiO3 materials [66]. The increasing temperature facilitates the formation of conducting paths and the potential barrier decreases through the material. Therefore, it is important to gain information about

Table 1. Summary of the BZT–BCT film tunnelling parameters as a function of temperature according to the Simmons model at highest bias voltage.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$G_0$ ($\Omega^{-1}$)</th>
<th>$\phi_0$ (V)</th>
<th>$\rho$ ($V^{-1}$)</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>$(5.80 \pm 0.1) \times 10^{-6}$</td>
<td>$0.48 \pm 0.01$</td>
<td>$57.6 \pm 0.05$</td>
<td>$1.00 \pm 0.01$</td>
</tr>
<tr>
<td>300</td>
<td>$(6.83 \pm 0.1) \times 10^{-6}$</td>
<td>$0.45 \pm 0.01$</td>
<td>$60.5 \pm 0.05$</td>
<td>$0.99 \pm 0.01$</td>
</tr>
<tr>
<td>325</td>
<td>$(8.21 \pm 0.1) \times 10^{-6}$</td>
<td>$0.42 \pm 0.01$</td>
<td>$62.5 \pm 0.05$</td>
<td>$1.01 \pm 0.01$</td>
</tr>
<tr>
<td>350</td>
<td>$(8.73 \pm 0.1) \times 10^{-6}$</td>
<td>$0.39 \pm 0.01$</td>
<td>$60.8 \pm 0.05$</td>
<td>$1.02 \pm 0.01$</td>
</tr>
<tr>
<td>375</td>
<td>$(9.58 \pm 0.1) \times 10^{-6}$</td>
<td>$0.37 \pm 0.01$</td>
<td>$59.3 \pm 0.05$</td>
<td>$0.92 \pm 0.01$</td>
</tr>
<tr>
<td>400</td>
<td>$(1.45 \pm 0.1) \times 10^{-5}$</td>
<td>$0.33 \pm 0.01$</td>
<td>$62.7 \pm 0.05$</td>
<td>$0.94 \pm 0.01$</td>
</tr>
<tr>
<td>425</td>
<td>$(1.92 \pm 0.1) \times 10^{-5}$</td>
<td>$0.31 \pm 0.01$</td>
<td>$66.2 \pm 0.05$</td>
<td>$0.94 \pm 0.01$</td>
</tr>
<tr>
<td>450</td>
<td>$(2.71 \pm 0.1) \times 10^{-5}$</td>
<td>$0.29 \pm 0.01$</td>
<td>$68.8 \pm 0.05$</td>
<td>$0.88 \pm 0.01$</td>
</tr>
</tbody>
</table>
the grain boundary in our BCZT material. We will do this in a forthcoming publication.

In order to compare our extracted values of barrier height for the BCZT on the LSCO with theoretical values, the barrier height can be calculated as the difference between the work function (ϕM) of LSCO and the electron affinity (χ) of the BCZT film. Here, ϕM = 4.2 to 4.6 eV for LSCO [67] and χ = 4.15 eV for BaTiO3 [68] and χ = 3.83 eV for CaTiO3 [69]. Thus, we have taken ϕM = 4.40 ± 0.2 eV and χ = 3.99 ± 0.16 eV. Therefore, ϕ0 could be approximately between 0.37 to 0.45 eV. Our experimental values found in the fitting were in the range of 0.30 eV to 0.48 eV. Therefore, we concluded that the Simmons model renders realistic physical parameters. Finally the values of the shape factor (ρ) varying between 57 to 68 V suggest that at higher temperatures the tunnelling current rises faster than the Ohmic, and the higher ρ is, the steeper the curve is. All this indicates that the leakage current of the BCZT thin film is based on electrode-limited conduction mechanisms. In general, it was seen that the conduction mechanism in dielectric BCZT is influenced by factors such as temperature, bias voltage (of the electric field), the electrode material and the device structure (MIM).

Dielectric properties of BZT–BCT thin films

In order to understand the dc electric field effect on the dielectric properties of BZT–BCT thin films, the dielectric properties were measured at different dc bias fields (±40 V) at different frequencies. Furthermore, the observation of the C–V butterfly curve and hysteresis loop suggest that the BZT–BCT thin films display ferroelectric behaviour and have a tetragonal structure. Figures 4(e) and (f) present the dc electric-field dependence of the capacitance density and tan δ (the dielectric loss) curves of the BZT–BCT thin films, which was measured in the frequency range of 10–100 kHz at room temperature. A broad dielectric phenomenon is observed throughout the range of frequencies measured. Dielectric properties follow a general trend: as the frequency increases, the dielectric constant decreases and the dielectric loss values increase. As the frequency increases, the capacitance density for the film was gradually decreased and was caused by the electronic polarisation. The high value of capacitance density at low frequency is attributed to different types of polarisations such as electronic, ionic, and interfacial polarisation at room temperature. As the applied field increases, both the capacitance density and the dielectric loss decreased.

Conclusions

In conclusion, based on the experimental observations, (Ba0.95Ca0.05)(Zn0.17Ti0.83)O3–BZT–BCT epitaxial thin films were grown (100) on MgO using PLD at higher deposition and annealing temperatures (700°–750 °C). The epitaxy of films with an in-plane tetragonal symmetry (c < a) was confirmed with HR-XRD RSMs. Tetragonal perovskite crystalline lattice structures were also confirmed with Raman spectroscopy. Dense and crack-free films with perovskite structure were obtained through PLD. The P–E hysteresis loops have shown saturated hysteresis loops with ferroelectric imprint behaviour due to defect dipoles or oxygen vacancies. Large recoverable energy (39.11 J cm⁻³) with a high dielectric breakdown field (2.08 MV cm⁻¹ before the dielectric breakdown occurred), was obtained for the thin films. PFM was deployed to study the ferroelectric response of the BZT–BCT films. The colour contrast demonstrates the switchable ferroelectric response of the films. Furthermore, the out-of-plane PFM phase hysteresis loop versus the tip voltage curves indicates their ferroelectric nature. From the dc electronic transport of thin films, it is found that the conduction mechanism of the films is consistent with a tunnelling behaviour and the electronic current may be predicted by the Simmons’ model. These results confirm the successful preparation of BZT–BCT epitaxial films with ferroelectric and moderate leakage current behaviour, which might be useful in capacitor applications.

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References
