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To cite this article: H Béa *et al* 2011 *J. Phys.: Condens. Matter* **23** 142201

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Nanoscale polarization switching mechanisms in multiferroic BiFeO₃ thin films

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Received 28 January 2011, in final form 14 February 2011

Published 18 March 2011

Online at stacks.iop.org/JPhysCM/23/142201**Abstract**

Ferroelectric switching in BiFeO₃ multiferroic thin films was studied by piezoresponse force microscopy, as a function of the tip voltage and sweep direction, for samples with two different intrinsic domain structures. In all films, the switched polarization direction follows the in-plane and out-of-plane components of the highly inhomogeneous electric field applied by the microscope tip. In films with ‘bubble-like’ intrinsic domains, we observed in-plane switching assisted by out-of-plane switching for lower voltage values, and independent in-plane and out-of-plane switching for higher voltages, in both cases allowing full control of the ferroelectric polarization depending on the tip voltage polarity and sweep direction. In films with ‘stripe-like’ intrinsic domains, independent in-plane and out-of-plane switching was observed, but unswitched stripe domains prevented full control of the ferroelectric polarization over large areas. We correlate the observed switching behavior with the field-driven onset of a highly distorted tetragonal phase predicted by *ab initio* calculations, which leads to a very high in-plane susceptibility during the return to the non-distorted monoclinic phase when the field is decreased. Depending on the specific strain and disorder present in the sample, the transition towards the highly distorted phase may be asymmetrized, and easier to reach when an electric field opposite to the out-of-plane polarization direction is applied.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The recent explosion of multiferroic research has focused in particular on the rich fundamental physics [1–3] and potential applications [4, 5] of magnetoelectric (ME) materials. The primary challenge is reliable room-temperature control of magnetic ordering via applied electric fields or vice versa. One of the currently most studied single-phase multiferroics is BiFeO₃ (BFO) [6], showing ferroelectricity, ferroelasticity and antiferromagnetism at room temperature. In this material,

despite its relatively weak ME coefficient [7], rotation of the antiferromagnetic (AF) direction under applied electric fields has been demonstrated in both single crystals [8] and thin films [9]. In the latter, this was subsequently used to control exchange bias [10, 11], and to electrically set the magnetization of metallic layers coupled to BFO [12]. In spite of these application-oriented advances, open questions remain about the ME coupling, and especially about its mechanisms at the nanoscale, the proposed regime for future device implementation.

Quantitative studies have been rendered challenging by the complex ferroelectric structure of BFO, with eight equivalent polarization variants along the body diagonals of

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the pseudocubic unit cell, and the AF vector in the plane perpendicular to the polarization [13]. This structure gives rise to domains separated by three different types of domain walls— 71° , ferroelastic and ferroelectric; 109° , ferroelastic and ferroelectric; and 180° , purely ferroelectric [9]—which may be present in different proportions in nominally similar BFO thin films, depending on film growth parameters, and substrate and electrode configurations. Understanding and controlling the switching between these different possible polarization states, and their effect on the magnetic ordering of the films, is a key first step towards device applications.

Until now, nanoscale studies of ferroelectric switching dynamics in BFO [9, 12, 14, 15] have generally considered the AF plane as being orthogonal to the polarization vector throughout the switching process. In this scenario 109° switching would be associated with rotation of the AF vector, and thus electric field control of the magnetic order, while 180° switching should leave the AF vector unaffected. However, both from Landau theory [16, 17] and symmetry considerations [18], domain walls in materials with different coupled order parameters, such as ferroelectricity and magnetic ordering, can in fact present a chiral character, with local enhancement of one order parameter correlating with the decrease of another. Ferroelectric polarization switching by nucleation and subsequent domain wall motion may therefore be a significantly more complex process from the point of view of the antiferromagnetic (and possibly locally ferromagnetic) ordering in the films. This is especially important in thin films where many more domain walls may be present than in bulk crystals. In such films, in some cases, a ‘fractal’ domain configuration significantly increases the effective length of the domain walls to be considered [19]. In addition, strain [20, 21] or pinning by disorder [22–24] present in the thin films may play an important role in stabilizing metastable domain and domain wall configurations. In fact, recent studies of new functionalities at domain walls in BFO suggest that migration of defects to the position of the domain wall may play a significant role in phenomena such as locally increased conductivity [25, 26], or possible ferromagnetism [17].

Moreover, recent *ab initio* work on BFO in applied electric fields [27] suggests that even the simplest assumptions based on the zero-field structure of the material may need to be reconsidered when investigating switching dynamics. Lisenkov and co-workers examined the series of phase transitions induced in a rhombohedral BFO unit cell (polarization along [111]) under the application of an electric field along $[00\bar{1}]$. First, the increase in the out-of-plane polarization component under the applied field was calculated to induce a transition towards a monoclinic Cc symmetry, in which switching of the out-of-plane polarization component under suitably high fields can occur with no change in the in-plane polarization components, and in which the AF vector remains orthogonal to the polarization direction. However, these calculations also predicted that a further increase of the electric field should induce a transition to tetragonal $P4mm$ symmetry, in which the polarization (~ 1.5 times larger than in the monoclinic phase) and the AF vector are parallel and lie purely along the $[00\bar{1}]$ direction. Similar electric-field-driven structural changes have been observed in rhombohedral

piezoelectric perovskites [28]. In BFO, a highly distorted $P4mm$ phase has previously been calculated to be metastable, and quite close in energy to the rhombohedral phase, even in a zero electric field [29–31]. More recently, *ab initio* work looking at the effect of biaxial strain established that, for large compressive strains (higher than -4.5%) such a highly distorted tetragonal phase is not in fact the most stable state of the material, and instead a highly distorted monoclinic structure (either Cm [32] or Cc [33]) with a significantly elongated (001) axis is expected.

