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Multiferroic BiFeO₃ films: domain structure and polarization dynamics

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BiFeO₃ simultaneously shows antiferromagnetic and ferroelectric order with high transition temperatures, i.e. $T_N \sim 370^{\circ}$ C and $T_C \sim 830^{\circ}$ C, respectively. Naturally, it has been inferred that coupling exists between the magnetic and ferroelectric order parameters like in the multiferroic manganites with low transition temperatures. A thorough investigation of the ferroelectric properties of BiFeO₃ is therefore in line with the understanding of its multiferroic behaviour. Here, we review the ferroelectric properties of epitaxial (001) oriented BiFeO₃ films grown by different techniques on several substrates. Structural characterization along with ferroelectric quantitative analysis point at the high quality of the films. Emphasis is put on identifying the various polarization variants and domain dynamics under an applied bias. In these studies, to unravel the intricate ferroelectric domain structure, piezo-force microscopy scans have been taken along the principal crystallographic directions. Two cases have been analysed. First, a 600 nm thick film grown on SrTiO₃ (001) with a thin SrRuO₃ underlayer exhibits a mosaic domain pattern due to the presence of both up and down polarization domains. Mainly four polarization domains have been identified in this case, which correspond to two structural domains. Second, epitaxial BiFeO₃ films grown on $DyScO_3$ (110) and miscut $SrTiO_3$ (001) with a thin $SrRuO_3$ underlayer show stripe patterns, with mainly two down polarization domains. A single structural domain of orthorhombic SrRuO₃ epitaxial underlayer induces this changes in the domain structure of BiFeO₃. The suppression of up domains by changing the substrate conditions prove the possibility of ferroelectric domain engineering. The three possible polarization switching mechanisms, namely 71 and 109° rotations, as well as 180° rotation, have been identified by following the domain dynamics in a two-domain epitaxial BiFeO₃ film. Interestingly, 180° polarization reversal seems to be the most favorable switching mechanism in epitaxial films under an applied bias along [001]. The observation of both ferroelastic and ferroelectric switching processes open exciting possibilities for the optimization of BiFeO₃'s ferroelectric properties and investigation of magnetoelectric coupling in epitaxial films. A recent photoemission study using

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linearly polarized X-rays proved the coupling between the ferroelectric and antiferromagnetic domain structures.

Keywords: Multiferroic; Ferroelectric; Ferroelastic; Piezoresponse; PFM; Domains; Domain walls; Switching; Antiferromagnetic; Magnetoelectric coupling

1. Introduction

The whole field of multiferroics [1–4] has been rejuvenated by the recent reports on large room temperature ferroelectric polarization and strong piezoelectric response in epitaxial BiFeO₃ films [5–11]. This is in sharp contrast to the weak polarization observed earlier on bulk ceramics [12], but in very good agreement with the recent theoretical results [13–17]. The main reason why BiFeO₃ has captured so much attention is that this material simultaneously shows antiferromagnetic and ferroelectric order with the corresponding transition temperatures well above room temperature, i.e. $T_N \sim 370^{\circ}$ C and $T_C \sim 830^{\circ}$ C, respectively [18]. Therefore, questions have arisen as whether the corresponding order parameters couple to each other [5, 13, 14, 19], as in the case of some multiferroic manganites with low transition temperatures [20–22]. It was not until very recently when the coupling between the antiferromagnetic and ferroelectric order in epitaxial BiFeO₃ films has been proven [23]. Moreover, the possibility of growing high quality epitaxial BiFeO₃ thin films has enabled the observation of weak magnetism as well [5, 24, 25], but its origin is not yet fully established [26, 27].

The structure of BiFeO₃ (sketched in figure 1) is characterized by two distorted perovskite blocks ($a_r = 3.96 \text{ Å}$, $\alpha_r = 0.6^\circ$) connected along their body diagonal (figure 1a), denoted as pseudocubic $\langle 111 \rangle$, to build the rhombohedral unit cell [28, 29]. We note here that all Miller indices used throughout this article are based on the pseudo-cubic lattice, unless otherwise specified. The two oxygen octahedra in the connected perovskite units are rotated clockwise and counterclockwise around this axis by $13.8(3)^{\circ}$, with the Fe cation shifted by 0.135 Å along the same axis away from the centre of an oxygen octahedron (figure 1b). The ferroelectric state is realized by a large displacement of the Bi ions relative to the FeO_6 octahedra (figure 1c). Two important consequences result from this atomic arrangement. First, polarization lies along the (111), leading to the formation of eight possible polarization variants (P_i^{\pm} with $i = \overline{1, 4}$; "+" and "-" stand for up and down polarization directions, respectively). These eight polarization directions correspond to four structural variants [8, 29–33]. Second, Fe magnetic moments couple ferromagnetically within the pseudocubic {111} planes, and antiferromagnetically between adjacent planes [13]. Since the coupling between ferroelectricity and magnetism in BiFeO₃ is determined by rotations of the oxygen octahedra [13], 71° (P_i^{\pm} to P_{i+2}^{\mp}) and 109° (P_i^{\pm} to P_{i+1}^{\pm}) rotations of polarization from one (111) axis to the other three (111) axes, rather than 180° switching along the same (111) axis (P_i^{\pm} to P_i^{\mp}), might lead to changes in the magnetic configuration.

Above all, $BiFeO_3$ is a good ferroelectric/piezoelectric material. But in contrast to the traditional Pb-based ferroelectrics, it is environmentally friendly. The implementation of $BiFeO_3$ in non-volatile memory applications is nonetheless critically dependent on understanding its ferroelectric domain structure and the polarization



Figure 1. The unit cell of BiFeO₃ (001) viewed along different directions. (a) threedimensional representation, (b) unit cell viewed along the pseudocubic $\langle 111 \rangle$ direction parallel with the Fe displacement (polarization axis), (c) a view along a pseudocubic $\langle 110 \rangle$ axis perpendicular to the polarization direction.

switching mechanisms. These aspects have been recently unraveled [8, 9], and in contrast to the case of mechanical stress-induced polarization switching [29, 34], 180° ferroelectric switching of polarization was observed under applied electrical bias conditions [9]. These results open the possibility of customizing the ferroelectric properties to enable the rapid implementation of the ferroelectric BiFeO₃ with the existing data storage technologies.

In this article we will review the main results concerning the growth, ferroelectric domain structure, and domain dynamics in epitaxial BiFeO₃ films. Using of the piezo-force microscopy (PFM) technique [39–41], the intricate domain structure has been successfully unravelled, and it was found that polarization switches via different mechanisms: 180° reversal, 71 and 109° rotations.

