Local properties of the surface layer(s) of BiFeO₃ single crystals

Neus Domingo,¹ Jackeline Narvaez,¹ Marin Alexe,² and Gustau Catalan^{1,3}

¹*Centre d'Investigació en Nanociència i Nanotecnologia CIN2 (CSIC-ICN), Campus UAB, 08193 Bellaterra, Spain*

²*Max Planck Institute of Microstructure Physics, 06120 Halle, Germany*

³*ICREA, Institució Catalana de Recerca i Estudis Avançats, 08010 Barcelona, Spain*

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The surface of BiFeO₃ single crystals has been characterized at the local level using several AFM-based techniques. We have observed the presence of two different epilayers showing electrical and mechanical properties different from those of the bulk: a ferroelectrically “dead” outer skin of 5 nm sitting upon a subsurface layer that displays an extremely fine pattern of hierarchical self-ordered nanodomains. Based on the size of the nanodomains and applying a Kittel-like analysis, we argue that the nanotwinned region should be confined in a layer less than a micron deep. The superficial phase transition at $T^* = 275^\circ\text{C}$ is restricted to the outer skin layer (the “dead” layer), while the nanotwinned layer is insensitive to this transition. In view of the photovoltaic properties and spin-dependent transport of domain walls in BiFeO₃, the existence of nanodomains (and thus a high density of domain walls) in bulk single crystals is likely to be relevant for understanding their functional properties. © 2013 AIP Publishing LLC
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I. INTRODUCTION

Recent studies have reported the existence of a surface (“skin”) layer in BiFeO₃ that is fundamentally different from the bulk of the material.^{1–3} A combination of techniques have been used to determine that this surface layer has a different symmetry (probably monoclinic), different electronic structure, and different phase diagram, including at least two phase transitions, at 275°C (also known as the T^* transition)¹ and -133°C ,⁴ not present in the sub-surface bulk compound. There is also evidence that the so-called Polomska transition at 185°C may also be skin-related.⁵ All the studies so far have, however, relied on spatially averaged techniques (X-ray diffraction, impedance analysis, infrared spectroscopy, and so on) to characterize the overall behaviour of the layer; in order to gain knowledge of the characteristics of the surface layer at the microscopic level, it is desirable to complement these studies with a local probe investigation. Here we report the results of such investigation.

Atomic force microscopy has been used in this work to characterize the surface layer of BiFeO₃ single crystals. These studies have allowed us to determine the thickness of the surface layer (~ 5 nm) as well as its mechanical and electrical properties. Surprisingly, our measurements have also evidenced an extremely fine array of self-organized nanodomains, with periodicities in the range of only a few tens of nanometers. As we argue below, these nanodomains are present neither in the outer skin of the crystal nor in its bulk, but in a micrometric sub-surface layer.

II. EXPERIMENTAL DETAILS

The samples studied are single crystals of BiFeO₃, grown using the method proposed by Kubel and Schmid,⁶

polished mechano-chemically with the surface parallel to the (001) plane. The crystals are the same for which the presence of a skin layer with two distinct phase transitions (at $T^* = 275^\circ\text{C}$ and -133°C) have been reported.¹

The surface was characterized by scanning probe microscopy (SPM), using an atomic force microscope (AFM), model MFP-3D from Asylum Research. Piezoresponse force microscopy (PFM) is used to characterize the electro-mechanical response of piezoelectric materials. Typically, a conductive cantilever is scanned over the sample surface in contact mode, while an AC bias is applied to the tip and the induced contraction and expansion of the sample are detected by the deflexion of the tip.^{7–9} PFM measurements can be done either at a fixed frequency or in resonance mode, that is, working at the contact resonance frequency (Dual Amplitude Resonance Tracking (DART)).¹⁰ DART mode allows tracking the contact resonance frequency (which strongly depends on the contact mechanics as the tip scans over the surface) by working simultaneously at two frequencies on each side of the resonance peak and monitoring its difference. When working in DART mode, the PFM signal is amplified due to the resonance conditions and thus becomes very convenient to study samples for which the real expansion and contraction is below the noise level of AFM deflexion measurement. Temperature control was afforded between room temperature and 300°C using Asylum's Polyheater stage. Finally, as well as surface topography and ferroelectric/piezoelectric response, we characterized the surface potential using Kelvin Probe Force Microscopy (KPFM).^{11,12} KPFM measures the working function potential of the surface by applying an ac voltage to the tip during the lift mode and cancelling the induced amplitude of oscillation by compensating the surface potential with a DC bias applied to the tip.