The electric-field-driven transition to such a tetragonal or quasi-tetragonal symmetry should strongly affect the switching behavior in BFO thin films, and was the motivation for our study of local ferroelectric polarization switching under different applied electric fields, a first step towards understanding both the ferroelectric and magnetic nature of the switching process.

In this paper, we present a piezoresponse force microscopy (PFM) study of polarization switching dynamics in BFO thin films under a biased PFM tip. We observe that depending on the tip bias, polarity and sweeping direction, in addition to sample growth parameters (and thus as-grown domain structure), the in-plane polarization may be fully controlled independently of the out-of-plane polarization. We propose here a phenomenological model of switching in BFO thin films to explain the control of the in-plane component of the polarization when a PFM tip applies an inhomogeneous electric field, i.e. a weak in-plane field combined with a stronger out-of-plane electric field. Our model argues that such switching may be understood more fundamentally as the combined effect of the small in-plane electric field applied by the tip and the onset of a highly distorted tetragonal phase due to the concomitant high out-of-plane field, as predicted from *ab initio* calculations [27]. To fully explain our measurements, we additionally take into account the effects of depolarizing fields resulting from the presence of the surrounding unswitched material, and possible asymmetrizing effects due to disorder or strain specific to the sample.

2. Materials and methods

For these studies, we used 50–70 nm thick BFO films deposited on 35 nm thick SrRuO_3 bottom electrodes on (001)-oriented SrTiO_3 (STO) substrates by pulsed laser deposition [34] and radio-frequency-magnetron sputtering. The films showed 2 nm and 0.4 nm rms surface roughness, respectively, and their high crystalline quality was confirmed by x-ray diffraction (see [35] for the 70 nm laser-deposited sample, with similar results obtained for the 50 nm sputtered sample). Representative topographical scans of the sample surface are shown in figures 1(a) and (d). As a function of the growth conditions and, in particular, depending on the growth rate, the intrinsic domain configuration in BFO thin films has been observed to vary considerably [36]. In our study, the intrinsic domains are rounded and more irregular for the pulsed-laser-grown samples (henceforth referred to as ‘bubble-like’ films), with an intrinsic domain structure somewhat correlated with the surface morphology, as can be seen in the vertical and

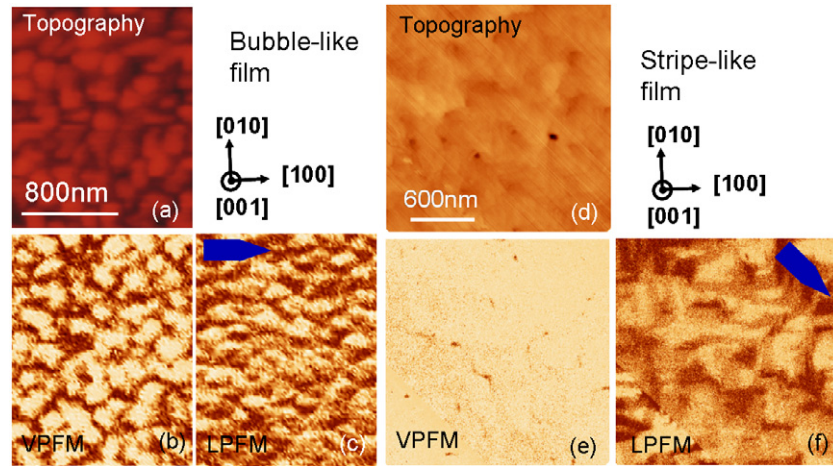


Figure 1. (a) Topography, (b) VPFM, and (c) LPFM in laser-deposited films with ‘bubble-like’ intrinsic domains, showing all eight polarization variants, and a domain structure somewhat correlated with the surface morphology. (d) Topography, (e) VPFM, and (f) LPFM in sputtered films with ‘stripe-like’ intrinsic domains, showing only the four ‘down’ polarization variants, and a domain structure largely independent of the surface morphology, much smoother in these films. In both LPFM images (c) and (f), the cantilever orientation during the measurement is given. The pseudocubic axis orientations are also represented.

lateral PFM measurements (VPFM and LPFM, respectively) shown in figures 1(b) and (c), and presenting all eight variants of the polarization as-grown [19]. The sputtered samples (henceforth referred to as ‘stripe-like’ films, similarly to [36]) meanwhile present only the four ‘down’ polarization components, giving bright contrast in the VPFM image and more regular, somewhat linear domains observed in LPFM (figures 1(e) and (f)).

In these films, we wrote domain structures by scanning a conductive atomic force microscope (AFM) tip (μmasch NCS18/Cr–Au) with an applied voltage in the desired pattern, using a *Nanoscope V Dimension*. To image the full out-of-plane and in-plane polarization components, both VPFM and LPFM measurements were carried out concurrently (0° scan)⁵. In the ‘bubble-like’ films with higher surface roughness only cantilever deflection (in the VPFM measurements), and cantilever torsion (in the LPFM measurements) was induced by the local piezoresponse of the films, necessitating a second LPFM scan at 90° for complete information about the in-plane polarization orientation, since the cantilever torsion provides information only about the in-plane polarization components perpendicular to the cantilever axis. In the ‘stripe-like’ films, possibly because of the lower surface roughness, we also observe a buckling of the cantilever in response to an in-plane piezoresponse along the cantilever axis [37–39]. This is particularly visible when the cantilever is oriented along the $[100]$ direction (see figures 3(b), (e), (h)) and is less

clear when it is along $[1\bar{1}0]$ as in figure 1(e). In this case, the VPFM signal is not completely homogeneous, presenting faintly darker regions corresponding to a noisier phase and to a decrease in the VPFM amplitude (data not shown). Since this information could be used to map out the polarization orientation parallel and antiparallel to the cantilever axis, in the case of the ‘stripe-like’ films, only one VPFM and LPFM scan, taken concurrently, was necessary to reconstruct the total polarization configuration. In the discussion and analysis which follows, all the PFM images we show are the phase signal.