2. The growth of epitaxial BiFeO₃ films

2.1. Pulsed laser deposition

Epitaxial BiFeO₃ films have been grown by pulsed laser deposition (PLD) on (001) oriented $SrTiO_3$ as well as on (110) oriented $DyScO_3$ substrates. A 50–100 nm thick conducting $SrRuO_3$ underlayer [44] is typically grown to enable electrical characterization in a capacitor geometry. The lattice constants of films and

substrates are summarized in table 1. Both SrRuO₃ and BiFeO₃ films are deposited in an oxygen atmosphere of 1×10^{-1} Torr at a constant temperature of 670°C. Figure 2(a) shows a θ -2 θ X-ray diffraction scan of a few tens of nm thick epitaxial BiFeO₃ film. The film is (001) oriented and no second phases have been detected under these growth conditions. The good films crystallinity is confirmed by the narrow FWHM of the 002 peak rocking curve (figure 2b), and the transmission electron microscopy data (figure 2c). The arrow in figure 2(c) points along the BiFeO₃/SrRuO₃ interface. Because of the lattice mismatch between BiFeO₃ and the epitaxial SrRuO₃ underlayer grown on SrTiO₃ (001), the BiFeO₃ lattice is compressed in plane and consequently elongated out of plane due to the Poisson ratio, or limited compressibility. Below about 30 nm, the films are fully epitaxially strained. Strain begins to relax at a thickness of about 20–40 nm and the BiFeO₃ lattice constant approaches the bulk value.

To understand the structure of the thin $BiFeO_3$ films, high-resolution XRD (HRXRD) measurements were performed. For this purpose, $BiFeO_3$ films were grown directly on $SrTiO_3$ (001) substrates to eliminate the $SrRuO_3$ peaks. The presence of non-degenerate rhombohedral diffraction peaks such as 113 or 210 is a good fingerprint of a structure with a symmetry lower than tetragonal, e.g. rhombohedral or monoclinic. The $BiFeO_3$ films with thicknesses larger than 30 nm exhibit such non-degenerate peaks, indicating a rhombohedral-like structure,



Table 1. The lattice constants of substrates and films.

Figure 2. The structure of PLD-grown epitaxial BiFeO₃ films. Typical (a) θ -2 θ X-ray diffraction spectrum, (b) 002 peak rocking curve, and (c) cross-section high-resolution transmission electron micrograph of thin BiFeO₃ films on SrTiO₃ (001).

as discussed below. No 113 peak was resolved in the HRXRD measurements performed on thinner $BiFeO_3$ films.

2.2. Liquid delivery metal-organic chemical vapour deposition

A metalorganic chemical vapour deposition (MOCVD) reactor equipped with a liquid delivery system was also used to grow epitaxial BiFeO₃ films [10]. As liquid metalorganic precursors, we used Tris(2,2,6,6-tetramethyl-3,5-heptanedionate)bismuth(III) [Bi(thd)₃] and Tris(2,2,6,6-tetramethyl-3,5-heptanedionate)iron(III) [Fe(thd)₃] dissolved in tetrahydrofuran, both based on β -diketonates. Their intrinsic similarity in organometallic chemistry makes them reasonably compatible. The showerhead we used with our reaction chamber is heated with oil to avoid condensation of vapourized precursors and achieve a uniform film deposition on a 2 inch area. The system has 13 heating controllers that adjust the temperature downstream from the vapourizer and enables us to obtain a thermally stable growth condition.

As we previously reported for the case of MOCVD-grown Pb (Zr, Ti)O₃ films [46], we found that the composition and structure of $BiFeO_3$ films are extremely sensitive to the substrate temperature, precursor delivery ratio and vapourizer temperature. The variation of films composition with different precursor supply ratios is shown in figure 3(a). The volumetric liquid source supply mixing ratio of Bi/(Bi + Fe) was varied from 0.50 to 0.85 and the growth temperature was fixed at 650°C. The mixing ratio stands for the volumetric ratio of liquid sources at room temperature, and not the actual gas mixing ratio in the reactor chamber. A stoichiometric composition was obtained from a Bi/(Bi + Fe) liquid source mixing ratio of 0.70. The higher supply ratio of Bi precursor with respect to Fe precursor required to achieve stoichiometric composition in films is a consequence of the low vapour pressure of Bi(thd)₃ as compared with the one of Fe(thd)₃. At 190°C the vapour pressure of $Fe(thd)_3$ is about 2.5 times higher than that of $Bi(thd)_3$. In addition, Bi(thd)₃ is not completely vapourized and leaves a $\sim 30\%$ nonvolatile residue, as deduced from thermogravimetric analysis. The incomplete vapourization of $Bi(thd)_3$ may be the reason for the needed high supply ratio of Bi precursor.

For comparison, we also plot in figure 3(a) the change of Pb atomic content ratio obtained from our previous MOCVD growth of Pb (Zr, Ti)O₃ at the same temperature, i.e. 650° C [46]. The growth window of BiFeO₃ is much narrower than that of Pb (Zr, Ti)O₃ as can be seen in figure 3(a). The composition change in the Bi/(Bi + Fe) ratio shows an almost linear behaviour with the liquid source mixing ratio, while there is a relatively wide plateau for the Pb (Zr, Ti)O₃ growth process. This is generally explained by a "Pb self-regulating" mechanism at high temperature growth processes and is used as the "growth window" [47, 48].

The changes in the microstructure of films with different compositions have been determined by a typical θ -2 θ X-ray diffraction scan. Only the 001 diffraction peaks of BiFeO₃, SrRuO₃, and SrTiO₃ were observed for films with the stoichiometric composition, and no second phases were detected (figure 3c). The out-of-plane lattice constant calculated from the 002 peak of a 150 nm thick BiFeO₃ film is 4.03 Å. This value is larger than the bulk lattice constant (3.96 Å) because of the in-plane compressive strain induced by the substrate (SrRuO₃/SrTiO₃(001)). For Fe- and Bi-rich films (marked with (I) and (III), respectively), additional second phase peaks such as 024 α -Fe₂O₃ (rhombohedral), R3c, a = 5.112 Å, c = 13.82 Å), or 002



Rutherford backscattering and energy disperse spectrometry, for precursor mixing ratio prepared at growth temperature of 650° C. Atomic percentage ratio in Pb(Zr_xTi_{1-x})O₃ (from Ref. [46]) is also plotted at the same scale for comparison. θ - 2θ X-ray diffraction scans for (b) Fe-rich phase (\bigstar : α -Fe₂O₃), The structure and composition of MOCVD-grown films. (a) Relation between Bi and Fe atomic percentage in BiFeO₃ films as measured by (c) stoichiometric composition and (d) Bi-rich phase (O: β -Bi₂O₃). Figure 3.

and 220 β -Bi₂O₃ (tetragonal, $P\bar{4}2_1c$, a=7.741 Å, c=5.634 Å) were observed (figure 3b and d).

After optimizing the Bi: Fe ratio in the precursors, epitaxial BiFeO₃ films have been grown on single crystalline (001) oriented $SrTiO_3$ and $SrTiO_3/Si$. To facilitate the heteroepitaxial growth and to introduce a conducting perovskite bottom electrode, we used a 70 nm thick, epitaxial $SrRuO_3$ underlayer deposited by PLD.