III. RESULTS

A. Nano-domains

The BiFeO_3 single crystal presents bulk ferroelectric and ferroelastic domains distributed in a quadrant arrangement, optically observable using standard birefringence, and consistent with the polarization axis pointing alternately along the diagonals of the unit cell. Note that birefringence is only sensitive to the in-plane projection of the polar axis but cannot actually convey information on the direction of the polarization in each domain.

On the contrary, local measurements of superficial piezoresponse by PFM show an unexpected self-organized array of very narrow stripe domains superimposed onto the bulk domain structure, as can be observed in Figure 1. The

FIG. 1. (a) Polarized optical microscopy image of the center of a rosette-like BiFeO_3 single crystal with the (001) plane parallel to the surface. Bulk domains are distinguishable using standard birefringence. (b) PFM image (amplitude) of the same $40\ \mu\text{m} \times 40\ \mu\text{m}$ area. A distribution of stripe domains is observable on the whole area, over imposed to the bulk domains. Domain walls are observable as a change in the preferred stripe orientations. The inset shows the FFT image of the PFM amplitude. The stripe domains are running along only 4 preferred directions in the whole crystal. The PFM image was taken with an Olympus AC240TM conductive tip (2 N/m, Pt coating) at a fixed frequency $f = 280\ \text{kHz}$ and $V_{\text{ac}} = 2.5\ \text{V}$.

stripe domains show a very regular periodicity of about 80 nm with a homogenous distribution within all the quadrants. They are running along four preferred directions of the plane different from the crystallographic axis, as shown by the FFT transform of the amplitude PFM image. On each quadrant, the stripes follow two single directions separated by angles of roughly 52° or 128° (acute angles change from 51° to 54° and obtuse angles go from 126° to 130°), while the relative rotation about preferred directions among different quadrants takes values around 37° (see Figure 2). Bulk domain walls are observable as a break in the symmetry of the stripe domain distribution (see red arrow of Figure 2).

To attempt to determine the polar orientation within each domain and thus the type of domain wall, PFM investigations and vectorial analysis were performed at high resolution (Figure 3). Vertical PFM (VPFM) is used to measure the out of plane component of the polarization, while lateral PFM (LPFM) response gives signal of the in-plane polarization component. From the VPFM images, it is possible to observe that contiguous stripes show a phase contrast of 180° (Figure 3(e)), indicating an opposition of the vertical polarization component among these domains. Yet, two types of domain walls are distinguishable as dark lines in the amplitude VPFM image (Figure 3(c)), one completely straight and the other one with an irregular zigzag shape. In order to determine the in-plane component of the polarization, amplitude and phase LPFM images were measured. These show further complexity: while the straight domain walls are still clearly seen, the zigzag shaped domain walls are hidden below a complex distribution of nanodomains that seem to be parallel to the bulk crystalline axis. Unfortunately, the apparent nanodomain width is of about 13 nm which is below the tip radius of our conductive AFM tip. This implies that conventional vector-PFM analysis might be influenced by cross-talk among different domains, preventing the resolution of the shape and type of the domain walls, i.e., 71° , 109° , or 180° . Further work with super-sharp conductive AFM tips is currently undergoing.