3. PFM switching measurements

3.1. Films with ‘bubble-like’ intrinsic domains

In the ‘bubble-like’ polydomain BFO films, we prepolarized wide horizontal domains with alternating positive and negative voltage on a $3 \times 3 \mu\text{m}^2$ area (slow scan axis $[0\bar{1}0]$), then scanned the tip along $[010]$ and $[0\bar{1}0]$ with either positive or negative voltage, creating narrower vertical lines, as is schematically indicated in figure 2(a).

The wide horizontal domains written with negative voltage (‘up’ polarization, regions 1, 3, 5) show a dark VPFM contrast (figure 2(b)), while the ones written with positive voltage are bright (regions 2, 4, 6). As expected, for vertical lines crossing a wide horizontal domain prepolarized with the opposite polarity, the out-of-plane polarization component is reversed, but no change occurs for regions of the same polarity. In the LPFM images (figures 2(c) and (d)), we observe that the in-plane configuration of the polarization is also clearly modified compared to the as-grown film (figure 2(f)). In negatively prepolarized horizontal domains (region 1), the LPFM signal along $[100]$ in figure 2(c) presents a bright contrast (in-plane polarization along $[100]$), while a predominantly dark contrast is obtained for the positively prepolarized horizontal domains

⁵ LPFM and VPFM measurements were carried out at 20 kHz, 3–4 V ac. The VPFM measurements show stable phase from one image to another, and a single initial comparison to a reference domain structure written with positive and negative voltage suffices to determine the out-of-plane polarization component in subsequent measurements. For the LPFM measurements, in our specific setup the phase signal may change from one image to another, and thus a reference was necessary for each image. For this purpose, we used a linear domain written at 45° with a negative voltage, for which we thus have a known in-plane configuration (in-plane polarization oriented towards the tip during the writing sweep; see sections 3 and 4) which will give a non-zero signal in LPFM measurements performed at both 0° and 90° .

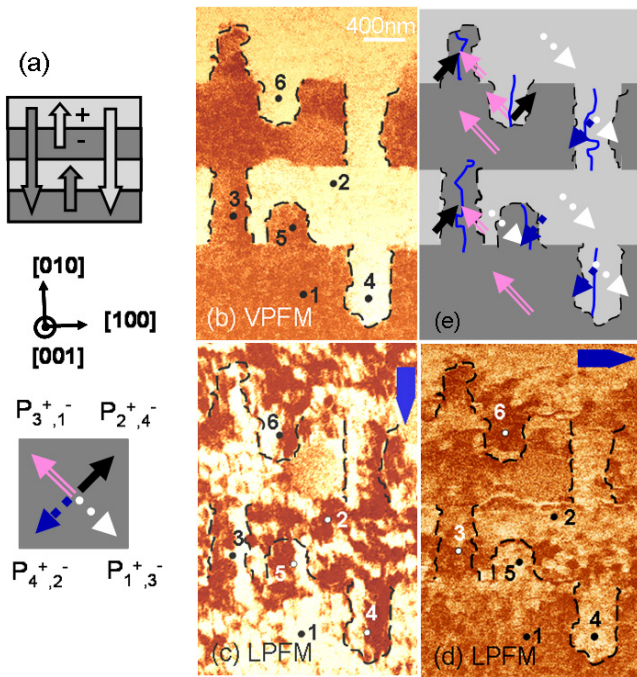


Figure 2. (a) Upper: writing pattern used to create horizontal and vertical line domains in the ‘bubble-like’ film, with dark gray corresponding to -12 V, and light gray to $+12$ V, and arrows indicating the sweep direction. Middle: axis orientation. Lower: representation and attribution of the in-plane components of the polarization. (b) 0° VPFM, (c) 0° and (d) 90° LPFM images of the resulting domain configuration. The scale and crystalline orientations indicated are the same for all the images (b)–(d). For the numbers, see the main text. A blue cantilever is represented in (c) and (d) to indicate its orientation during LPFM measurements. The black dashed lines in (b)–(d) correspond to domain walls between out-of-plane polarization components, written with the vertical tip sweeps. (e) Map of predominant polarization in the written regions with both out-of-plane (bright and dark gray), and in-plane (arrows) polarization components, coded as indicated in the adjoining key. The blue solid lines correspond to 71° domain wall while the black dashed lines are a mixture of 71° , 109° and 180° domain walls (except around region 4, where clearly assignable 109° (left) and 180° (right) domain walls are observed).

(region 2) (in-plane polarization primarily along $[100]$ with some $[\bar{1}00]$ components). During the vertical tip sweeps along $[010]$ or $[0\bar{1}0]$, the in-plane component of the polarization was also modified, but only in the specific regions in which the out-of-plane polarization was concurrently reversed (outlined in black)⁶. The characteristic pattern observed in these regions (dark LPFM contrast on the right of the cantilever and bright on its left for the negative-voltage-written lines (regions 3, 5), and the opposite for positive-voltage-written lines (regions 4, 6)), correlates with the in-plane component of the electric field perpendicular to the cantilever axis during writing (see following) and is directed towards the tip for negative voltage and away from the tip for positive voltage.