2.3. High-rate off-axis sputtering

High quality epitaxial BiFeO₃ films have been grown on (001) oriented $SrTiO_3$ substrates and on DyScO₃ (110) substrates by high-rate off-axis sputtering [11]. This method enables the growth of complex oxide thin films with extremely smooth surfaces [43]. The three-dimensional strain states and crystal structure of the BiFeO₃ films were determined by high resolution X-ray diffraction (HRXRD).

Miscut (001) oriented SrTiO₃ substrates have also been used for the growth of epitaxial BiFeO₃ films. The miscut angles were 0.8 and 4° toward [100]. An epitaxial 100 nm thick SrRuO₃ bottom electrode was grown using the same technique [44] to enable electrical characterization. The substrate was kept at a constant temperature of 690°C during the growth of BiFeO₃. To compensate the Bi-loss in the films, stoichiometric targets with 5% excess Bi₂O₃ have been used. We have also determined the chemical composition of BiFeO₃ films and targets using wavelength dispersive spectrometry (WDS). The films are found to be nearly stoichiometry with the Bi: Fe ratio of 1.0 ± 0.03 .

The substrates' miscut angle has a strong influence on films microstructure [45]. With increasing the miscut angle the volatile species, Bi, tightly binds to the edge and kink site, rather than to a terrace. Thus, we believe that the role of substrate miscut is to maintain film stoichiometry by decreasing the propensity for volatile species to desorb and maintain the step-flow growth up to large thicknesses. Due to the large miscut angle, the steps and terraces align perpendicular to the miscut direction.

Shown in figure 4 are X-ray θ -2 θ scans of 60 and 600 nm thick BiFeO₃ grown on SrTiO₃ (001). There is a systematic variation of the 002 peaks towards lower diffraction angle with reducing the film thickness. This indicates that the out-of-plane lattice parameters of thinner films are larger than those of thicker films. This is a result of the biaxial compressive strain in the BiFeO₃ lattice. The full width at half maximum (FWHM) of the rocking curve for 002 BiFeO₃ reflection ranges from 0.35 to 0.42° for 60–600 nm thick films. These values confirm the high crystalline quality of our films.

The in-plane epitaxial arrangement of the (001) oriented BiFeO₃ films was studied using azimuthal scans. Initially we have taken the off-axis scans of the 101 reflections of (001) SrTiO₃. The peak position of (101) SrTiO₃ is exactly at 0,90,180,270° due to the cubic symmetry. However, the pseudocubic lattice 101^{C} reflection of BiFeO₃ is $\pm 0^{\circ}$ shifted from the phi values for cubic or *c*-axis tetragonal structure. Also, multiple peaks of BiFeO₃ were observed in off-axis scans. This suggests that BiFeO₃ does not posses the tetragonal symmetry. To determine the crystal structure of films, we have taken off-axis scans of the rhombohedral non-degenerate 210^{R} reflection of BiFeO₃ as shown in figure 4(b). The 210^{R} scan was performed for the BiFeO₃ films grown directly on SrTiO₃ substrates because all orthorhombic



Figure 4. The structure of sputter-grown films. (a) θ -2 θ X-ray diffraction scans for 60- and 600 nm thick BiFeO₃ films grown by sputtering, (b) off-axis ϕ scan of the rhombohedral non-degenerate 210^R reflection of BiFeO₃.

reflections of SrRuO₃ overlap with those of BiFeO₃. The 60 nm thick film shows the same behaviour. This confirms the rhombohedral structure of the thin films.

3. Ferroelectric properties: macroscopic, quantitative analysis

The epitaxial BiFeO₃ films grown by the different physical and chemical deposition methods described above show similar macroscopic ferroelectric properties if grown on the same type of substrates. The P-E hysteresis loops have been measured using a Radiant Technology 6000 ferroelectric tester, at frequencies of 0.1-20 kHz. The switchable polarization as a function of applied voltage has been measured as well. For this purpose, Pt and Pt/SrRuO₃ top electrodes have been lithographically



Figure 5. Ferroelectric properties of PLD-, MOCVD-, and sputter-grown films. (a) Polarization, (b) switched polarization, and (c) perpendicular piezoresponse *vs.* applied electric field.

patterned using a lift-off process. To quantitatively measure the piezoelectric response, an atomic force microscope-based setup has been employed (Multimode-AFM from Veeco-DI, equipped with a Nanoscope IIIa controller).

The results obtained for 200 nm thick films grown on SrRuO₃/SrTiO₃ (001) by various methods are summarized in figure 5. Typical P-E hysteresis loops are shown in figure 5(a). The loops are square-like and well saturated with $P_{\rm S} \approx 60 \,\mu {\rm C \, cm^{-2}}$, pointing at a reduced leakage. The measured spontaneous polarization in the films grown by PLD, MOCVD, and sputtering are in very good agreement with the calculated value for single crystal BiFeO₃ (~60 $\mu {\rm C \, cm^{-2}}$ along (100)) [5, 15]. Typical switched polarization data *versus* applied field are shown in figure 5(b) for the three growth methods. Again, the measured saturated switchable polarization ($P \approx 2P_{\rm r}$) of ~120 $\mu {\rm C \, cm^{-2}}$ is in agreement with the expected value for good ferroelectric BiFeO₃ films. Quantitative piezoelectric data are shown in figure 5(c). The loops are square-like, with a perpendicular converse piezoelectric coefficient (d_{33}) of ~50 pm V⁻¹. All these results indicate high quality epitaxial BiFeO₃ film.

4. Nanoscale domain structure and domain dynamics

Ferroelectric domains occur to minimize the elastic and electrostatic energies. Their shapes and sizes are a direct consequence of various stresses, which in thin films reflect the quality of epitaxial growth. In particular, the onset of certain domain configurations is dictated by lattice, structure and thermal expansion coefficient mismatch, film thickness, and temperature [35–38]. The various polarization switching mechanisms depend on the allowed polarization configurations, which in turn are reflected in the equilibrium domain structure. Therefore, unravelling the ferroelectric domain structure is critical for a thorough understanding of possible switching mechanisms.

In this section, we first present a brief roadmap to understanding the piezocontrast, and then we move on to the main up do date results on domain structure in 001 oriented epitaxial $BiFeO_3$ films. Based on these findings, we will discuss afterwards the possible electrical bias-induced polarization switching mechanisms as deduced from the changes in domain structure.