B. Surface and sub-surface layers

To determine whether the observed nanodomains are related to the reported skin transition of BiFeO_3 (BFO) at $548 \pm 5\ \text{K}$, we have studied the superficial PFM response as a function of temperature up to 300°C . Figure 4 shows that the domain structure survives completely intact up to 300°C , the maximum achievable temperature of our heater. In other words, the nanodomains are insensitive to the skin transition and therefore apparently unrelated to it.

In contrast to the ferroelectric domains, the surface morphology does experience a sudden change at the transition temperature of approximately 275°C . The contact force from the scanning AFM tip, typically around 250 nN, starts to induce delamination of the outer skin at precisely that temperature. In addition, after several heating and cooling cycles, several “cracks” appear on the surface layer.

FIG. 2. PFM image (amplitude) of an area close to a bulk domain wall. The red arrow shows the position of the bulk domain wall. The inset shows the FFT image of the PFM amplitude. The stripe domains of the same quadrant show a relative angle orientation of 128° , while the relative rotation with respect to the other quadrant in this case is 37.5° . The PFM image was taken with an Olympus AC240TM conductive tip (2 N/m, Pt coating) in DART mode, at a contact resonance frequency of $f_{rc} \sim 290$ kHz and $V_{ac} = 1$ V.

We interpret both observations as a consequence of different thermal expansion of the skin layer and the bulk material, as reported by Martí *et al.*¹ At T^* , the skin layer suddenly expands, while the bulk does not change; the transition associated with a sudden mismatch in thermal

expansion causes elastic stresses between the skin layer and the bulk, which are relieved by cracking and/or delamination of the surface layer. The topography of the skin layer is shown in Figure 5(a).¹

Comparison between the skin and the revealed sub-skin areas confirms the presence of the stripe domain pattern at the sub surface layer, at a level below the outer skin (see Figures 6(a)–6(f)). To determine the electric properties of the skin and the sub-skin surfaces, KPFM measurements were also performed around the cracks (Figures 6(g) and 6(h)). Strong contrast of up to hundreds of mV is observed in some cases, indicating a higher surface potential for the sub-surface layer compared to the skin, confirming the charge-depletion of the surface layer already stated by impedance spectroscopy and x-ray photoelectron spectroscopy.¹

IV. DISCUSSION

Domain size is generally dependent on boundary conditions and sample dimensions. Kittel's law gives the lower bound for ferroic domain size, assuming completely unscreened interfacial fields. In these ideal conditions, the width w of the stripe domains is related to their depth d by a square root law:^{13–15} $w = A\sqrt{d}$, where A is some appropriate constant. As mentioned, this assumes perfect unscreening; when the interfacial fields are screened, the domain size will be bigger than w .¹⁴ Likewise, as emphasized by Catalan *et al.*,¹⁶ d may not be the thickness of the sample but the depth to which the domains penetrate within the sample. This can be smaller than the sample

FIG. 3. DART PFM measurements: (a) topography and (b) deflection images of $1.5 \mu\text{m}^2$ area of BiFeO_3 surface. Calculated RMS roughness is 288.37 nm. Amplitude DART PFM image of (c) out-of-plane and (d) in-plane polarization. Phase PFM image of (e) out-of-plane and (f) in-plane polarization. The in-plane signal is measured in the y-axis direction. Measurements were done with a conductive μmach DPER14 tip (6 N/m, PtIr coating), at $V_{ac} = 2.5$ V and a contact resonance frequency of $f_{rc} \sim 665$ kHz for the out-of-plane signal and 1.27 MHz for the in-plane one.

