Revealing the interplay of structural phase transitions and ferroelectric switching in mixed phase BiFeO$_3$

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Epitaxially strained BiFeO$_3$ thin films with co-existing tetragonal- and rhombohedral-like phases exhibit a range of intriguing functional properties, often strongly related to the unique microstructure of the film. Here we report enhancements in electromechanical response during simultaneous nanoscale application of electric field and localised stress. These enhancements manifest in the form of peaks, or humps, in the piezoresponse hysteresis loops obtained under select polarity of applied electric field, corresponding nominally to a downward polarisation. Using a variation of band excitation piezoresponse force spectroscopy to collect electromechanical hysteresis loops and to simultaneously monitor the elastic behaviour during switching, we develop a comprehensive picture of the complex interplay of ferroelastic structural transitions and ferroelectric switching and its impact on the overall functional response. Such an understanding is a crucial step towards realising practical electronic devices, such as pressure sensors, incorporating this promising material.

Keywords: phase transitions, polarization rotation, mixed-phase ferroelectric, piezoresponse force microscopy, Nanoscale stress

1. Introduction

Mixed phase BiFeO$_3$ (BFO) films have recently attracted significant attention due to remarkable enhancement of functional properties such as enhanced spontaneous magnetisation, 11 enhanced electromechanical response 12, 3 and conduction at interfaces 4, 5. Bulk BFO adopts a rhombohedral (R) unit cell in the $R3c$ space group 6 with polarisation along the $\langle 111 \rangle_c$ pseudocubic directions. 7 When grown on substrates with large in-plane compressive strain (approximately $< -4.5 \%$), 8 very thin BFO films can adopt a monoclinic unit cell that is approximately tetragonal (T) 8 with polarisation along the $\langle 001 \rangle_c$ pseudocubic axes. For thicknesses above $\sim 60$ nm, the T-like phase becomes less favourable and there is a relaxation of the unit cell towards a more rhombohedral configuration. 9 This results in a mixed crystallographic phase microstructure, with alternating T- and R-like regions, as revealed by X-ray diffraction 9, 10 and scanning transmission electron microscopy. 10 The strain-driven phase competition gives rise to an effective morphotropic phase boundary (MPB), similar to those commonly observed in solid solutions such as PbZr$_x$Ti$_{1-x}$O$_3$. In MPB materials, the different structural phases are separated by small energetic barriers, making them susceptible to phase transitions when subjected to
external stimuli such as temperature, electric field and mechanical stress. Intriguingly, it is possible to deterministically and reversibly alter the phase population in BFO by application of electric field and nanoscale stress, thereby opening up a new route to further tune the hysteretic response during switching. However, challenges still remain in understanding the precise nature of the interplay of structural transitions and stress-mediated ferroelectric switching and the overall effect of this meshing of phenomena on the functional properties of the film. Such understanding could be pivotal to the development of future technological applications, such as pressure-sensors, photoresistive or magnetoelectronic devices, exploiting the enhanced properties that can accompany the mixed phase microstructure and its tuning through different stimuli.

Detailed studies of the effects of electric field on mixed phase BFO have been performed using scanning probe microscopy, revealing both R → T and T → R phase transitions. The advent of band excitation piezoresponse force spectroscopy (BEPS) has enabled the collection of nanoscale piezoelectric hysteresis loops and detailed study of the accompanying phase transitions. While electric field is relatively simple to exert on the nanoscale via an atomic force microscope (AFM) tip, it has been challenging to achieve controlled stress-induced phase transitions in a typical AFM setup. Recently, however, nanoscale phase transitions have been achieved in mixed phase BFO and PZT by precise control of forces applied through the AFM tip. When combined with BEPS, this approach can allow for elucidation of the contributions of ferroelastic switching and ferroelectric switching to the overall hysteretic response, as we have previously demonstrated in PZT films. Here, we follow a similar approach and perform BEPS as a function of force (up to ~ 1 μN) applied to the sample surface via the AFM tip. To deconvolute the effects of stress and electric field, we first investigate the individual effects of application of an external electric field by BEPS measurements, and stress through nanoindentation experiments, before probing the combined effect of these two extrinsic stimuli and the impact on the overall switching behaviour under applied force, i.e. a force-voltage experiment. Both the elastic and ferroelectric properties have been studied, through variations in the contact resonance frequency and the piezoresponse, respectively. Notably, enhancements are found in the piezoresponse when subjecting the film to nanoscale stress. We attribute the enhanced electromechanical response to R/T phase boundary motion, due to both electric field and stress-induced T → R transitions. This combined approach allows for elucidation of the complex interplay between stress-mediated structural phase transitions and ferroelectric switching in this intriguing material system.