4.1. Understanding the piezoelectric contrast

In ferroelectric materials, the piezoelectric effect is a direct manifestation of the presence of polarization. Therefore, PFM [39–41] is an indispensable tool for the study of polarization distribution within domains at nanoscale. Recently, PFM has been employed to study the ferroelectric domain structure and domain dynamics in 001 oriented epitaxial BiFeO₃ films [8, 9]. A DI-Veeco Multimode AFM equipped either with Nanoscope IV controller has been used to simultaneously record the out-of-plane (OP) and in-plane (IP) piezoresponse (PR) signals, with the aim of reconstructing the polarization vector in each domain. The scans have performed at ambient conditions, using an ac bias of 6.39 kHz (of e.g. $3.0 V_{pp}$ amplitude for the 600 nm thick films) applied to the conducting probe. To image the ferroelectric domains we mainly used the in-phase signals from the lock-in amplifiers (Stanford Research Systems SR830). To confirm the results obtained from imaging the in-phase PR, amplitude and phase imaging experiments have been carried out as well. The PFM images have been recorded with the cantilever pointing along different directions to reconstruct the polarization direction [8, 49-51]. We will review the findings on domain structures in epitaxial BiFeO₃ films grown by sputtering on $SrTiO_3$ (001) [8, 9, 11], as well as on $DyScO_3$ (001).

The domain structure in rhombohedral ferroelectrics on a 001-type cubic surface can be rather complicated [8, 31] due to the possible coexistence of as many as 8 polarization variants [29, 30, 33]. To understand the PFM contrast [41], we schematically show the structure of rhombohedral $BiFeO_3$ (001) [29] in figure 6 together with the PFM cantilever oriented along, e.g. [110] (figure 6a). The ac biasexcited film's OP- and IP-PR are pictured in figure 7 for the P_{\perp}^+ and P_{\perp}^- domains in the geometry shown in figure 6. First, domains with up (\mathbf{P}_{i}^{+}) and down (\mathbf{P}_{i}^{-}) polarizations should give rise to opposite contrast in OP-PFM (black and white, respectively), because their OP-PR are in anti-phase (blue curve in figure 7). Second, domains with polarization vectors along the cantilever's long axis ($P_{2,4}^{\pm}$ in figure 6), do not give rise to IP-PFM signal (zero amplitude) for they do not produce any torque required for IP imaging [49]. Instrumental offsets often make these domains appear with a non-zero PR signal. Third, domains with polarization pointing to the right (P_1^+ , P_3^- in figure 6) with respect to the cantilever's long axis should produce an opposite tone as compared with domains having polarization pointing to the left (P_3^+, P_1^-) in figure 6). The reason for this is the antiphase IP-PR signals produced by these domains (red curve in figure 7).



Figure 6. A schematic of the four different structural variants in (001) rhombohedral films along with an AFM cantilever oriented along [$\overline{1}10$]. $P_i^{\pm}(i = \overline{1,4})$ stand for the polarization vectors. The central unit represents a detailed perovskite building block of the rhombohedral structure.



Figure 7. A schematic of the out-of-plane and in-plane piezoelectric response from two domains with the polarization vector pointing as shown. The black curve represents the ac bias applied to the tip, and the coloured curves stand for the out-of-plane (blue) and in-plane (red) piezoresponses.



Figure 8. Typical (a), (b) amplitude, (c), (d) phase, and (e), (f) in-phase PFM images taken with the cantilever along one of the BiFeO₃'s pseudocubic $\langle 110 \rangle$ axes. (a), (c), (e) are OP–PFM and (b), (d), (f) are IP–PFM images. The bars are 500 nm.

To illustrate these cases, we show in figure 8 amplitude, phase and in-phase PFM images taken on a 130 nm thick BiFeO₃ (001) film. The information provided by amplitude images (figure 8a and b) contains the magnitude of PR. These images show two tones, with the brown one standing for zero PR. These scans clearly reveal the presence of domain walls (zero OP–PR stripes in figure 8a), as well as large areas with zero IP–PR (figure 8b). The latter correspond to domains with the IP polarization component either parallel or antiparallel with the cantilever, that is, along two colinear $\langle 110 \rangle$ directions.

The phase images (figure 8c and d) provide a great deal of information about the direction of polarization in domains, but scans along different crystallographic directions are necessary to reconstruct the vector direction. The dominant dark tone in the OP phase image in figure 8(c) stands for a phase value of $+170^{\circ}$, while the white tone represents a phase value of -10° . Thus, the two domains are 180° apart in phase with the dominant one pointing down, as expected for a SrRuO₃ underlayer (which behaves as an element-like metal), and verified by performing poling experiments (see the next subsection). The dark and white domains in the IP phase image (figure 8d) stand for +160 and -20° , respectively. Following the same line of reasoning for the IP phase images as before, one finds that dark and white domains are characterized by opposite polarization directions with respect to the cantilever's axis. Knowing that one IP polarization component is parallel or antiparallel with the cantilever, i.e. along one of the (110) axes, one would expect that all IP polarization components point along the other orthogonal (110) directions for symmetry reasons [29]. This finding was confirmed by scanning along different crystallographic directions [8, 9]. Other important characteristic of the IP-phase image (figure 8d) is the occurrence of noisy image contrast. Within these domains, the phase signal fluctuates between -180 and $+180^{\circ}$ due to the lack of PR signal. This is in agreement with the observation of zero-amplitude domains in figure 8(b).

The in-phase images (figure 8e and f) contain all the information obtained from the corresponding amplitude and phase images and are therefore sufficient for the study of ferroelectric domain structure and domain dynamics, as we show in the following section. Based on the observation of allowed domain configurations, we establish the rule here that light and dark IP tones stand for right and left polarization components, respectively, with respect to the cantilever's long axis.

4.2. Equilibrium domain pattern

First, we analyse a 600 nm thick BiFeO₃ film grown by sputtering on a zeromiscut SrTiO₃ (001) substrate with a conductive SrRuO₃ underlayer. A mosaic-like ferroelectric domain structure was observed in both OP and IP–PFM images (figures 9 and 10). By locally poling the film at negative and positive biases above the threshold value we found that the dark and light regions in the OP–PFM images are domains with up and down OP polarization components, respectively. An additional weak contrast can be distinguished in the OP–PFM images, which matches the IP–PFM domain pattern. This weak contrast accounts for about 15% of the signal measured between the up and down polarization states. This can be understood as a consequence of a mechanical effect, which arises from the different relative orientations of the polarization vector with respect to both the cantilever's long axis and clamping point.



Figure 9. The mosaic ferroelectric domain structure of a 600 nm BiFeO₃ film grown on SrRuO₃/SrTiO₃ (001). (a), (d), (g) are OP–PFM and (b), (e), (h) are IP–PFM images taken at 3 $V_{\rm pp}$ with the cantilever pointing along the directions marked on the figure (c), (f), (i) IP–PR signal measured along the lines in the corresponding PFM images. Spikes in the plots are due to domain walls. The bars are 1 µm.



Figure 10. The mosaic ferroelectric domain structure of a 600 nm BiFeO₃ film grown on SrRuO₃/SrTiO₃ (001). (a), (d), (g) are OP–PFM and (b), (e), (h) are IP–PFM images taken at 3 $V_{\rm pp}$ with the cantilever pointing along the directions marked on the figure (c), (f), (i) IP–PR signal measured along the lines in the corresponding PFM images. The bars are 1 µm.