FIG. 4. DART PFM measurements of a $1\,\mu\text{m} \times 1\,\mu\text{m}$ area measured at $T = 300\,^{\circ}\text{C}$ (a), (b) and at room temperature (c)–(e). (a) Amplitude PFM image of out-of-plane polarization and (b) phase PFM image with a contrast signal of 180° . Striped nanodomains still exist over the skin phase transition temperature observed at $275\,^{\circ}\text{C}$. (c) Topography image of a wider area of $1.8\,\mu\text{m} \times 1.8\,\mu\text{m}$ on the same region, and the corresponding amplitude PFM image (d) and phase PFM image (e) of the out-of-plane polarization, measured at room temperature for comparison. To perform this measurements, a Nanosensors EFM conductive tip (2 N/m, PtIr coating) in DART mode, at a contact resonance frequency of $f_{\text{rc}} \sim 335\,\text{kHz}$ and $V_{\text{ac}} = 3\,\text{V}$.

thickness, as occasionally observed.¹⁷ Therefore, although Kittel's law is usually interpreted as a lower bound on the equilibrium domain width w , it also sets an upper bound on the domain depth d .

In order to find this depth for our samples, we can use the “universal” form of Kittel's law normalized in terms of the domain wall thickness,^{16,18} $d = \frac{w^2}{\delta G}$ (Refs. 19 and 20), where d is the domain depth, w is the domain width of 40 nm as calculated from FFT, δ is the domain wall thickness, taken as 2 nm,¹⁶ and G is a constant with a value of $G \sim 2.5$,¹⁸ and we obtain a value for the domain penetration depth of $d \sim 320\,\text{nm}$. This value is more than one order of magnitude bigger than the thickness of the outer skin layer as measured by X-ray diffraction and AFM (about 5 nm) but still several orders of magnitude thinner than the single crystal sample, which is nearly 1 mm thick. We can therefore state the presence of not only one but two different skins as shown in a scheme in Figure 5(c): a very thin outer skin layer of about 5 nm and a subsurface layer of several hundreds of nanometers thick that displays a very complex nanodomain structure superimposed onto the bulk single crystal domain structure.

The properties of the two epilayers are rather different. The outer skin has a different structure from the interior and also different phase transitions.^{1,4} It also has a lower electronic density as inferred from impedance measurements¹ and from the KPFM measurements in the present work that show a lower surface potential for the outer skin. The PFM measurements indicate that the ferroelectric contrast between the domains is less marked when probed through this epilayer, which suggests that it is not itself ferroelectric, and the

FIG. 5. (a) Topography image of an area of $10 \times 10\,\mu\text{m}$ showing several cracks produced on the surface after reiteration of thermal cycles. (b) Section profiles of yellow line and red line of previous image, respectively. The average thickness of the cracks is measured to be around 5 nm. (c) Scheme of the structure of the bulk BiFeO_3 single crystal. There is a skin layer of about 5 nm (purple layer), and underneath we find a thicker subsurface layer of several hundreds of nanometers with complex nanodomain structure (striped region) overimposed to the bulk domain configuration of the single crystal.

tribological measurements also confirm visible elastic contrast between a homogeneous epilayer and a ferroelectrically/ferroelastically textured subsurface. All in all, then, the 5 nm epilayer appears to be a ferroelectrically and ferroelastically “dead” layer whose intrinsic properties are enhanced by some aging effects coming up after several thermal cycling, that help to decouple the skin from the crystal bulk.

FIG. 6. Topography of two different cracks (a), (b) in $3\ \mu\text{m} \times 3\ \mu\text{m}$ image area; (c) and (d) are the corresponding out-of-plane amplitude of PFM signal; (e) and (f) are the out-of-plane PFM signal phase. The range is 180° . (g) and (h) are the KPFM images of the two cracks, with a voltage range of 400 mV for (g) and 25 mV for (h). For sample (a) measurements were done with a conductive $\mu\text{masch DPER14}$ tip (6 N/m, PtIr coating), in DART mode, at a contact resonance frequency of $f_{\text{rc}} \sim 746\ \text{kHz}$ and $V_{\text{ac}} = 3.5\ \text{V}$, while for sample (b) measurements were done with an Olympus AC240TM conductive tip (2 N/m, Pt coating) in DART mode, at a contact resonance frequency of $f_{\text{rc}} \sim 336\ \text{kHz}$ and $V_{\text{ac}} = 2\ \text{V}$. In both cases, KPFM was done in lift mode by applying an $V_{\text{ac}} = 1\ \text{V}$ to the tip.

