Flux Closure Vortexlike Domain Structures in Ferroelectric Thin Films

Y. Ivry,[1,*] D. P. Chu,[2] J. F. Scott,[3] and C. Durkan[1,†]

[1]*Nanoscience Centre, University of Cambridge, 11 JJ Thomson Avenue, Cambridge, CB3-0FF, United Kingdeom*
[2]*Electrical Engineering Division, University of Cambridge, 9 JJ Thomson Avenue, Cambridge, CB3-0FA, United Kingdom*
[3]*Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge, United Kingdom*

(Received 2 February 2010; published 19 May 2010)

Enhanced piezoresponse force microscopy was used to study flux closure vortexlike structures of 90° ferroelastic domains at the nanoscale in thin ferroelectric lead zirconium titanate (PZT) films. Using an external electric field, a vortexlike structure was induced far away from a grain boundary, indicating that physical edges are not necessary for nucleation contrary to previous suggestions. We demonstrate two different configurations of vortexlike structures, one of which has not been observed before. The stability of these structures is found to be size dependent, supporting previous predictions.

DOI: 10.1103/PhysRevLett.104.207602 PACS numbers: 77.80.Dj, 77.80.bn

The study of domains and domain walls in nanoferroelectrics began primarily with the work of Gruverman *et al.* [1] in the mid 1990s and Ganpule *et al.* [2] in 2002, who showed that the wall structure was metastable. More recently, the study of vortexlike domain configurations in ferroelectrics has been carried out theoretically [3–5] and experimentally [6,7]. Vortex domains are already well known in magnetic systems, but there are significant differences between magnetic and ferroelectric vortices. Magnetic vortices occur when the magnetization of an in-plane magnetic material circulates around a point with such rapid spatial variation, generally through geometric constraints, while attempting to achieve flux closure, that it is forced out of plane. In ferroelectrics, a vortex is a structure that achieves flux closure without the necessity to switch from in-plane to out-of-plane polarization. Also, magnetic nanodots exhibit vortex-antivortex pairs [8], whereas these have rarely been seen in ferroelectric nanodots [9]. Although spins satisfy the Bloch equations, which are first order, ferroelectric domain walls satisfy Landau-Khalatnikov equations and Landau-Lifshitz-Gilbert equations, which have an empirical damping constant. Additionally, there is a significant difference in the time scales associated with free ferroelectric domain wall motion (which may be ballistic over very short distances) and the case of oxygen pinning, leading to relaxation time constants in the order 0.01–0.1 ps and ~50 ns, respectively [10]. This is indicative of the wide range of domain wall and relaxation behavior in ferroelectrics, particularly as compared to ferromagnetics.

Many ferroelectrics are also ferroelastics, with hysteresis in their stress-strain relationships (exceptions are those materials that preserve crystal class at their Curie temperatures). In such systems, the electric polarization is strongly linked to the local mechanical strain and there is an intimate interplay between the ferroelectric and ferroelastic domain configurations [11]. It has been predicted that in these systems polarization vortices should be accompanied by a vortexlike structure of ferroelastic domains (non-180° domains) [4,5]. In fact, recently, a vortexlike behavior of 90° domains has been observed in patterned submicron cuboids (nanodots) of the ferroelectric material $BaTiO_3$, revealing a quadrant striped domain structure [9]. There are several reports on the evolution of ferroelectric [12,13] domains, as well as theoretical studies of ferroelastic domains and vortices [14]. However, the experimental methods that have been used in the above works could not observe both the 90° and 180° domain (i.e., ferroelastic and ferroelectric) distributions simultaneously, nor can they observe ferroelastic domain evolution. Generally it has been found [15–18] that piezoresponse force microscopy (PFM) is the ideal technique with which to address these issues, affording high spatial resolution. Indeed, Balke *et al.* [8] have recently demonstrated a degree of control over ferroelastic domains at the micron scale. However, nanoscale characterization and control has so far not been demonstrated. Specifically, there are three questions to be answered.

(1) Is geometric confinement to a small volume a prerequisite for the formation of vortexlike domain structures, or can they exist in large-area films? It is not yet known whether such a structure is formed due to the boundary conditions imposed by the geometry of the material or whether it is formed to stabilize large electromechanical deformations at the local scale in order to form a larger-scale field closure irrespective of the local geometry. Currently, since both polarization vortices and 90° quadrants have been independently observed only in nanodots, there is an obvious tendency to believe that the driving mechanism is dictated by the geometry of the pattern constituting nucleation points, rather than local variations in the electromechanical field [9].