The scans in figure 10 were acquired with the cantilever pointing along the same axes as in figure 9, but in opposite directions. The reason for doing this is to independently confirm the $\langle 111 \rangle$ polarization vector directions. Due to the complicated domain pattern observed in the PFM scans, one cannot *a priori* assume that the interpretations based on scans along just one direction are accurate and sufficient. To do so, the sample has been rotated with increments of 45°. The images have not been recorded in exactly the same area, and we will show that this is not necessary because a set of rules concerning the orientation of polarization can been derived in this particular case.

The IP projection of the $\langle 111 \rangle$ polarization vectors on a (001) surface lie along the pseudocubic $\langle 110 \rangle$ axes. Thus, PFM scans taken with the cantilever pointing in opposite directions along one of the $\langle 110 \rangle$ axes provide the same contrast levels for the IP-polarization components as scans taken with the cantilever along the other $\langle 110 \rangle$ axis. Indeed, this was confirmed in these scans, and therefore only one set of data is shown in figures 9(g), (h) and 10(g), h. This IP information, corroborated with the two possible OP orientations enable a complete 3D description of polarization orientation as shown earlier [30, 49, 50].

OP contrast	IP contrast		Dessible
	[010]	[010]	orientations
Dark (up) Light (down)	Dark (left) Light (right)	Light (right) Dark (left)	[-111], [-1-11] [1-1-1], [11-1]

Table 2. The possible polarization orientations deduced from the OP- and IP-PFM images in figures 9(d), (e) and 10(d), (e).

The IP-PFM images taken with the cantilever pointing along the (100) axes (figures 9b, e and 10b, e) exhibit two contrast levels, while scans performed with the cantilever pointing along (110) show three levels (figures 9h and 10h). Line profiles across the images in figures 9(b) and 10(b) reveal PR signal magnitudes of \sim 2.9 and \sim 1.2 V in both images. For scans taken with the cantilever pointing along the other (100) axis (figures 9e and 10e), the two levels correspond to ~ 2.7 and $\sim 1.3 - 1.5$ V (figures 9f and 10f). Since only two levels are observed in these IP-PFM images and the corresponding PR signals are the same for scans performed with the cantilever pointing oppositely along the same axis, the IP-polarization components symmetrically straddle each of the (100) axes. Thus, we make the inference that these components can only lie along (110), in agreement with the Kubel and Schmid's model [29]. This is confirmed by the IP-PFM scans taken with the cantilever pointing along the (110) axes (figures 9h and 10h). In these images, the PR signal corresponding to the light brown colour ($\sim 1.7 \text{ V}$ in figure 9i and $\sim 2.0 \text{ V}$ in figure 10i), changes only slightly as the sample is rotated by 180°. Therefore, the IP polarization components of these domains lie along the cantilever's axis. Rotating the sample by 180° (figure 10g, h) inverts the IP-PR almost symmetrically about the neutral level (light brown domains). The neutral level is also observed in the IP-PFM images taken with the cantilever along the other two orthogonal (110) axes (not shown), confirming the $\langle 111 \rangle$ orientation of polarization.

In the images taken with the cantilever pointing along [010] (figure 9d, e) and [010] (figure 10d, e), most of the domains with 'up' polarization are predominantly one colour in the IP–PFM images, while domains with down polarization exhibit the opposite IP contrast. The possible orientations of polarization resulting from these findings are summarized in table 2. Thus, the domain structure is mainly characterized by four polarization vectors oriented oppositely along two body diagonals, which form an angle of 71° with each other. A minute amount of the other four variants (circled in figures 9d, e and 10d, e) is also seen.

The main polarization directions in the mosaic domain structure are schematically shown in figure 11(a) and are identified in the OP-PFM scan in figure 11(b) taken with the cantilever pointing along [110]. Shown in figure 11(c) is the corresponding IP-PFM image. The domains were labelled according to the different polarization directions in figure 1, namely P_3^+ and P_4^+ for up polarization domains, and P_3^- , P_4^- , for down polarization domains, as deduced from the levels in figure 11(c). Note that there is a small degree of uncertainty for IP-polarization components along the scanning direction due to the occasional occurrence of the other two variants. These variants are identified among the domains with IP polarization components perpendicular to the cantilever's long axis, and are marked with * in figure 11(b). Both ferroelectric $(P_3^+ - P_3^-, P_4^+ - P_4^-)$ and ferroelastic



Figure 11. Reconstructed polarization distribution in the mosaic domain pattern. (a) A 3D sketch of the main polarization directions, (b) OP and (c) corresponding IP–PFM images taken at $3 V_{pp}$ along [110]. The arrows in (b) represent the directions of IP polarization components, as deduced from (c). Some of the domains in (c) are marked as in figure 6. The bars in (b) and (c) are 1 μ m.

 $(P_3^+ - P_4^-, P_3^+ - P_4^+, P_4^+ - P_3^-, P_3^- - P_4^-)$ domain walls can be distinguished. Consideration of IP components only in figure 11(b) can be misleading, since it appears that head-to-head domains exist. In fact, by taking into account the OP components, one finds that this is an allowed configuration which leads to formation of ferroelectric domain walls (see figure 11).

If the miscut angle of the $SrTiO_3(001)$ substrate is increased from zero to e.g. 0.8° , a dramatic change in the domain structure is observed [9]. This is somewhat in contrast to the case of tetragonal $PbZr_{0,2}Ti_{0,8}O_3$, where changes are more subtle [42]. Shown in figure 12 are OP and IP-PFM images acquired by scanning with the cantilever along [100] (figure 12a and b), [010] (figure 12d and e) and [110] (figure 12g and h). From the mostly white tone seen in the OP-PFM, we deduce that the film is predominantly polarized in the down direction (P_i). A small fraction of up domains (black, P_i^+) are observed as well. A stripe pattern is visible in all scans, but the corresponding PR signal in the OP-PFM images accounts for only $\sim 15\%$ of the signal measured between the up and down polarization states. We attribute this to an electromechanical effect induced by the non-orthogonal cantilever-polarization vector orientation as discussed above. Since information from scans with the cantilever along opposite directions is needed to reconstruct the polarization direction in the domains [8, 49–51], such images are shown in figure 13. They were acquired along [100] (figure 13a and b), [010] (figure 13d and e) and $\overline{[110]}$ (figure 13g and h). The images were not taken in precisely the same area. Because of the simple domain pattern which characterizes the films grown on miscut SrTiO₃, this does not preclude the precise determination of polarization direction within domains. For symmetry reasons, the scans taken with the cantilever along [110] and [110] provide no additional information, and are therefore not shown.