In contrast, the sub-surface layer displays a bright KPFM signal indicative of higher surface potential, presumably due to the polar discontinuity at the (001) surface. It also shows a distinct self-ordered pattern of hierarchical nanodomains that cover the entire crystal to a depth of a few hundreds of nanometers and that are visible as clear piezoelectric contrast in the PFM. According to X-rays, in the sub-surface layer, the crystal still has the conventional bulk BiFeO_3 symmetry, so this ferroelectric domain pattern must be compatible with $R3c$ symmetry. As mentioned earlier, proper vectorial analysis of the PFM phase contrast is prevented by the extremely narrow size of the domains. Further work is required to increase the lateral resolution of the vectorial-PFM measurements and determine the nanodomain orientation.

V. CONCLUSION

The surface of BiFeO_3 single crystals has been characterized at the local level using a range of scanning probe microscopy based techniques. Surface stress introduced by the sudden thermal expansion at $T^* \sim 280^\circ\text{C}$ causes the skin to “crack” revealing the sub-surface layer. This has allowed to directly measure the exact thickness of the skin layer (5 nm) and to confirm that it is ferroelectrically and ferroelastically dead.

Meanwhile, piezoresponse force microscopy also reveals the presence of an extremely fine pattern of self-ordered domains. Basic Kittel-type arguments suggest that these domains cannot be present throughout the bulk of the sample but, rather, should be confined to a layer of a few hundred nanometers depth. This nanodomain layer sits between the bulk of the crystal and its outer dead layer. The actual symmetry as well as the origin of these domains

remains to be determined. Of particular relevance here is the transmission electron microscopy study of Berger *et al.*,²¹ performed on the same type of samples. These authors see strikingly similar domain patterns to those reported here, even though the plane orientation of their TEM samples, (110), is different from those in the PFM study, (001). Although the presence of these domains in cross-sectional samples may suggest that the domains are present across the film, it is worth bearing in mind that TEM-transparent samples are fairly thin (less than 100 nm) and may therefore not be directly comparable to the bulk/core of BiFeO_3 . The preparation process of TEM samples is also intrinsically aggressive, and we do not know its effect on the domain configuration.

Although there is enough evidence by now to suggest that the 5 nm outer skin of BiFeO_3 is a universal or at least very widespread feature for all BiFeO_3 samples,^{1,4} we cannot confirm whether the sub-surface nanotwinned layer is also general or specific of the single crystals looked at in this study. Another interesting and almost intrinsically unresolvable question is whether when the sub-skin layer of the crystals is revealed by delamination a new skin forms on the revealed surface. Non-destructive tests capable of probing a few nanometers into the sample would be ideal to try to answer such questions. At any rate, our results confirm that the functional and structural properties of the surface of BiFeO_3 are different from its interior. They also reveal more complexity than initially thought: even in nominally simple single crystals, multiple layers that are coherent with the bulk of the crystal but have different properties and/or domain arrangements can appear.

In previous works, the potential impact of the outer skin layer on spintronic (exchange bias) experiments was mentioned. Here we want to bring up another equally important

issue: given that the domain walls of BiFeO₃ are known to have different properties from the domains themselves, the presence of such a fine pattern of spontaneous nanodomains on the surface of the films will probably have a substantial effect on its properties. In particular, we note that the domain walls of BiFeO₃ are thought to have a strong photovoltaic effect^{22,23} and possess unexpected spin-dependent transport properties.²⁴

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¹X. Martí, P. Ferrer, J. Herrero-Albillos, J. Narvaez, V. Holy, N. Barrett, M. Alexe, and G. Catalan, *Phys. Rev. Lett.* **106**, 236101 (2011).

²G. Xu, D. Viehland, J. F. Li, P. M. Gehring, and G. Shirane, *Phys. Rev. B* **68**, 212410 (2003).