(2) Do these vortexlike structures occur spontaneously in ferroelectric films? Can they also be driven by applied external fields? Do they always nucleate on grain boundaries or external surfaces?

(3) Does the external geometry and size dictate the formation of such structures in the way that they do in mag-

netic nanodots? If so, what boundary conditions are essential?

In this Letter we address all of these questions, showing that vortexlike domains in ferroelectric films occur in large-area films, not just nanodots, that they occur spontaneously and can also be produced by external fields, and that they are not limited by nucleation on grain boundaries.

Enhanced piezoresponse force microscopy (EPFM) [19] is a technique based on conventional PFM, but utilizing the cantilever dynamics to allow high-resolution ($\sim$1 nm) mapping of ferroelectric and ferroelastic domains simultaneously with the topography of thin films. We used EPFM to study vortexlike behavior in 60 nm thick polycrystalline films of predominantly (110) lead zirconium titanate [PZT (30/70)], which was deposited on an Ir electrode [15,19]. Using this technique, we have recently reported on ferroelastic domain structures in PZT [20].

Figures 1(a)–1(c) show the topography and the native ferroelectric and ferroelastic domain distribution in a 1.1 μm $\times$ 1.1 μm area of the film. A closer look at the highlighted area reveals that the ferroelastic domains in this region [stripes in Fig. 1(b)] arrange to form a closed structure, consisting of bundles of ferroelastic domains similar to those reported in Ref. [14]. Moreover, the phase image [Fig. 1(c)] shows that this structure forms a polarization vortex similar to that reported in Ref. [6]. Given that the material is (110) oriented, and that the ferroelastic domains are separated by 90° walls, the polarization within each domain makes an angle of 45° with the wall, and 90° with the polarization in adjacent domains. As shown in Fig. 1(d), this causes the global average of polarization $\langle P_\perp \rangle$ normal to the grain boundary to vanish, whereas $\langle P_\parallel \rangle$ parallel to the grain boundary is large. This arises from the minimization of depolarization fields around the perimeter of the grain. This willingness to minimize depolarization suggests that grain boundaries act as polar discontinuities, a finding that is consistent with the correlation between grain size and critical temperature found in previous studies on ferroelectric powders. The central area can therefore be regarded as a vortex disclination, or topological defect. Within this framework, $\langle P(r, \theta) \rangle$ in this grain can be described by a winding number of value ± 1 as discussed by Roytburd and others [21,22]. Such winding numbers have recently been used to describe polarization distributions around $BaTiO_3$ nanowires [23]. The general characteristics of depolarization fields in ferroelectric nanodomains have been reported elsewhere [24–27]. In nanoparticles or nanograins, Schilling *et al.* have shown [9] that the domain pattern in three-dimensional nanostructures depends upon the aspect ratio of the lateral sizes; zigzag in-plane polarized structures form on the larger faces or facets, whereas the out-of-plane polarizations are restricted to the face of smallest area, giving "barber-pole" stripes. This minimizes globally the depolarization energy.

The fact that the 90° vortexlike structure was observed in a small grain is consistent with the suggestion that this structure arises due to geometrical restrictions, by nucleating from the grain boundaries. Nonetheless, a careful look at the ferroelastic domains at the edges of the adjacent grains shows that some of them are of the same orientation as those of the vortexlike structure in the small grain. Therefore, one can deduce that it is not necessarily the geometry that originates the vortexlike structure, although it may be partly responsible for the orientation of the ferroelastic domains. Given that one of the two previously proposed mechanisms in Ref. [9] is correct, it is most likely that the vortexlike structure is formed to accommodate the local variations in stress and polarization fields at the macroscopic scale. This may explain why the structure is not confined to a single grain, as neighboring grains in polycrystalline materials may assume the same crystallographic orientation to reduce the macroscopic stress [21]. This can also explain the observation of a polarization vortex in polycrystalline ferroelectrics that has been reported by Gruverman *et al.* [28]. If indeed this is the case, one should be able to form vortexlike structures that are not restricted to a specific geometric pattern without deforming the physical structure of the material. Moreover, it implies that it may be possible to form and deform vortexlike structures also in geometries other than patterned features at the nanoscale. This may be done for instance by adjusting the electromechanical stresses locally, which in turn may be introduced through a variable local external electric field.