Two important observations can be made regarding the IP–PFM images taken with the cantilever along the $\langle 100 \rangle$ axes (figures 12b, e and 13b, e). First, the stripe domain is barely visible for scans with the cantilever along [100] (figure 12b) and [$\overline{100}$] (figure 13b), and the corresponding line profiles shown in figures 12(c) and 13(c)



Figure 12. The stripe ferroelectric domain structure of a 600 nm BiFeO₃ film grown on SrRuO₃/0.8° miscut-SrTiO₃ (001). (a), (d), (g) are OP–PFM and (b), (e), (h) are IP–PFM images taken at 3 V_{pp} with the cantilever along the crystallographic directions marked on the figures (c), (f), (i) line profiles taken at 3 V_{pp} along the directions marked in the in-plane PFM images shown in (b), (e), and (h), respectively. Shown with a black arrow in (a), (d), (g) is the miscut direction. The bars are 2 µm.

confirm that the PR difference between domains is very low. This fact tells us that the IP components of polarization have the same magnitude and direction with respect to the cantilever's long axis in each image (within the precision of cantilever alignment along the crystallographic axes). Second, the images in figures 12(b) and 13(b) show different overall tones, which translates into different PR signals, as shown in figures 12(c) and 13(c). These two PR signals have approximately the same values as the maximum and minimum PR signals measured for scans taken with the cantilever along [010] (figure 12e) and [010] (figure 13e). Considering the contrast formation mechanism for OP- and IP-PFM as discussed above (figures 6 and 7) and the fact that polarization can only lie along $\langle 111 \rangle$ [29], two polarization vectors with IP components along $[\overline{110}]$ (P_{1}^{-}) and $[1\overline{10}]$ (P_{4}^{-}) are enough to account for the observed IP-PFM contrast. A minor amount of other variants can be distinguished as well, which are reminiscent of the more complicated domain pattern seen in films grown on substrates with a smaller miscut angle [8].

The existence of mainly two distinct domains can be proven by analysing the IP–PFM images taken along [110] (figure 12h) and [110] (figure 13h). The neutral tone given by IP polarization components parallel/antiparallel to the scanning direction is seen (light brown), which corresponds to a PR magnitude of ~1.5 V (figure 12i). White (figure 12h) and dark brown domains (figure 13h) are seen as the scanning direction is reversed. These domains correspond, respectively, to PR values



Figure 13. The stripe ferroelectric domain structure of a 600 nm BiFeO₃ film grown on SrRuO₃/0.8° miscut-SrTiO₃ (001). (a), (d), (g) are OP–PFM and (b), (e), (h) are IP–PFM images taken at 3 V_{pp} with the cantilever along opposite directions with respect to the scans shown in figure 12 (c), (f), (i) line profiles taken at 3 V_{pp} along the directions marked in the in-plane PFM images shown in (b), (e), and (h), respectively. The black arrow in (a), (d), (g) points along the miscut direction. The bars are 2 µm.

of ~3.0 (figure 12i) and ~0.0 V (figure 13i), that is symmetric around ~1.5 V. Using the same arguments as in the previous paragraph, we find that the domains which change colour in figures 12(h) and 13(h) as the scanning direction is reversed are characterized by a polarization vector along $[1\overline{11}]$ (P_4^- in figure 6). From figures 12(b) and 13(b) as well as from the PFM data acquired along $[\overline{110}]$ and $[\underline{110}]$ (not shown) we conclude that polarization in the light brown domain lies along $[\overline{111}]$ (P_1^- in figure 6). Finally, the IP–PR magnitude along $\langle 110 \rangle$ (~3.0 V) is about $\sqrt{2}$ times the magnitude along $\langle 100 \rangle$ (~2.2 V).

The two polarization vectors point along $[\overline{111}]$ (P_1^-) and $[1\overline{11}]$ (P_4^-). A minor amount of other variants was distinguished as well, which are reminiscent of the more complicated pattern seen in films grown on non-vicinal substrates [8]. Shown in figure 14(a) and (b) are OP- and IP-PFM images taken with the cantilever along $[\overline{110}]$, as sketched in figure 6. The IP polarization components in several domains are marked with arrows in figure 14(b) and we labelled them according to the notation in figure 6. A 3D sketch of the two polarization vectors in the stripe domain is shown in figure 14(c) and infers the presence of ferroelastic domain walls.

We have shown so far that altering the substrate miscut angle has a dramatic influence on the ferroelectric domain structure, which might in turn affect the polarization switching mechanisms. By changing substrates' lattice constant and symmetry, as well as films' thickness, one can modify the domain structure and



Figure 14. Reconstructed polarization distribution in the stripe domain pattern. (a) OPand (b) IP-PFM images taken with the cantilever along $[\bar{1}10]$ (c) A 3D sketch of the polarization directions in the stripe domain. The bars are 1 µm. Representative polarization vectors in (b) and (c) are marked as in figure 1.



Figure 15. Ferroelectric domain structure in a 600 nm thick epitaxial BiFeO₃ film grown on SrRuO₃/DyScO₃ (110). (a) is OP–PFM, (b) and (c) are corresponding IP–PFM images taken along two orthogonal $\langle 110 \rangle$ directions. The bars are 2 µm. The red arrows point along the cantilever's long axis. A 3 V_{pp} -bias was applied to the cantilever during scanning.

consequently the switching behaviour. To illustrate the role of substrate lattice constant, we analyse in the following the ferroelectric domain structure of a 600 nm thick epitaxial BiFeO₃ films grown by sputtering on DyScO₃ (110), with a SrRuO₃ underlayer. The corresponding lattice parameters are listed in table 1.

The PFM images shown in figrue 15 have been recorded in precisely the same area with the cantilever pointing along two orthogonal $\langle 110 \rangle$ directions (marked with red arrows in figure 15b and c). Following the colour code listed in table 2 one can identify mainly two ferroelectric domains with down polarization ($P_{i,i+1}^-$, for a unique *i*). The corresponding in-plane components of polarization are marked in figure 15(b) and (c) with black and white arrows. A small amount of up polarization domains can be seen as well in the OP–PFM scan (black in figure 15a). A similar analysis to the one performed in the case of a 600 nm thick BiFeO₃ grown on zero miscut SrTiO₃ (001) [8] reveals that these up polarization domains: $P_{i,i,+1}^+$, for the same *i* as in the $P_{i,i,+1}^-$ domains. Other important characteristic of this film is the onset of large, elongated domains as in the case of the 600 nm thick film grown on miscut SrTiO₃ (001).

A brief discussion is needed here to account for the observed stripe domain patterns in the epitaxial BiFeO₃ films grown on DyScO₃ (110) and miscut SrTiO₃ (001). This domain configuration contains only two out of eight possible polarization variants. The two polarization variants in the stripe pattern belong to two distinct structural variants with the domain walls running along the pseudocubic $\langle 100 \rangle$ direction. Such a domain structure was observed earlier in (001) oriented epitaxial $PbZr_{0.80}Ti_{0.20}O_3$ and $PbZr_{0.65}Ti_{0.35}O_3$ films and was seen as a consequence of mechanical and charge compatibility conditions [31]. It was recently found both theoretically, by performing phase-field simulations [52], and experimentally, by reducing the growth rate of the underlying SrRuO₃ layer, that a similar domain structure forms in thin epitaxial BiFeO₃ films as well [53]. At low deposition rates, the growth mode changes from step-bunching to step-flow [54] and a single domain epitaxial SrRuO₃ underlayer forms, which promotes the growth of stripe domain BiFeO₃ epitaxial films [53].