2. Experimental Methods

Samples were grown epitaxially by pulsed laser deposition of LaScCoO3 (5 nm) and BiFeO3 (50 nm) on a (001) oriented LaAlO3 substrate. We have previously confirmed epitaxy by scanning transmission electron microscopy. Scanning probe microscopy measurements were performed on an
Asylum Cypher equipped with a Zurich Instruments external lock-in amplifier (HF2LI) and using PPP- EFM Pt/Ir probes with a nominal force constant of 2.8 N/m and purchased from Nanosensors. BEPS measurements were performed using a National Instruments module controlled via a LabView interface. Force-voltage measurements were realised by performing BEPS as a function of force (up to ~ 1 μN) applied to the sample surface via the atomic force microscope (AFM) tip. A DC “write” bias, $V_{DC}$, as a step function with a triangular periodic envelope was applied to the sample through the AFM tip in contact with the surface. The piezoresponse was measured through application of an AC “read” voltage, $V_{AC}$. The “write” bias was not applied during the read cycle to minimise the impact of capacitive forces. The frequency of $V_{AC}$ was excited over a range spanning the contact resonance frequency. Hence the resulting piezoresponse hysteresis loops are a function of excitation frequency and DC bias (applied immediately prior to the measurement). In the force-voltage embodiment, BEPS measurements were repeated over a grid with discrete spatial points, for a variety of cantilever loading forces (determined by the contact mode feedback setpoint and the calibrated cantilever stiffness) and the desired number of cycles (repetitions). This approach results in a multidimensional dataset of the form of \{$x \times y \times V_{DC}$ steps $\times v_{mod} \times$ cycles $\times$ applied force\}, where $x$ and $y$ are spatial coordinates, and $v_{mod}$ is the modulation frequency of $V_{AC}$. All of the hysteresis loops and contact resonance data discussed herein refer to those measured from the vertical (out-of-plane) motion of the cantilever acquired in vertical piezoresponse force microscopy (VPFM) mode. Measurements were performed with an increasing force branch followed by a decreasing one. Forces ranged from 20 to 1220 nN in increments of 200 nN, with $V_{AC} = 1.0$ V and $V_{DC}$ varying over 44 steps as 0 → +15 → 0 → -15 → 0 V in increments of 1.4 V. Both biases were applied to the AFM tip and the measurements were repeated over 2 cycles to account for issues such as poor tip-sample contact.$^{[20]}$ The resulting data were fitted using a simple harmonic oscillator model$^{[24]}$ using custom MATLAB scripts. Nanoindentation measurements were performed in an identical manner, except with an arbitrarily small value of $V_{DC}$ [max] = 10 mV, far below the thresholds for ferroelastic or ferroelectric switching. For the nanoindentation experiment, average values of the amplitude, $A$, and contact resonance frequency, $\omega_0$, were calculated for each force as the average over the 5 points and the 44 measurement steps, i.e. average\{$x \times y \times V_{DC}$ steps\}. All force-voltage data were collected from grids of 5 × 5 points and in vertical PFM (VPFM) mode. Piezoresponse loops were calculated as $A \cos \phi$ where $A$ is amplitude and $\phi$ is phase.

3. Results

3.1. Electric Field-Induced Phase Transitions

Before studying the combined effects of electric field and stress, it is informative to first consider their individual effects on phase transitions. Application of an electric field through an AFM tip at fixed points$^{[2, 9, 14, 18]}$ and during scanning$^{[2, 14, 25]}$ has previously been demonstrated to drive phase transitions
in BFO and provides a promising route towards nanoscale control of the functional properties. As such, we begin by considering electric field-induced phase transitions and their effect on the hysteretic response.