⁶ That is why, since the as-grown films present a slightly preferential ‘down’ out-of-plane polarization orientation, in the negatively prepolarized horizontal domains (region 1) we obtain a monodomain configuration, while in the positively prepolarized horizontal domains (region 2) the in-plane configuration was not fully controlled due to the lack of the concomitant out-of-plane switching.

The LPFM signal along $[010]$, with the cantilever rotated by 90° (figure 2(d)), shows that the negatively prepolarized wide domains (region 1) present a dark contrast (polarization along $[010]$), while the positively prepolarized wide domains show a predominantly bright contrast (polarization along $[0\bar{1}0]$). For the vertical lines, we again observe in-plane switching only where the out-of-plane polarization component was switched at the same time (dashed-black-outlined regions). In these measurements, however, the LPFM contrast depends on both the voltage polarity and the tip sweep direction during writing. For vertical lines negatively written along $[0\bar{1}0]$ (region 3) dark contrast is observed whereas for vertical lines negatively written along $[010]$, the contrast is bright (region 5). Positively written vertical lines present the opposite behavior: when sweeping along $[010]$ the contrast is bright (region 4), while along $[0\bar{1}0]$ the contrast is dark (region 6). Combining the information from the VPFM and two LPFM scans allows us to map out the full polarization orientation for the written domain structure, as summarized in figure 2(e). We stress here that only the predominant polarization orientation in each region is reported. As presented in figure 2(e), the domain walls separating both sides of the vertical lines are nominally charged 71° domain walls and should thus be metastable. However, these domain walls remained completely stable during the five month duration of the study, and may thus have been stabilized by defects or disorder.

From these data, we can conclude that for the electric field range used (± 12 V over a 70 nm film), in-plane polarization switching in the ‘bubble-like’ BFO films has to be assisted by out-of-plane polarization switching, and the resulting in-plane polarization orientation depends on both the applied voltage polarity and the tip scanning direction. Specifically, for a negative voltage we obtain that the in-plane component of the polarization along the direction of the sweep (parallel or antiparallel to $[010]$) aligns opposite to the tip sweeping direction. When applying a higher voltage (22 V, data not shown), it was also possible to change in-plane configuration of some regions where the polarization was already oriented down, i.e. without switching the out-of-plane component of the polarization.

With a specific combination of tip voltage and direction in sequential writing passes, we can therefore engineer a desired domain structure in the ‘bubble-like’ film, with full control over both in-plane and out-of-plane polarization components.

3.2. Films with ‘stripe-like’ intrinsic domains

We next carried out similar measurements to those described in section 3.3 in a ‘stripe-like’ film, as shown in figure 3. On this sample, we have written two sets of two rectangles with negative voltage (-8 V) by sweeping the tip with its slow scan axis along either $[\bar{1}\bar{1}0]$ (figures 3(a)–(c)) or $[110]$ (figures 3(d)–(f)) as shown in the right column. In both cases, the out-of-plane polarization has been switched in these regions, as indicated by the dark contrast in the VPFM image, and as confirmed by a measurement made with the cantilever rotated by 90° to distinguish deflection from buckling contributions in the VPFM signal (not shown).

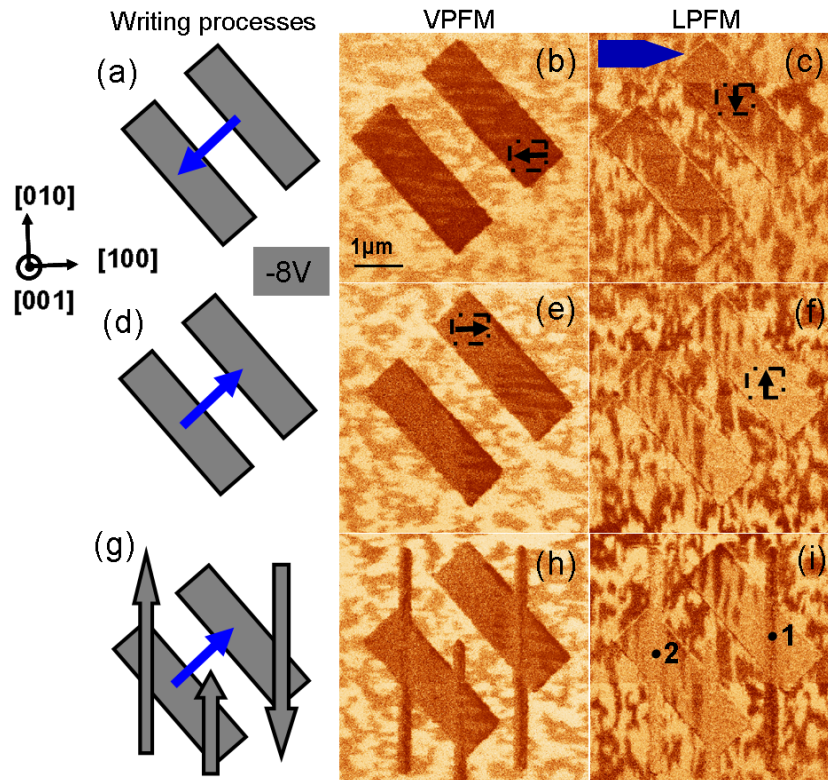


Figure 3. (a), (d), (g) Writing patterns used to create large domains and thin vertical lines in the ‘stripe-like’ film, with dark gray corresponding to -8 V, and arrows indicating the sweep direction. For the wide domains, the blue arrows tilted at 45° indicate the slow scan axis. (b), (e), (h) VPFM and (c), (f), (i) LPFM images of the resulting domain configuration. The scale and crystalline orientations indicated are the same for all the images. For the numbers, see text. The local in-plane direction of polarization along $[100]$ (b) and (e) and $[010]$ (c) and (f), corresponding to the observed color contrast, is indicated by the arrows in a box for a given region.