³P. M. Gehring, W. Chen, Z. G. Ye, and G. Shirane, *J. Phys.: Condens. Matter* **16**, 7113 (2004).

⁴R. Jarrier, X. Martí, J. Herrero-Albillos, P. Ferrer, R. Haumont, P. Gemeiner, G. Geneste, P. Berthet, T. Schülli, P. Cevc, R. Blinc, S. S. Wong, T.-J. Park, M. Alexe, M. A. Carpenter, J. F. Scott, G. Catalan, and B. Dkhil, *Phys. Rev. B* **85**, 184104 (2012).

⁵A. Kumar, J. F. Scott, and R. S. Katiyar, *Phys. Rev. B* **85**, 224410 (2012).

⁶F. Kubel and H. Schmid, *J. Cryst. Growth* **129**, 515–524 (1993).

⁷S. V. Kalinin, E. Karapetian, and M. Kachanov, *Phys. Rev. B* **70**, 184101 (2004).

⁸A. Gruverman, P. M. Vilarinho, Y. Rosenwaks, and A. Kingon, *Scanning Probe Microscopy: Characterization, Nanofabrication and Device Application of Functional Materials* (Springer, Netherlands, 2005), Vol. 186, pp. 223–249.

⁹E. Soergel, *J. Phys. D: Appl. Phys.* **44**, 464003 (2011).

¹⁰B. J. Rodríguez, C. Callahan, S. V. Kalinin, and R. Proksch, *Nanotechnology* **18**, 475504 (2007).

¹¹M. Nonnenmacher, M. P. O'Boyle, and H. K. Wickramasinghe, *Appl. Phys. Lett.* **58**, 2921–2923 (1991).

¹²W. Melitz, J. Shen, A. C. Kummel, and S. Lee, *Surf. Sci. Rep.* **66**, 1–27 (2011).

¹³C. Kittel, *Phys. Rev.* **70**, 965–971 (1946).

¹⁴T. Mitsui and J. Furuichi, *Phys. Rev.* **90**, 193–202 (1953).

¹⁵A. L. Roitburd, *Phys. Status Solidi A* **37**, 329–339 (1976).

¹⁶G. Catalan, J. Seidel, R. Ramesh, and J. F. Scott, *Rev. Mod. Phys.* **84**, 119–156 (2012).

¹⁷V. Y. Shur, E. L. Rumyantsev, E. V. Nikolaeva, E. I. Shishkin, D. V. Fursov, R. G. Batchko, L. A. Eyres, M. M. Fejer, and R. L. Byer, *Appl. Phys. Lett.* **76**, 143–145 (2000).

¹⁸A. Tabyaoui, A. Ainane, M. Saber, and I. Lukyanchuk, *Phys. Scr.* **72**, 265 (2005).

¹⁹J. F. Scott, *J. Phys.: Condens. Matter* **18**, R361 (2006).

²⁰G. Catalan, J. F. Scott, A. Schilling, and J. M. Gregg, *J. Phys.: Condens. Matter* **19**, 022201 (2007).

²¹A. Berger, D. Hesse, A. Hähnel, M. Arredondo, and M. Alexe, *Phys. Rev. B* **85**, 064104 (2012).

²²S. Y. Yang, J. Seidel, S. J. Byrnes, P. Shafer, C. H. Yang, M. D. Rossell, P. Yu, Y. H. Chu, J. F. Scott, J. W. Ager, L. W. Martin, and R. Ramesh, *Nat. Nanotechnol.* **5**, 143–147 (2010).

²³M. Alexe and D. Hesse, *Nat. Commun.* **2**, 256 (2011).

²⁴Q. He, C. H. Yeh, J. C. Yang, G. Singh-Bhalla, C. W. Liang, P. W. Chiu, G. Catalan, L. W. Martin, Y. H. Chu, J. F. Scott, and R. Ramesh, *Phys. Rev. Lett.* **108**, 067203 (2012).