The as-grown BFO film adopts an R/T mixed phase microstructure with uniform out-of-plane polarisation pointing down towards the substrate, along the [00\(\overline{1}\)]_c axis. The R-phase has in-plane polarisation components directed along the \(\langle 110\rangle_c\) directions. The top panel of fig. 1a shows an AFM height image of the as-grown BFO film, where R-phase needles can be seen as the dark striations embedded within the lighter T-phase matrix. Scanning this region with a large DC bias applied to the AFM tip \(V_{dc} = +14\) V here) erases the R-phase, leaving the T-phase region in the bottom panel. In this instance the poled T-phase retains the same out-of-plane polarisation as the as-grown film. It has previously been reported\[^{14}\] that subsequent application at a fixed point of an electric field antiparallel to the initial polarisation direction can induce the formation of R/T-phase rosette patterns, as shown in the PFM images in fig. 1b. These images show a region of pre-poled T-phase with two rosette patterns after application of a tip bias of -10 V at two distinct points. The R-phase needles which are aligned
approximately along the vertical and horizontal axes of the images appear as the dark striations in the topography image (top panel) with bright edges in the amplitude image (centre) due to the enhanced piezoelectric coefficient, $d_{33}$, at the R/T interfaces.\cite{2} The needles are clustered around the switched T-phase points, which are demarked by dark domain walls in the amplitude image. Directly under the tip, the strong electric field switches the polarisation of the T-phase by 180° to point along [001]c, as can be seen from the bright regions in the phase image (bottom panel of fig. 1b); the surrounding T-phase retains polarisation along [00 1]c. Due to the geometry of the AFM tip, the electric field is highly localised and so its in-plane components increase rapidly in the region surrounding the tip.\cite{26} These in-plane electric field components nucleate the R-phase which maintains the same out-of-plane polarisation as the surrounding, unprobed regions. Similar behaviour has been observed in single phase, monodomain BFO grown on SrTiO$_3$ where simultaneous application of electric field and stress to a moving AFM tip was shown to generate a trailing flexoelectric field, causing polarisation rotations in the rhombohedral unit cell of that film.\cite{25}

The rosette behaviour can be understood in the context of an energetics argument: the path of least energy to rotate a tetragonal (001) polarisation by 180° is via the rhombohedral (111) diagonals.\cite{27} For example, a polarisation rotation from [00$ar{1}$] to [11$ar{1}$] then [001] requires less energy than that to rotate directly from [00$ar{1}$] to [001], as demonstrated theoretically for La-doped BFO.\cite{18} Similar ferroelastic-mediated ferroelectric switching has also been observed in a variety of other systems.\cite{28-31} Furthermore, the above processes are reversible such that the rosettes can be erased by subsequent application of an electric field of the opposing polarity.\cite{14}

Fig. 1c shows a typical averaged piezoresponse hysteresis loop collected at a force of 20 nN from a pre-poled T-phase region (as in fig. 1a). This location shows ferroelectric switching (full phase inversion at voltage inversion), with coercive biases, $V_{c}$, of $\pm$ 5.5 V. A small doubling up of the loop can be seen at large positive $V_{DC}$ and will be discussed below.

### 3.2. Stress-Mediated Phase Transitions

Previous studies have demonstrated phase transitions in BFO\cite{16} and PZT\cite{22} through application of nanoscale stress via an AFM tip due to alteration of the energies associated with stabilising the different phases. Therefore, a systematic nanoindentation characterisation of the BFO films was performed to reveal the impact of nanoscale stress on the evolution of the microstructure. Figs 2a,b show AFM topography images of the microstructure of the as-grown film and a pre-poled T-phase region before (top panel) and after (bottom) nanoindentation. The corresponding PFM data are shown in section S1 of the supporting information. In the as-grown film in fig. 2a, no change in microstructure is observed upon application of force. Conversely, 5 sets of R-phase needles are observed at the nanoindented points
in the pre-poled area in fig. 2b. These data suggest that the as-grown film is stable enough to resist the influence of point stress, whereas the pre-poled T-phase region is far more malleable. The as-grown film has an optimal R-phase population imposed by the growth conditions (substrate mismatch, growth temperature, film thickness, etc.), whereas the pre-poled region is initially in a purely T-phase state. As a result, there are different energetic conditions for the two regions: the pre-poled region is in a metastable state, which can be readily altered by application of relatively low external forces. The as-grown region, on the other hand, is far more stable and would conceivably require far larger external forces to nucleate additional R-phase and overcome the energy penalty imposed by the introduction of further internal stresses between the R- and T-phases. In effect, the T-phase regions in the as-grown film are “clamped” in place. Crucially, the stress-mediated R-phase needles are approximately 200 – 300 nm long and 100 nm wide, far in excess of the estimated tip diameter of ~ 50 nm (see electron micrographs in section S2 of the supporting information), demonstrating that they are not simply due to tip-induced film damage.
FIG 2 Stress-mediated phase transitions. AFM height images of (a) the as-grown film and (b) the pre-poled T-phase region before (top) and after (bottom) nanoindentation on 5 points; the colour scale is 0 – 8 nm. No discernible change can be seen in (a), whereas localised R-phase needles can be seen as dark striations in (b). (c,d) Corresponding plots of $A$ and $\Delta \omega_0$, respectively, as measured by BEPS. These results were averaged over the 5 nanoindented points and 44 ‘steps’ from (a,b), see experimental section for details.