Considering the in-plane signals, we see that in the LPFM phase images (figures 3(c) and (f)), unlike in the case of the ‘bubble-like’ films, the written regions remain strongly polydomain—although they present a predominant contrast, we always observe a number of stripe domains of opposite in-plane polarization orientation. Similarly, in these regions the buckling contribution to the VPFM signal is not homogeneous, and is composed of either a predominantly dark contrast with brighter-contrast stripe domains (figure 3(b)) or the opposite, dark-contrast stripe domains within a predominantly brighter-contrast region (figure 3(e)). However, when comparing the sets of measurements of figures 3(b), (c) (e) and (f), we clearly see that the predominant contrasts in the written regions are opposite, thus revealing opposite in-plane components of the polarization both along $[100]$ (see boxes and arrows in figures 3(b) and (e)) and $[010]$ directions (see boxes and arrows in figures 3(c) and (f)). To summarize, the predominant in-plane polarization direction was switched in a reverse manner when the slow scan axis during writing was along $[110]$ or $[\bar{1}\bar{1}0]$, in agreement with the conclusions obtained for the ‘bubble-like’ film. However, in the ‘stripe-like’ film, although a specific combination of tip voltage and direction can therefore be used to engineer a predominant polarization orientation, the intrinsic stripe-like features resist switching, an effect also observed in strongly stripe-patterned films [14].

As for the ‘bubble-like’ film, we then wrote vertical lines with negative tip voltage, sweeping along the directions

indicated (figure 3(g)), and measured the resulting domain pattern (figures 3(h) and (i)). Strikingly, and unlike what we observe in the ‘bubble-like’ film, the in-plane component of the polarization was modified even where the out-of-plane polarization was not switched. This can be seen in particular in figure 3(i), where a dark (region 1) or bright (region 2) line appears in the previously written rectangle (compare figures 3(f) and (i)). The in-plane contrast of the written lines along $[100]$ (from the buckling signal in figure 3(h), where the signal is brighter (resp. darker) on the left (resp. right) part of the lines) is similar to that obtained for the negative-voltage-written lines in the ‘bubble-like’ film, i.e. oriented perpendicular to, and directed towards the tip. Along the $[010]$ direction (from LPFM in figure 3(i)), the contrast also depends on the sweeping direction: a bright contrast is obtained for the tip sweeping along $[010]$ and a dark contrast for the $[0\bar{1}0]$ direction⁷.

Thus, in the ‘stripe-like’ films, where in-plane switching may occur independently of out-of-plane switching, for a negative voltage we obtain that the in-plane component of the polarization along the direction of the sweep (parallel or antiparallel to $[010]$) aligns with the tip sweeping direction, unlike in the ‘bubble-like’ films.

⁷ We stress here that the phase reference has changed between images of figures 2 and 3 due to our setup and the contrast in LPFM images is reversed.

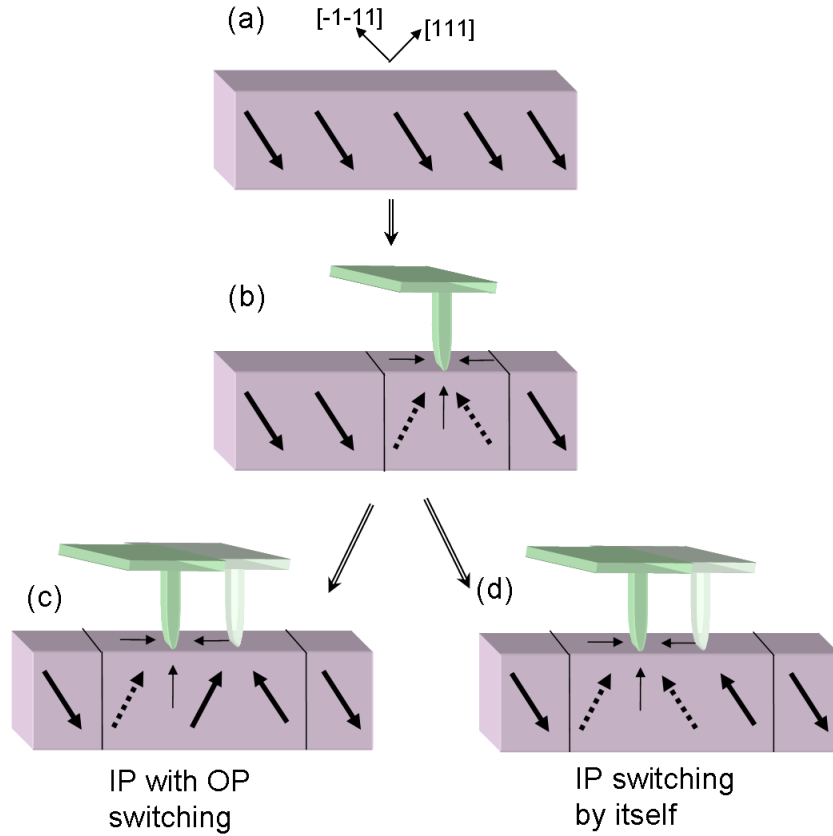


Figure 4. Schematic representation of the switching mechanism starting (a) with a homogeneous $[11\bar{1}]$ polarization (wide arrows). Under a negative tip voltage (-12 V for the ‘bubble-like’ samples, -8 V for the ‘stripe-like’ samples), the polarization switches (dashed wide arrows) (b) following the direction of both out-of-plane and in-plane field (small narrow arrows, not on scale). (c) In the ‘bubble-like’ film, when the tip sweeps leftwards, the in-plane polarization is switched concurrently with out-of-plane polarization, resulting in a predominant polarization along $[111]$, giving an in-plane polarization component opposite to the tip sweeping direction. (d) In the ‘stripe-like’ film, when the tip sweeps leftwards, the in-plane switching occurs independently of out-of-plane switching, giving an in-plane polarization component aligned with the tip sweeping direction. The shaded tip in (c) and (d) represents the previous tip position.