4.3. The switching of ferroelectric polarization

4.3.1. Imaging the switching of polarization by PFM. Following the same procedure as above, one can identify all electric field-induced polarization switching mechanisms in epitaxial BiFeO₃ films. In addition to in-phase imaging experiments, amplitude and phase scans have been performed as well to confirm the switching results. Such an approach is illustrated in figure 16. To locally switch the films, a dc bias was applied to the conducting AFM probe while scanning over the desired area. The poled area is conspicuous in all the OP images (figure 16a, c and d), confirming film switching. While the interpretation of OP images is straightforward, the colour changes in IP scans correspond to several switching processes. By considering the contrast formation mechanism as sketched in figure 7 for the geometrical alignment depicted in figure 6, the relation between PFM colour change and different switching processes are summarized in table 3. Following this colour code, we could identify all three possible switching mechanisms in figure 16(f), and from now on, we will only be focusing on the in-phase PFM scans.

4.3.2. Polarization switching in a two-domain epitaxial BiFeO₃ film. We particularize now these rules to the case of a (001) BiFeO₃ film which shows a simple domain pattern, namely a 600 nm thick film grown on a vicinal $SrTiO_3$ (001) substrate.



Figure 16. Typical (a), (b) amplitude, (c), (d) phase, and (e), (f) in-phase PFM images taken after negative bias poling with the cantilever along one of the BiFeO₃'s pseudocubic $\langle 110 \rangle$ axes. (a), (c), (e) are OP–PFM and (b), (d), (f) are IP–PFM. The images were taken in the same area as in figure 8. The bars are 500 nm.

Could also in a	PFM with cantilever along $\langle 110 \rangle$		
mechanism	In-plane	Out-of-plane	
71°	Unchanged light (*) Unchanged dark/white		
109°	Light ↔ white Light ↔ dark	White \leftrightarrow dark	
180°	Unchanged light(*) Dark ↔ white		

Table 3.The correspondence between PFM colour change and switching
mechanisms for the alignment sketched in figure 6.

(*) Indiscernible without sample rotation.



Figure 17. Polarization switching in a stripe domain film. PFM images taken with the cantilever along [$\overline{1}10$]. (a) Before and (b), (c) after poling at -12 V. (a) and (b) are IP–PFM and (c) is OP–PFM image, (d) same image as in (b) with the dark brown stripe pattern from (a) superimposed as a grey tone. The bars are 1 µm.

Shown in figure 17 are IP– and OP–PFM images taken before and after electrical poling with the cantilever along [$\overline{1}10$], as sketched in figure 6. We marked with arrows the IP polarization components in several domains in figure 17(a) and (b) and label them according to the notation in figure 6. By applying a -12 V dc bias on the probe during scanning, polarization flips upwards and the OP–PR contrast in the corresponding area reverses (figure 17c), while the IP domain pattern undergoes important modifications (figure 17b).

The modification of the domain pattern seen in the IP–PFM after OP poling (figure 17b) is due to polarization switching and to the displacement as well as creation of ferroelastic domain walls. The fact that we were able to displace and create ferroelastic domain walls in a continuous film suggests that they are somewhat more mobile than the ferroelastic domain walls in tetragonal ferroelectrics [55]. Referring now to the geometrical alignment sketched in figure 6 and the colour

change listed in table 3, the main polarization switching processes can be identified by following the IP contrast changes as follows: (i) unchanged light tone: either $P_4^- \rightarrow P_2^+$ (71° switching), or $P_4^- \rightarrow P_4^+$ (180° switching); (ii) unchanged dark tone: $P_1^- \rightarrow P_3^+$ (71° switching); (iii) dark to light: either $P_1^- \rightarrow P_4^+$, or $P_1^- \rightarrow P_2^+$ (109° switching); (iv) light to dark: $P_4^- \rightarrow P_3^+$ (109° switching); (v) light to white: $P_4^- \rightarrow P_1^+$ (109° switching); and (vi) dark to white: $P_1^- \rightarrow P_1^+$ (180° switching).

To facilitate the identification of all these switching mechanisms we show in figure 17(d) the IP–PFM image acquired after poling, on which we superimposed the dark brown IP domains of the as-grown film from figure 17(a) as a grey pattern. By only following the grey tone change to dark brown in figure 17(d), light brown, and white, one can resolve all three possible polarization switching processes: 71, 109, and 180°. Several such mechanisms are marked in figure 17(d). The switching process corresponding to case (i) cannot be unequivocally determined without sample rotation, and is therefore not considered here. It is interesting to note that ferroelastic switching (71 and 109°) is generally not observed in tetragonal ferroelectrics. As a general result of this poling experiment one can mention the complete change of the overall stripe pattern due to 109° ferroelastic switching.

Another interesting result is depicted in figure 18. After electrically poling the film at -14 V, the overall stripe pattern has been preserved (compare figure 18a and b). The complete down to up polarization switching is confirmed by the OP-PFM image shown in figure 18(c). Several domains in figure 18(a) and (b) have been indexed according to the geometrical alignment shown in figure 6. To identify the switching mechanisms, we show in figure 18(d) the switched domains from figure 18(b) with the as-grown pattern from figure 18(a) superimposed as grey stripes. The dark brown domains (P_1^-) in figure 18(a) generally turn white (P_1^+) after poling (figure 18b), which corresponds to 180° switching. The picture in figure 18(d) shows that the switched white domains do not precisely match the initially dark brown domains (P_1^-) in figure 18(a) (grey in figure 18d). This difference accounts for the occurrence of 109° switching.



Figure 18. Polarization switching in a stripe domain film. PFM images taken with the cantilever along $[\bar{1}10]$ (a) before and (b), (c) after poling at -14 V. (a) and (b) are IP-PFM and (c) is OP-PFM image, (d) same image as in (b) with the dark brown stripe pattern from (a) superimposed as a grey tone. The bars are 1 µm.

To understand the evolution of domain switching, we carried out field-dependent experiments. Shown in figure 19 are IP–PFM images taken before poling (figure 19a, d and g) and after poling at -8 V (figure 19b), -10 V (figure 19e), and -16 V (figure 19h) along with the corresponding OP–PFM scans (figure 19c, f and i). These images were acquired only few microns away from each other, with the cantilever along [110]. The ragged appearance of the IP pattern in figure 19(b) is due to incomplete switching as one can deduce from the OP scan shown in figure 19(c). The dark domains in figure 19(b) (except the one circled) did not change their OP tone either. Following the contrast change as above, we found that 180° polarization reversal is the dominant mechanism under these conditions. The circled domain in figure 19(b) is the only one which occurred as a results of 71 and 109° polarization switching.