Figs 2c,d show plots of $A$ and the relative changes in $\omega_0$, respectively, as a function of force during nanoindentation. The values were averaged over all measurement steps (see experimental section) and all of the 5 nanoindented points. The relative change in $\omega_0$ is defined as $\Delta \omega_0 = [ \omega_0'' - \omega_0' ] / \omega_0' \times 100$ where $\omega_0'$ is the mean amplitude at a force of 20 nN and $\omega_0''$ is that at any given force. The error bars are determined by the corresponding ±1σ standard deviation. In fig. 2c, the as-grown film (black curve) shows $A$ values that remain largely constant with a variation of less than ±6% between 20 and 1220 nN. For the pre-poled region (dashed red curve) and at low force, $A$ remains similar to the as-grown film with only small increases up to 420 nN. Beyond this force, however, there is a continuous increase in amplitude, up to a maximum of 31 ± 7 at 1220 nN, representing a remarkable increase – in excess of 700% – compared to the lowest force of 20 nN. Similarly large increases in electromechanical response are known to arise due to ferroelastic transitions, leading to the introduction of large interfacial strains in phase change systems\cite{27,32,37} and thus the data here strongly suggest the onset of structural T → R phase transitions around 420 nN. In contrast to the data in fig. 2 where R-phase rosettes were formed around the tip, here the R-phase needles are nucleated directly at the point of contact and therefore provide a greater contribution to the locally-measured electromechanical response. Increased stress (force) has previously been demonstrated to enhance the R-phase population in this system,\cite{16} consistent with the increasing trend of the amplitude with applied force observed here. Further evidence of these T → R transitions can be seen in fig 2d.

For the as-grown film there is a steady increase in $\Delta \omega_0$ (fig. 2d) corresponding to a stiffening of the tip-sample contact which we attribute to the increased contact radius with increased force: assuming Hertzian contact\cite{38} and a tip radius of 25 nm, we find estimated values for the contact radius, $a_{ts}$, of ~ 2 nm at 20 nN and ~ 20 nm at 1220 nN. Full details of the calculations are given in section S2 of the supporting information. In the pre-poled region, on the other hand, there is a gradual decrease in $\Delta \omega_0$ beyond a force of ~ 420 - 620 nN, which suggests a slight softening of the underlying material, consistent with the enhanced amplitude in fig. 2c and is similar to previous reports of T → R transitions in La-doped BFO grown on LAO.\cite{18,39} Similar to the increases in $A$, the continued decrease in $\Delta \omega_0$ with applied force is likely due to increased R-phase population with increased force. Crucially, these results demonstrate two possible means of identifying BFO R/T phase transitions during switching experiments. Thus, by combining these nanoindentation measurements with the ferroelectric switching ones discussed in section A above, it is possible to track the phase change behaviour while the system
is subject to both external stress and electric field, both of which can influence the electromechanical response.

3.3. Stress-Mediated Hysteretic Response

It is well known that phase change systems such as those with an MPB can exhibit enhanced electromechanical response due to phase transitions;\cite{34} this opens an avenue for direct, local enhancement of functionality of these BFO thin films. Thus, having discussed the individual effects of electric field and stress, we now consider their combined effects on the electromechanical hysteretic response by means of force-voltage spectroscopy. Fig. 3a shows a $4 \times 4 \, \mu m^2$ region of the BFO film pre-poled into the T-phase state with polarisation directed along $[00\bar{1}]_c$, and fig. 3b shows the same region after the force-voltage experiment. In fig. 3b, stress-written R-phase needles can be seen within the T-phase matrix and are clustered in proximity of the switched points. The latter are evident in the VPFM amplitude and phase images shown in figs. 3c,d, respectively. They are bordered by dark regions at the $180^\circ$ domain walls in the A image (fig 3c) and they appear with bright contrast in the phase image (fig. 3d) due to $180^\circ$ out-of-plane rotation of the polarisation to $[001]_c$ after switching. Elongation and doubling up of the switched points into a figure 8-like pattern is observed in the same images, which may be due to an irregular tip shape/degradation of the conductive tip coating, caused by the large forces employed, or to due to a small shift in the tip location due to the large topographic changes associated with the R/T phase transitions during the experiment. Nevertheless, this is not anticipated to affect the results here and we observe no clear contributions to the BEPS data.