3.3. Phenomenological schema of switching dynamics in the two types of films

We summarize these observations of two opposite switching mechanisms for the ‘bubble-like’ and ‘stripe-like’ films in a highly simplified schematic representation. Starting from a monodomain (figure 4(a)), switching of both in-plane and out-of-plane components of the polarization is depicted in figure 4(b) for an electric field applied along both the in-plane and out-of-plane axes, as expected for a negatively biased PFM tip (see section 4 for more detailed consideration of the electric field). For a tip sweeping leftwards with negative applied voltage the out-of-plane switching-assisted in-plane switching in ‘bubble-like’ film leads to figure 4(c), with a predominant in-plane component opposite to the tip sweeping direction, while independent out-of-plane and in-plane switching in the ‘stripe-like’ film leads to figure 4(d), with a predominant in-plane component along the tip sweeping direction.

4. Modeling electric fields at the AFM tip

To understand the observed switching of the in-plane polarization components in both samples, we first need to

consider the electric field generated by the biased AFM tip. Using *COMSOL Multiphysics*, we modeled the electric field of a realistically shaped tip⁸ with a bias of -12 V, in contact with a 70 nm thick insulating film, on top of a grounded metal electrode. We chose 100 for the value of the dielectric permittivity of the film (reported values at room temperature of 75 in single crystals [40]). Thin films of (001)-oriented BFO show a monoclinic structure rather than the rhombohedral symmetry of their bulk single crystal counterparts [41], suggesting an anisotropy in the functional properties induced by the compressive in-plane strain, including both an anisotropic dielectric permittivity, and the possibility of easier in-plane switching (lower effective coercive field). The bulk BFO values for the pseudocubic $a = b = c$ lattice parameters are 3.965 Å [42]. In our case, the pseudocubic in-plane and out-of-plane lattice constants for the ‘bubble-like’ and ‘stripe-like’ films were $a = 3.905$ Å, $c = 4.1$ Å and $a = 3.905$ Å, $c = 4.08$ Å, respectively, suggesting a relatively small anisotropy.

When modeling the electric field, we therefore considered both the case of an isotropic dielectric response, and an

⁸ Opening angle: 40° , radius of apex: 50 nm, tip length: $20\ \mu\text{m}$, in agreement with manufacturer descriptions of the tip shape.

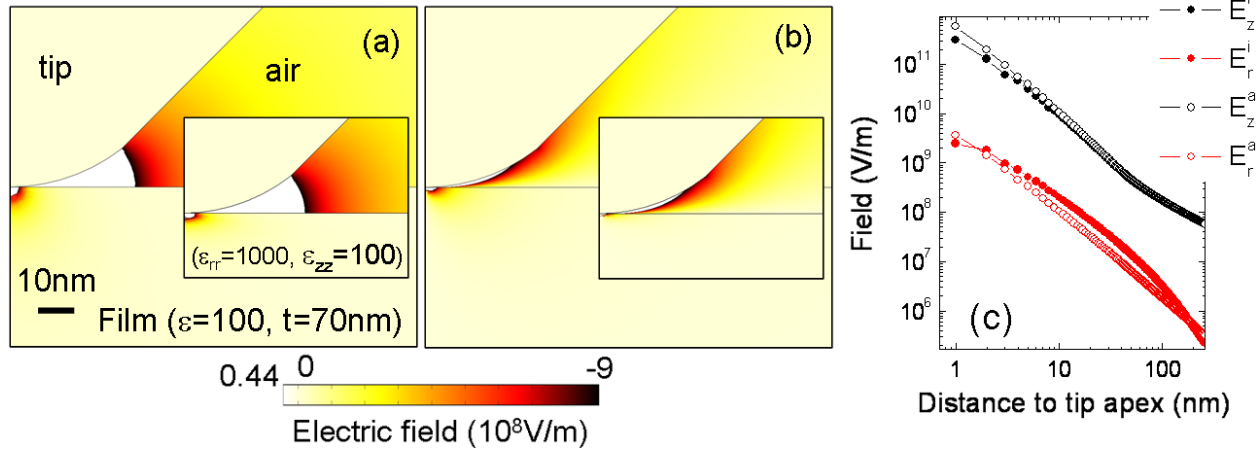


Figure 5. (a) Out-of-plane (E_z) and (b) in-plane (E_r) electrical field with -12 V applied to the tip and an isotropic dielectric permittivity $\epsilon = 100$. The insets show the fields immediately around the tip in the case of an anisotropic dielectric permittivity, with $\epsilon_{\text{out-of-plane}} = 100$ and $\epsilon_{\text{in-plane}} = 1000$. White regions correspond to out-of-range fields. (c) Log-log plot of E_z and E_r at the film surface as a function of the distance from tip apex for both the isotropic, labeled ‘i’, and anisotropic, labeled ‘a’, case.

anisotropic dielectric tensor with an in-plane response ten times higher than the out-of-plane response. Such anisotropy could be due to the anisotropic unit cell, but a factor of ten is probably strongly overestimated. In both cases, the electric field is highly inhomogeneous with both an out-of-plane (E_z , figure 5(a)) and a radially symmetric in-plane component (E_r , figure 5(b)) rapidly decreasing with distance from the tip apex (figure 5(c)). However, as plotted in figure 5(c), the in-plane field is significantly (two orders of magnitude) lower in intensity than the out-of-plane field (in both isotropic and anisotropic cases). Thus, from simply considering the electric field profile, in-plane polarization switching using the tip is expected to be significantly more difficult than out-of-plane polarization switching. Although this effect may be somewhat mitigated if the effective coercive field is lower in the in-plane direction, we nonetheless do not expect a two order of magnitude difference between the out-of-plane and in-plane effective coercive fields.