At an applied bias of -10 V (figure 19e and f), the switching is still incomplete (white domains within the black poled area figure 19f). Beside 180° polarization reversal, 71° (unchanged dark tone in figure 19e), and 109° polarization rotations (dark to light and vice versa in figure 19e) become conspicuous. Therefore, our experimental results suggest that at low biases 180° polarization reversal is more favourable than 71 and 109° polarization rotations in epitaxial films under an electric field applied along (100).

As the applied bias is increased to -16 V (figure 19h and i), 71 and 109° polarization rotations are the dominant switching mechanisms. At high applied biases, sufficient energy may be supplied to the film to allow a rhombohedral to monoclinic phase transition, which is known to accompany polarization rotations in rhombohedral ferroelectrics [56]. Finally, as seen in figure 19(e) and (h), and in figures 17(b) and 18(b), the stripe domain pattern undergoes changes also outside the poled area, due to changes in the strain conditions as the result of ferroelastic domain displacement/creation.



Figure 19. Bias dependence of polarization switching. (a), (d), (g) IP–PFM images taken with the cantilever along [$\overline{110}$] before poling, and after poling at (b) -8 V, (e) -10 V, and (h) -16 V. The corresponding OP–PFM images taken after poling are shown in (c), (f) and (i). The bars are 1 µm.

5. Future directions

5.1. Decreasing the coercive field

The lead zirconate titanate (PbZr_xTi_{1-x}O₃) family of ferroelectric materials has been extensively used in applications such as micro-electro-mechanical systems and data storage. However, the critical drawback of PbZr_xTi_{1-x}O₃ is its toxicity due to the lead content. Since the international community has been aggressively moving towards banning the use of lead in electronic components, the star of Pb-based ferroelectric materials seems to be fading quickly. Thus, a substitute is stringently needed, and attention has been focused on BiFeO₃, due to its good ferroelectric properties. Significant progress has been recently demonstrated on the integration of BiFeO₃ on Si (001) substrates by using a SrTiO₃ template layer with an SrRuO₃ bottom electrode [6, 10]. However, the epitaxial BiFeO₃ films grown on Si (001) show coercive fields of 200 kV cm⁻¹ and a large leakage level, which block their pathway to device applications. Lowering the coercive field to values below 100 kV cm⁻¹ as well as reducing leakage have thus become critical issues.

To achieve these aims, one could for instance follow the La-substitution procedure at the A^{3+} -site as in the case of tetragonal PbZr_xTi_{1-x}O₃ [57, 58]. Rare-earth substitutions at the Bi³⁺ site have been attempted in the past [59]. For instance, it was found that La-substitution, both the ferroelectric Curie temperature and lattice constant decrease with increasing La concentration [60, 61]. Most recently, it has been reported that La-substitution at the Bi site improves the electrical properties of BiFeO₃ to some extent [62–64], but no insights on the actual role of dopant has been given up to date. Therefore, further efforts have to be directed on understanding the mechanisms responsible for the large coercive fields and leakage currents.

5.2. Ferroelectric-antiferromagnetic coupling

BiFeO₃ has the remarkable property of simultaneously being a very good ferroelectric and antiferromagnetic at room temperature. Naturally, the question as whether there is any coupling between the corresponding order parameters arises. This seems possible because the antiferromagnetic easy plane is determined by the relative orientation between the Fe cation and oxygen octahedra. Polarization rotation results in a modification of the oxygen configuration around the shifting Fe cation. This might affect the superexchange interaction between the Fe cations, which in turn alters the local magnetic order. Beyond any doubt, the technological potential of a room temperature electrically tunable antiferromagnet are huge. Despite this, only a few experimental and theoretical works aimed at elucidating this aspect [5, 13, 19, 23], mainly because of the difficulty in disseminating between the ferroelectric and magnetic contributions.

Just recently, using PFM and photoemission electron microscopy (PEEM) with linearly polarized X-ray, a strong correlation between the ferroelectric and antiferromagnetic domain structures of an epitaxial BiFeO₃ film was observed by Zhao *et al.* [23]. By analyzing the local changes in the ferroelectric and antiferromagnetic domain structures following the application of an electrical bias, it was shown that ferroelastic switching leads to a reorientation of the antiferromagnetic easy plane [23].

6. Summary

The domain structure and domain dynamics in (001) oriented epitaxial BiFeO₃ films under an applied electric field have been reviewed. Single crystalline films with smooth surfaces and good ferroelectric properties have been grown by various methods such as PLD, MOCVD, and high-rate off-axis sputtering. In all these films, saturation polarization values of ~60 μ C cm⁻² and converse perpendicular piezoresponse coefficients of ~50 pm V⁻¹ have been obtained. The equilibrium ferroelectric domain structure in these films strongly depends on the substrate conditions, and has been investigated by PFM. A 600 nm thick epitaxial BiFeO₃ film grown on SrTiO₃ (001) with a thin epitaxial SrRuO₃ underlayer shows a mosaic-type domain pattern, with both up and down polarization domains. By taking OP– and IP–PFM scans along the principal crystallographic directions it was found that two distinct structural variants with both up and down polarizations (i.e. four polarization variants), account for the main features of the equilibrium domain structure. The two up (down) polarization vectors lie along two (111) which form and angle of 71° with each other.

Significantly different domain patterns have been observed on epitaxial BiFeO₃ films of the same thickness (600 nm) grown on DyScO₃ (110) and miscut SrTiO₃ (001) with a SrRuO₃ underlayer. IP– and OP–PFM scans performed along different crystallographic directions on as-grown films reveal the existence of two structural variants with only down polarizations (i.e. two polarization variants). These two polarization vectors lie along two (111) axes which form an angle of 71° with each other. Therefore, by growing on miscut SrTiO₃ (001) or DyScO₃ (110), the up polarization domains are suppressed, and the down polarization domains form stripes running along (100).

Upon electrically poling the films along [001] dramatic changes in the ferroelectric domain patterns have been observed. These changes are conspicuous in the IP–PFM images and are a result of ferroelastic domain wall creation and displacement. All possible switching mechanisms, namely 71 and 109° polarization rotation, as well as 180° polarization reversal are observed. Interestingly, the later is the dominant mechanism at low fields, but is generally accompanied by ferroelastic switching as well.

The importance of understanding the polarization switching in thin epitaxial $BiFeO_3$ films is twofold. First, this enables the possibility of tuning the ferroelectric properties by domain engineering. Second, the direct observation of polarization rotation opens the exciting opportunity to investigate the coupling between the ferroelectric and antiferromagnetic order parameters at room temperature. Significant effort is currently aimed at addressing these two issues and the most recent results are meeting the expectations.

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