In the VPFM amplitude image in fig. 3b, reductions in amplitude can be seen at the $180^\circ$ domain walls, around which rosette-like patterns of R-phase are present. Such patterns expand beyond the switched location immediately below the tip, more strongly so at the free-edges of the force-voltage-written area. Furthermore, far weaker striations angled at $\sim 45^\circ$ in the surrounding T-phase can be seen from this image and much more clearly in the lateral PFM (LPFM) images in section S3 of the supporting information. In VPFM they likely arise due to cross-talk (cantilever buckling) from small $\langle 110 \rangle$ monoclinic distortions.\cite{14} Similar features have been observed by LPFM to form flux closure states in a comparable mixed phase BFO system.\cite{19} These are distinct from the crystallographic terraces of the T-phase that can be seen as the pale striations in the height images (figs 3a,b) which are roughly aligned along the horizontal axes of the images that run along the degenerate in-plane $\langle 100 \rangle_c$ directions. The clustering of the R-phase needles arises from the “phase malleability” of the film: the bias-written T-phase is metastable, resulting in easier transitions between phases than in the as-grown film. This is consistent with the significantly lower susceptibility of the as-grown film to applied stress explored in section 3.2 above.
FIG 3 Stress-mediated hysteretic response. (a) Height image of a pre-poled T-phase region. VPFM (b) height, (c) amplitude and (d) phase images after performing a 5 × 5 point force-voltage experiment over the region shown in (a). The colour scales are 0 – 8.5 nm (height), 0 – 0.8 a.u (amplitude) and ±180° (phase). (e) Piezoresponse, Acosφ, loops averaged over all 25 points. At 20 nN the loops adopt the familiar form whereas at forces greater than 420 nN the loops double up, forming humps of enhanced piezoresponse when $V_{DC}$ is between the positive coercive value and $+15$ V.

The averaged piezoresponse ($Acos\phi$) hysteresis loops are shown in fig. 3e. A selection of forces from the decreasing force branch is shown here; the full range is shown in section S3 of the supporting information. The corresponding loops for increasing force show near identical features. At the lowest forces of 20 – 220 nN, the loops adopt the familiar form reproducing the polarisation-electric field hysteresis curves. However, at higher force and at $V_{DC} \gtrsim 5 – 6$ V, there is a doubling up of the loops, forming ‘humps’. Similar features have been previously observed in BFO\cite{2,18} and PbZr$_{0.52}$Ti$_{0.48}$O$_3$ (PZT)\cite{22,40} thin films, and have been attributed to phase transformations\cite{2,22} and domain wall motion.\cite{40,41} Furthermore, the presence of humps in piezoelectric loops due to purely ferroelectric transitions has been shown to be due to differences in domain population between the remanence-to-saturation and saturation-to-remanence regions of the loops.\cite{41} In the present case, these would be the R-phases from the 180° rosette patterns as the electric field is increased towards saturation, i.e. as the rosettes are erased at $+V_{DC}$. At increasing contact force, the hump area and maximum piezoresponse increase, while the
coercive voltage decreases. A near identical trend is observed when performing the same experiment on the as-grown film without prior poling (see section S4 of the supporting information). We have also previously reported similar trends in a polycrystalline PZT film: it was suggested, with the aid of phase field simulations, that the humps arose from rearrangements of the domain structure due to electromechanically-induced motion of ferroelastic domain walls.\textsuperscript{[22]}