Coherently with this electric field model, we previously observed that in (111)-oriented films, application of an electric field with a microscope tip results in switching towards purely out-of-plane polarization variants [43], in agreement with other experiments [25]. In this case, the in-plane field is thus too weak to rotate the polarization in a strongly in-plane direction, and a purely out-of-plane variant is stabilized during switching. On the other hand, in the case of (001)-oriented films, all variants of the polarization have equivalent in-plane components. The electric field of the tip would render these variants slightly inequivalent, favoring those parallel to the radially symmetric in-plane field component around the tip. However, this in-plane field, being very small for the voltage range used, is probably far too weak to independently induce in-plane polarization switching. Nevertheless, since this in-plane electric field is generated by voltage applied to the tip, it will always be associated with a much stronger out-of-plane field, a key point for understanding our experimental results.

5. Discussion of domain switching dynamics in BFO

When considering the polarization switching, both in-plane and out-of-plane, observed in the BFO thin films, it is essential to consider the continuous application of the high out-of-plane electric field under the biased AFM tip. As predicted by first principles calculations, the application of such an out-of-plane electric field may induce tetragonal unit cell symmetry with the polarization along the field direction [27], or at the very least a significant elongation of the monoclinic unit cell [32]. When the field is subsequently decreased, the unit cell should go back to the remanent, undistorted monoclinic state⁹. At this point, in the absence of an in-plane electric field, the unit cell can go into one of the four possible monoclinic symmetries having the same out-of-plane component of the polarization as the tetragonal state, with equal probability. Therefore, during our measurements, if the out-of-plane electric field is high enough to induce the tetragonal phase, the polarization would present a zero in-plane component¹⁰, and very high sensitivity even to the very weak in-plane field generated by the tip as it moves across the surface of the sample. Thus, as the out-of-plane field decreases, a return to monoclinic unit cell symmetry with an in-plane polarization component along the local in-plane field direction would be favored. We note here that a similar, and possibly identical phase is present in phase field models of domain switching dynamics in BFO (see figure 1(B) in supplementary materials of [14]), where an out-of-plane polarization 1.5 times larger than in the rest of the film and an in-plane polarization close to zero is nucleated

⁹ In unstrained BFO films, experimental observations bear out this supposition: to our knowledge, no report of a remanent highly distorted tetragonal unit cell after electric field biasing in such films has been made. In strained BFO films, although electric field switching between low distorted and highly distorted phase has been reported [33, 44–46], we note that the unit cell remains monoclinic.

¹⁰ We note here that this may be a dynamic process, and in the presence of the small in-plane field there would still probably be a slight monoclinic distortion, similar to the very highly distorted quasi-tetragonal phase reported in strained BFO films [44, 45, 32, 33].

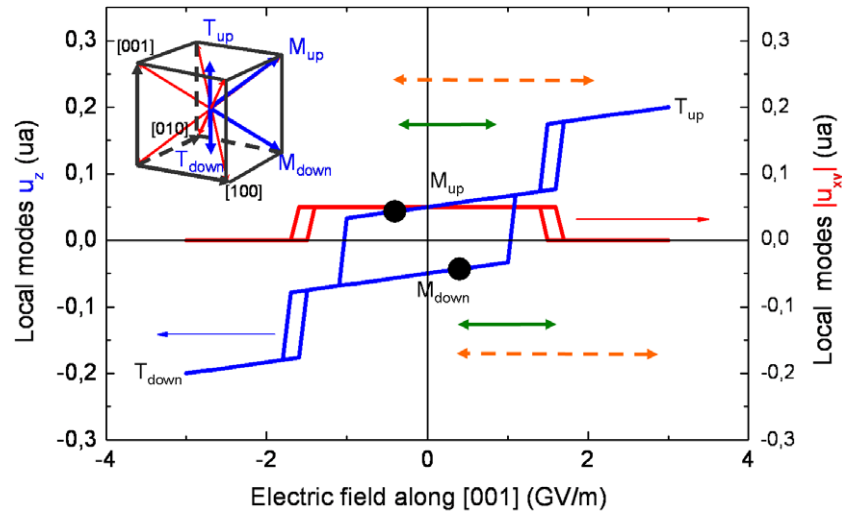


Figure 6. Expected hysteresis loop for out-of-plane (blue) and in-plane (red) polarization, proportional to local modes calculated from first principles [27]. Polarization directions in the monoclinic (M) and tetragonal (T) phases are schematically indicated on the pseudocubic unit cell (inset). The large dots correspond to the actual ‘zero applied field’ M_{up} or M_{down} state taking into account depolarizing field/disorder effects. The solid green arrows and dashed orange arrows represent the effect of applying lower or higher electric fields, respectively, from either M_{up} or M_{down} state.

just below the tip. We note also that both in the phase field modeling [14], and in our own simulations, the very high fields needed to induce a tetragonal or tetragonal-like distorted phase are generated only in the immediate vicinity of the AFM tip apex, within ~ 10 nm of the surface in a film that is 50–70 nm thick. However, once a domain is nucleated in this high-field region, it is probable that the coercive field for propagation, especially along the elongated out-of-plane direction, is much lower than the thermodynamic one. In addition, the presence of local defects within this volume may aid the initial nucleation process [47, 48].