To further explore whether a vortexlike structure can be formed without the aid of physical boundary constraints, we imaged a larger area [Fig. 2(a), 3 μm $\times$ 3μm)] and

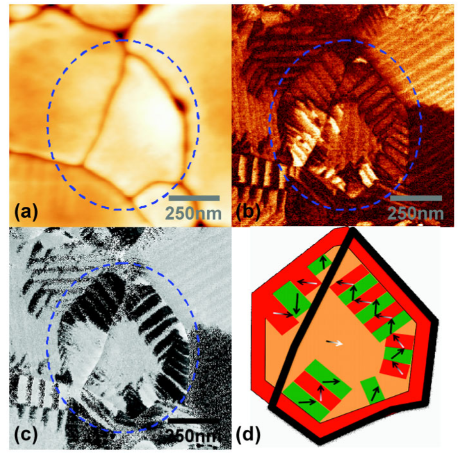

FIG. 1 (color online). EPFM imaging of a native vortexlike 90° domain structure within a macroscopic polarization vortex in polycrystalline PZT. (a) The topography of an area with a vortexlike structure of ferroelastic domains, (b) amplitude, and (c) the phase image of the same area demonstrates that the vortexlike structure forms a macroscopic polarization vortex. Panel (d) shows schematically what we have observed: a series of ferroelastic domains, i.e., *a* [medium gray (green)] and *c* [dark gray (red) and light gray (orange)] oriented regions. The polarization vectors [in-plane polarization indicated by black arrows within medium gray (green) shaded domains; out-of plane polarization indicated by shaded arrows] maintain a head-to tail configuration, and manage to attain flux closure.

allocated a small region within a large grain in an attempt to induce a vortexlike structure far away from the grain boundaries (highlighted) to eliminate the possibility of nucleation there. The native domain structure shows a random ferroelectric domain distribution with no detectable ordered ferroelastic domains. It should be noted that the surface was rather homogenous and that the rms roughness of the chosen area was 0.5 nm.

To induce large local variations in polarization and strain, we then scanned the area again while dividing it into smaller segments in which a voltage of either +10 V or −10 V dc [bright and dark regions superimposed on the topography image in Fig. 2(b)] was applied between the conducting AFM tip and the bottom electrode. The resultant imaged domain distribution showed that this process led to the formation of bundles of ferroelastic domains [Figs. 2(c) and 2(d)]. Finally, in an attempt to induce a polarization vortex, we scanned the same area again, while applying −10 V inside a central square and 10 V in the external frame [dark and bright areas superimposed on the topography image in Fig. 2(e)]. The uniformity in the latter written patterns is larger than in the patterns of the previous manipulation, allowing the previously obtained domains to constitute ‘‘building blocks’’ that may be capable of rearranging into a larger structure. Imaging the ensuing domain distribution reveals a vortexlike structure of 90° domain bundles [Figs. 2(f) and 2(g)] that comprises a macroscopic polarization vortex [sketched in Fig. 2(h)]. The fact that the vortexlike structure was formed far away from any grain boundaries indicates that they are not necessary for its formation. Note that the nanodomain pattern in Fig. 2(g) consists of a square array of side ca. 280 nm that has matched the domain wall orientation within an irregular grain boundary mosaic, despite the fact that the vortex was induced far away from any grain boundaries. Moreover, the topography shows no irregularities in the area of the vortex. However, at the center of the vortex, there is a bundle of ferroelastic domains oriented at approximately 45°, i.e., along the diagonal. Such domains in nanomagnets are well known—similar closure nanodomains extending across two to three Ti-rich islands in ilmenite have been reported [29].

Next, the stability of the manipulated vortexlike structure was explored. If the structure forms to compensate large local electromechanical deformations when forming a larger-scale polarization vortex, one would expect that the vortexlike 90° domain structure will deform when the small polarization vortex is replaced by a polarization distribution with larger domains. Thus, aiming to excite the vortexlike structure, we scanned a larger area while applying the voltage in the same manner as in the previous scan [Fig. 2(i)]. Subsequent imaging demonstrates that the striped domain configuration has been dramatically modified [Figs. 2(j) and 2(k)]. Furthermore, similar to the previous excitation, this last manipulation also formed a closed shape of alternating polarization. The fact that the vortexlike structure can be deformed with an external