4. Discussion

Field-induced structural phase transitions, resulting in changes in the piezoelectric coefficient,\textsuperscript{[2]} $d_{33}$, and in the Young’s modulus\textsuperscript{[39]} have been previously reported in BFO and similar materials systems.\textsuperscript{[21,42]} Such changes can be detected by BEPS via the related values of amplitude and contact resonance frequency, respectively.\textsuperscript{[21,42]} Therefore, in order to understand the hysteretic behaviour and the role of phase transitions mentioned in the previous section, it is informative to “unravel” the piezoresponse loops. Starting with the influence of purely electric field (no applied stress), fig. 4a shows plots of the “unraveled” loops of $A$, $\omega_0$ and $\varphi$ as a function of $V_{DC}$ for two consecutive cycles. These data correspond to the full loops shown in figure 1c. Using as markers the minima in $A$ and the 180° change in $\varphi$ around the coercive biases, it is possible to identify the regions corresponding to (i) – (iv) depicted in the plan view schematics in fig. 4b. These sketches follow the rosette formation and deletion pathway previously demonstrated in the literature.\textsuperscript{[14]} In order to minimise potential poor tip-sample contact effects\textsuperscript{[20]} at this low force, the data in fig. 4a are extracted from the decreasing force branch of a series of force-voltage measurements, where the force is first increased from 20 to 1220 nN and then decreased back to 20 nN. Since the $V_{DC}$ waveform finishes with “poling” at negative voltages, the initial state of the film in fig. 4a is a 180° rosette pattern created at the previous force of 220 nN, i.e. region (iii) of fig. 4b. This differs from the virgin state of the pre-poled T-phase however, due to the sequential nature of phase transitions in this system, the aforementioned 180° rosette is then fully erased once $V_{DC}$ reaches $\pm 7$ V.

In region (i) of fig. 4, the T-phase film’s polarisation is oriented along $[00\bar{1}]_c$ with positive values of $\varphi$. In region (ii), nucleation of the R-phase occurs leading to the formation of rosette patterns by the fringing fields around the tip, followed by switching around $V_c^-$. By the end of this region and the beginning of region (iii), there is a 180° change in $\varphi$ as the T-phase directly under the tip is switched to have polarisation along $[001]_c$, giving rise to the 180° rosettes shown in fig. 4b. The field is then decreased back through 0 V and into the positive nucleation and switching regime about $V_c^+$, where the rosette patterns that were created previously are deleted; this is depicted in panel (iv) of fig. 4b. Finally, going from region (iv) to (i) and once $V_{DC} > V_c^+$, there is another 180° phase change and the polarisation of the T-phase under the tip is switched back to $[00\bar{1}]_c$, returning the material to its original state.
FIG 4 Electric field-mediated hysteretic response at a low force of 20 nN. (a) “Unraveled” loops corresponding to the piezoresponse hysteresis curve reported in fig. 1c and showing $A$, $\omega_0$, and $\phi$ as a function of $V_{DC}$ over two cycles. Sequential regions (i-iv) are labelled and the vertical dashed red line corresponds to the end of cycle 1 and the beginning of cycle 2. (b) Schematic representations depicting the polarisation of the sample in the immediate vicinity of the tip-sample contact, during the field cycling through (i-iv) in (a). The dashed black square in (ii) marks the “direct field” region directly beneath the tip which undergoes 180° polarisation switching upon application of an above coercive voltage, as depicted in (iii).

Stepped variations in the plot of $\omega_0$ in fig. 4a can be seen between regions (i) and (iii) and are marked by the dashed green lines and arrows. These variations suggest a slight softening of the material in the presence of the 180° rosettes [region (iii)], relative to the pure T-phase in region (i). In the first cycle (left of the dashed red line), there is a slight decrease of $\omega_0$ by 0.2 kHz, and in cycle 2 (right) a larger value of 0.6 kHz is observed. This difference between cycles may be caused the underlying positive gradient of $\omega_0$ (hardening) that can be seen. It is likely that this gradient is due to variation in the quality of the tip-sample contact over time at this low force, a hypothesis corroborated by the fact that no such gradual hardening is observed at higher forces. Nevertheless, while the softening in region (iii) is subtle, it is consistent with the reductions in Young’s modulus observed after T → R phase transitions in a similar mixed phase BFO system.\(^{39}\) The fact that these T → R transitions do not occur directly beneath the tip but in the surrounding fringing fields is likely a contributing factor to the relatively small $\omega_0$ variations observed here. The amplitude, on the other hand, does not show such appreciable stepped variations between the different regions. There are substantial decreases (i.e. sharp minima) at the exact coercive values, where the average null polarisation results in consistent lowering of the resulting piezoelectric effect.
The stress-mediated hysteretic response would be expected to follow a similar route to that depicted in fig. 4 with sequential formation and deletion of rosette patterns. However, the addition of stress acts to alter the energetics related to the phase transitions.[16] This can be seen in fig. 5a, which shows plots of the “unraveled” loops of $A$, $\omega_0$ and $\varphi$ plotted in an identical manner to fig. 4b, but for a force of 820 nN (corresponding to fig. 3e), where significant stress-induced phase transitions are expected based on the nanoindentation results discussed earlier. Similar to fig. 4a, these data were extracted from the decreasing force branch of a series of measurements where the sample was previously subjected to measurements at a force of 1020 nN finishing with “poling” the sample at negative $V_{DC}$. This results in the initial state of the sample being in region (iii) from fig. 4 where 180° rosettes are present. However, the sequential nature of the phase transitions means that the sample is returned to region (i) once $V_{DC}$ reaches $\sim +10$ V.