We schematically illustrate this out-of-plane field-assisted in-plane switching in figure 6, based on the calculation results by Lisenkov *et al* [27]¹¹. The expected hysteresis loop shows the polarization switching possible between M_{up} and M_{down} variants (monoclinic unit cell) for moderate fields and the transition to a T_{up} or T_{down} (tetragonal unit cell) for higher fields. Two coercive fields are thus obtained, one corresponding to a switching of only the out-of-plane component of the polarization, where the symmetry remains monoclinic, and the second one linked to the monoclinic to tetragonal symmetry change, where the in-plane component of polarization goes to zero and the out-of-plane component is significantly increased.

In this scenario, we also need to take into account the effects of the depolarizing field due to the surrounding unit cells further from the tip, whose polarization will not be switched immediately, and which will shift the effective field below the tip, as compared to the applied field, either towards negative (for ‘up’ polarized surroundings) or towards positive (for ‘down’ polarized surroundings). More generally this effect may be further complicated by the presence of charged defects,

which could also asymmetrize the response, and varying strain due to lattice mismatch with different underlying substrates, which could change the width of the plateaus in the hysteresis. The ‘up’ and ‘down’ remanent states, i.e. with no applied field, are thus represented by the large dots on figure 6. A transition to the tetragonal phase, leading to further possible in-plane control, would thus be easier if the applied out-of-plane field is opposite to the out-of-plane polarization component; an in-plane switching of the polarization will be easier if assisted by an out-of-plane switching.

From this hysteresis loop schematic we expect that, depending on the depolarizing field/disorder effects, for a certain range of electric fields at the tip (see solid double arrows corresponding to a positive field starting from M_{up} and M_{down}), in-plane polarization switching would necessarily be associated with out-of-plane polarization switching, and reproduce the in-plane electric field distribution around the tip. As the biased tip sweeps across the BFO surface, in-plane switching would therefore be observed ‘downstream’ of the tip motion, with the final state thus depending on both the applied voltage polarity and the sweep direction, as schematically presented in figure 4.

This scenario shows very good agreement with the observed polarization switching in ‘bubble-like’ films with ± 12 V, shown in figure 2. In the vertical line domains, a single polarization state along [010] in each line is obtained (figure 2(d)), corresponding to the in-plane field ‘downstream’ of the tip motion. We can therefore use a combination of tip voltages and directions to engineer a desired configuration of domains and domain wall types in such samples.

From figure 6, we can also see that high enough electric fields (see dashed double arrows corresponding to a positive field starting from M_{up} and M_{down}) can overcome the sample-specific depolarizing field/disorder effects, and allow transition to the tetragonal phase even when applied in the same direction

¹¹ The transition fields calculated by Lisenkov *et al* [27] are relatively large but the out-of-plane field applied by the tip reaches similar values ~ 10 – 15 nm around the tip apex.

as the out-of-plane polarization component in the monoclinic phase, thus allowing in-plane polarization switching without concomitant out-of-plane switching. In our films, as explained previously, such independent in-plane switching was observed in some areas for the ‘bubble-like’ films when much higher voltages were applied (22 V, not shown) and for the ‘stripe-like’ film (−8 V, see figure 3). In that case, the switching is schematically represented by figures 4(a), (b) and (d), in which one can see that the resulting in-plane direction will be, for a negative voltage, the same as the tip sweeping direction, consistently with experiments (figure 3).

In addition, we note that simply out-of-plane switching with no in-plane change would also be possible if the phase remained monoclinic. Such purely out-of-plane switching was intermittently observed in some regions of the films but is less reproducible, probably because the plateau between the switching of the monoclinic phase and the onset of the tetragonal phase is relatively narrow.

6. Conclusion

To conclude, we have shown that the use of the highly inhomogeneous electric field provided by a biased sweeping PFM tip allows a control of the in-plane component of the polarization independently of the out-of-plane one in (001)-BFO thin films. The controlling parameters are the bias polarity and amplitude and the tip sweeping direction. Also, depending on the type of sample, i.e. ‘bubble-like’ versus ‘stripe-like’, differences in the switching dynamics are observed and have been attributed to the different morphologies and defect distribution and to the different depolarizing field resulting from the regions surrounding the initial nucleus generated in the very high field immediately under the tip. The in-plane switching occurring despite the very small in-plane component of the electric field is consistent with the electrically driven onset of tetragonal symmetry calculated by first principles [27]. In the presence of such a phase transition, the antiferromagnetic vector is expected to rotate from perpendicular to parallel to the polarization direction and the weak magnetic moment is expected to cancel [27] as the octahedra tilts are absent from the tetragonal phase. This configurational change still has to be confirmed or excluded experimentally, but a parallel configuration between the polarization and the antiferromagnetic vector and a zero weak magnetic moment would imply cancelation of the magnetoelectric coupling [49] and thus significant modifications of the behavior of domains and domain walls in BFO.

Acknowledgments

The authors thank J-M Triscone, K Bouzehouane and S Fusil for helpful discussions, and M Lopes and E Jacquet for technical assistance. This work was supported by the Swiss National Science Foundation through the NCCR MaNEP, and by the European Commission STREP project MaCoMuFi and FP7 project OxIDes. HB was supported by a Bourse d’Excellence from the University of Geneva.

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