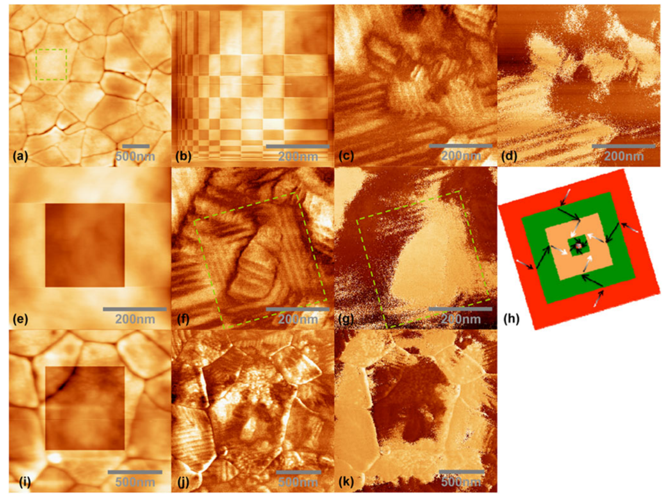

FIG. 2 (color online). Formation and deformation of a vortexlike 90° domain structure within a macroscopic polarization vortex. (a) The topography around and at the manipulated area. (b) Bright and darker patterns denote the areas that were scanned while 10 V and −10 V were applied between the tip and the bottom electrode superimposed on the topography. The resultant simultaneously imaged amplitude (c) and phase (d) reveal that small and randomly oriented 90° domain bundles were formed. (e) The second manipulation, in which 10 V (external bright frame) and −10 V (internal square) were applied to create a vortexlike 90° domain structure that is revealed in (f) the amplitude image, which in turn supports the polarization vortex that appears in (g) the phase image. (h) A sketch of the domain configuration, which takes the same format as observed in Ref. [8]. Note the different domain configuration here to that shown in Fig. 1—in this case, the domains are not oriented with respect to the grain boundary, although the entire structure has rotated by 45°. (i) The area was then manipulated on a larger scale, so that 10 V was applied at the external bright frame, whereas −10 V was applied at the internal dark square. The resultant domain image of the larger area shows that the stripes were destroyed (j), whereas the larger-scale 180° domains were written successfully (k).

electric field applied at this scale is not surprising, as it complies with traditional observations, in which the field closure that arises due to the polarization is not associated with the vortexlike structure. Moreover, it suggests that the vortexlike structure is a metastable excited state and scale dependent, in agreement with previous observations [9]. A comparison between Figs. 1(b) and 2(f) reveals that there are two ways in which flux closure may be attained—in Fig. 1(b), the ferroelastic domains are arranged radially, whereas in Fig. 2(f), they are azimuthal.

To locally release strain, ferroelectric thin films are bent, and the corrugation angle (α) is a measure of the released strain. The corrugation angle can be deduced from the width of the a stripes w_a, as given by [30] $\tan(\alpha) = \frac{c}{w_a}$, where c is the length of the longer side of the tetragonal unit cell. Hence, one can use the relative a-stripe width as a tool to determine the relative strain release in different areas. Implementing this to compare the native vortex with the artificially made vortex, one can see that w_a is constant throughout the native vortex. However, it should be noted that in this case strain may also be released at the grain boundary. On the other hand, in the artificially made vortex, w_a is narrower at the circumference and wider in the center, where there is a bundle of ferroelastic stripes oriented at 45° to the outer sides. That is, in the native vortex, strain is homogeneously released, while in the artificially made vortex the inner part is less strained than the circumference. This indicates that the core of the vortexlike structure is relatively relaxed, in agreement with the conclusion that the structure is originated to minimize the electromechanical energy.

We also note that in Fig. 1(b), the *c* domains within the outer parts of the vortexlike structure are polarized *up*, whereas those in the central area are polarized *down* (or vice versa), thus forming a true polarization vortex; whereas in contrast to this, in Fig. 2(f), one half of the central area of the vortexlike structure is polarized "up," whereas the other half is "down." This is presumably to compensate for the fact that the surrounding region is not polarized uniformly, so the polarization vortex is distorted. It should be noted that in both cases flux closure both in plane and out of plane is realized, and the factors determining which configuration will be adopted in any given case are as yet unclear. It is reasonable to postulate that the microstructure and the local stress distribution play a major role. We must also briefly consider the issue of polarization screening at the surface. It has been shown, both theoretically [31] and more recently experimentally using Kelvin-probe microscopy [32], that free charges compensate, and in some cases, overcompensate the polarization charge at the surface of ferroelectrics. Some of this free charge is intrinsic to the ferroelectric, and the rest is injected from the AFM tip during poling. Given the close spatial proximity (20–30 nm) of differently oriented domains in a polarization vortex, the overcompensated surface free charges are likely to mostly cancel each other out leaving the surface fully screened. The consequent reduction in the surface free energy may be a contributing factor in the stability of the vortexlike structures, and will play a greater role in determining the thermodynamic equilibrium within thinner films.