The stepped variations in $A$ and $\omega_0$ in fig. 5a are far more pronounced and more consistent across the two cycles than in the absence of stress in fig. 4b. This enables unequivocal identification of four distinct regions which are labelled (i) – (iv) and shaded to guide the eye. Initially, during cycle 1 and for low $V_{DC}$, a rosette pattern from the previous force of 1020 nN is present and due to potential tip-sample contact issues we begin the discussion at $V_{DC} \sim +15$ V in region (i). This regime shows an elevated plateau in $\omega_0$ and the lowest $A$, consistent with the T-down phase (polarisation along $[00\bar{1}]_c$ at large $+V_{DC}$). On the other hand, region (iii) shows decreased $\omega_0$ and enhanced $A$, consistent with the presence of 180° rosettes at high negative $V_{DC}$, as discussed above. Rosettes are created around the negative coercive value in region (ii) where $\omega_0$ decreases and those rosettes are erased in region (iv) where $\omega_0$ increases and maxima in $A$ are observed, i.e. where the humps in piezoresponse hysteresis curves are formed. These regions therefore arise as the result of various R/T phase transitions and are related to a combination of the electric field-induced formation and deletion of rosette patterns and stress-induced T $\rightarrow$ R transitions. It is noteworthy that at the end of region (iv) there are clear increases in amplitude due to the R $\rightarrow$ T transitions in the material, resulting in enhancements of the piezoelectric response. The opposing T $\rightarrow$ R transitions leading to region (ii) do not result in similar enhancements of the electromechanical amplitude since these transitions lead to reduced out-of-plane deformations. The likely transitions are depicted in the cross-sectional schematics in fig. 5b.
FIG 5 Force-voltage-mediated phase transitions. (a) Plots of $A$, $\omega_0$ and $\varphi$ as a function of $V_{DC}$ over two cycles and at a force of 820 nN. From these plots, 4 distinct regions can be identified with larger changes in $A$ and $\omega_0$ than for the low force in fig. 4. The dashed black lines highlight a region of moderately enhanced $A$ when decreasing $V_{DC}$ from +15 V towards remanence. (b) Schematic cross-sectional representation depicting the likely transitions accompanying the regions numbered (i)-(iv) in (a). For representative purposes the tip is sketched above the surface of the sample although it remains in contact throughout the experiment.

In region (i) (figs 5a,b), the positive bias stabilises the T-phase and both $A$ and $\omega_0$ remain relatively constant. The polarisation is uniformly directed along $[00\overline{1}]_c$, as shown by the positive and constant value of $\varphi$. We refer to this as T-down in contrast to T-up where the polarisation is along $[001]_c$. Upon decreasing $V_{DC}$ from +15 V towards negative coercive voltage, there is a gradual increase in $A$ – within a region demarked by the dashed black lines – to a value roughly halfway between the values for T-down at +15 V in (i), and those for the 180° rosette in (iii). Although certainly not conclusive, this suggests that there may be some stress-induced $T \rightarrow R$ transitions, either directly beneath the tip (as in...
the nanoindentation experiment) or around it, due to the altered boundary conditions upon application of force. This would lead to a mixed phase state, albeit with a lower R-phase population than in region (iii). It is possible that this R-phase population is not sufficient to produce a detectable $\omega_0$ shift in fig. 5a since this parameter is much less sensitive to phase population changes than $A$, as demonstrated by the nanoindentation experiments in section 3.2 above.

Region (ii) – the negative nucleation and growth regime – is the bias-induced rosette formation stage, as demonstrated earlier in figs 1 and 4. Around the negative coercive value there is a 180° phase shift (fig. 5a) due to switching of the polarisation of the T-phase to $[001]_c$. This is accompanied by the usual sharp dip in $A$ and abrupt changes in $\omega_0$. Beyond this region, at increasingly negative $V_{DC}$, the 180° rosettes of region (iii) are present. Here the amplitude is increased relative to the T-down region (i) and is accompanied by a softening of $\omega_0$ by $\sim 0.8$ kHz. This suggests a significant R/T mixed phase population surrounding the tip, sufficient to alter the elastic properties of the interrogated region of the sample. Finally, in region (iv) there is the rosette deletion process. This occurs as $V_{DC}$ is increased to large positive values and is the origin of the enhanced piezoresponse humps discussed in fig. 3e, which can be seen here as the large humps in amplitude between $V_c^+$ and the maximum bias in fig. 5a. We attribute these large increases in $A$ and the corresponding gradual increases in $\omega_0$ (hardening due to incremental conversion to T-phase with lower electromechanical response[3]) to R/T phase boundary motion due to both electric field[3] and stress-mediated T $\rightarrow$ R transitions, similar to the $d_{33}$ enhancements due to ferroelastic transitions in epitaxial PbZr$_{0.2}$Ti$_{0.8}$O$_3$ films[32] and other morphotropic phase boundary materials.[34-37] After the maximum $A$ (the inflection point of the hump), the material is predominantly in the T-phase and so $A$ decreases due to the lower $d_{33}$ of this phase.

To rationalise the humps of enhanced $A$ above the coercive field, we tentatively propose the route sketched in panel (iv) of fig. 5b. This depicts a polarisation reversal process in lieu of the simple rosette deletion shown in fig. 4b. For very low electric fields ($V_{DC} \sim 0$ V), the presence of the rosettes sketched in panel (iii) will most likely inhibit stress-induced T $\rightarrow$ R transitions due to new mechanical boundary conditions ensuring that the rosettes are stable. However, in the subcoercive regime, the electric field is weak and the fringing fields around the tip will favour R $\rightarrow$ T transitions of the rosettes, as shown in the earlier discussions. The stress applied through the AFM tip in this instance is known to alter the energetics of the system to favour a greater proportion of R-phase.[16] It would therefore be expected that the rosette deletion process would follow the route sketched in panel (iv) of fig 5b. Based on this argument, for $0 V < V_{DC} < V_c^+$ the R-down phases from the rosettes would convert to T-down due to the fringing fields, whereas there would be T-up $\rightarrow$ R-up directly underneath the tip (i.e. the “direct field” with small in-plane components). In essence, the R/T phase boundaries are effectively shunted.
inwards in this picture. For $V_{DC} \geq V_c^+$ there would then be rotation of the out-of-plane polarisation to $[00\bar{1}]_c \rightarrow (R/T\text{-up} \rightarrow R/T\text{-down})$ before final $R\text{-down} \rightarrow T\text{-down}$ conversion as $V_{DC}$ tends to +15 V. Note that this would also satisfy the path of least energy for polarisation switching since, for example, rotating through each of the individual $T \rightarrow [001]_c \rightarrow [11\bar{1}]_c \rightarrow T$ $[00\bar{1}]_c$ transitions requires less energy than a direct $180^\circ$ T-phase $[001]_c \rightarrow [00\bar{1}]_c$ transition.$^{[27]}$

5. Conclusions

In summary, we have employed a novel scanning probe microscopy technique to elucidate the stress-mediated hysteretic response of a mixed phase BFO system. We have shown that the observed functional behaviour arises due to a complex interplay of both structural and ferroelectric reorganisation with applied electric field and nanoscale stress. This manifests in the form of peaks, or humps, in electromechanical response at one given polarity of applied DC bias ($+V_{DC}$ when applied via the AFM tip). Through detailed study of the electromechanical responses we have provided a comprehensive picture of this complex stress-electric field interplay, leading to these unipolar humps. We find evidence that the enhanced electromechanical response arises from R/T phase boundary motion and that these phase boundaries can be reversibly created and erased over several cycles. The observations presented here provide an invaluable contribution to the development of structure-function relations in this technologically-relevant BFO system, a crucial step towards realising practical applications of this material. This ability to exert nanoscale control over both the mechanical and functional properties of thin films is especially attractive for use in devices such as pressure sensors and we anticipate that the approaches employed here will be of significant interest to other materials systems, especially those with morphotropic phase boundaries.

Supporting Information

See supporting information for additional PFM and BEPS data and calculation of contact radius.

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