To conclude, our results show that vortexlike 90° domain structures are not unique to nanodots and can also be found in polycrystalline films. Moreover, we showed that these structures may be both induced and deformed by an external electric field. We have observed two different flux-closure configurations, a quadrant azimuthal structure similar to that observed in Ref. [9] and a radial structure, which to our knowledge has not been observed before. Additionally, among the mechanisms that were previously proposed to explain the origin of vortexlike structures, our findings support the suggestion that these structures are formed to minimize the energy arising due to large local stress and charge variations when forming a polarization vortex, whereas they eliminate the necessity of a geometrical boundary for the nucleation of the structures.

This work was carried out as part of the Nokia-University of Cambridge collaboration in Nanotechnology. The authors would like to thank G. Catalan for useful discussions. Moreover, Y. I. would also like to acknowledge AJA, Wingate Foundation, FCO, AIA, and Bn'ai Brith for financial support.

*yachinivry@gmail.com
†cd229@eng.cam.ac.uk

[1] A. Gruverman *et al.*, J. Vac. Sci. Technol. B **14**, 602 (1996).
[2] C. S. Ganpule *et al.*, Phys. Rev. B **65**, 014101 (2001).
[3] I. I. Naumov *et al.*, Nature (London) **432**, 737 (2004).
[4] S. Prosandeev *et al.*, J. Phys. Condens. Matter **20**, 193201 (2008).
[5] J. Slutsker *et al.*, Phys. Rev. Lett. **100**, 087602 (2008).
[6] A. Gruverman *et al.*, J. Phys. Condens. Matter **20**, 342201 (2008).
[7] B. J. Rodriguez *et al.*, Nano Lett. **9**, 1127 (2009).
[8] N. Balke *et al.*, Nature Nanotech. **4**, 868 (2009).
[9] A. Schilling *et al.*, Nano Lett. **9**, 3359 (2009).
[10] An excellent overview is given in M. Motolskii *et al.*, Annu. Rev. Mater. Res. **37**, 271 (2007).
[11] V. Nagarajan *et al.*, Nature Mater. **2**, 43 (2003).
[12] A. Roytburd and V. Roytburd, Philos. Mag. **90**, 61 (2010).
[13] A. Artemev and A. Roytburd, Acta Mater. **58**, 1004 (2010).
[14] M. K. Roy *et al.*, Appl. Phys. Lett. **95**, 192905 (2009).
[15] C. Durkan *et al.*, Phys. Rev. B **60**, 16 198 (1999).
[16] N. Balke *et al.*, J. Am. Ceram. Soc. **92**, 1629 (2009).
[17] Y. Cho *et al.*, Ferroelectrics **292**, 171 (2003).
[18] A. Gruverman *et al.*, Phys. Rev. Lett. **100**, 097601 (2008).
[19] Y. Ivry *et al.*, Appl. Phys. Lett. **94**, 162903 (2009).
[20] Y. Ivry *et al.*, Nanotechnology **21**, 065702 (2010).
[21] A. L. Roytburd, J. Appl. Phys. **83**, 228 (1998).
[22] M. E. Drougard and R. Landauer, J. Appl. Phys. **30**, 1663 (1959).
[23] J. W. Hong *et al.*, arXiv:0908.3617v1.
[24] J. M. Gregg *et al.*, J. Phys. Condens. Matter **19**, 022201 (2007).
[25] J. M. Gregg *et al.*, J. Phys. Condens. Matter **19**, 132201 (2007).
[26] J. M. Gregg *et al.*, J. Phys. Condens. Matter **16**, 2253 (2004).
[27] J. M. Gregg *et al.*, J. Phys. Condens. Matter **16**, L451 (2004).
[28] A. Gruverman *et al.*, Appl. Phys. Lett. **93**, 242902 (2008).
[29] R. J. Harrison *et al.*, Proc. Natl. Acad. Sci. U.S.A. **99**, 16556 (2002).
[30] A. H. G. Vlooswijk *et al.*, Appl. Phys. Lett. **91**, 112901 (2007).
[31] A. N. Morozovska *et al.*, Phys. Rev. B **80**, 214110 (2009).
[32] Y. Kim *et al.*, Appl. Phys. Lett. **94**, 032907 (2009).