Domains in Ferroelectric Nanodots

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ABSTRACT

Almost free-standing single crystal mesoscale and nanoscale dots of ferroelectric BaTiO3 have been made by direct focused ion beam patterning of bulk single crystal material. The domain structures which appear in these single crystal dots, after cooling through the Curie temperature, were observed to form into quadrants, with each quadrant consisting of fine 90° stripe domains. The reason that these rather complex domain configurations form is uncertain, but we consider and discuss three possibilities for their genesis: first, that the quadrant features initially form to facilitate field-closure, but then develop 90° shape compensating stripe domains in order to accommodate disclination stresses; second, that they are the result of the impingement of domain packets which nucleate at the sidewalls of the dots forming “Forsbergh” patterns (essentially the result of phase transition kinetics); and third, that 90° domains form to conserve the shape of the nanodot as it is cooled through the Curie temperature but arrange into quadrant packets in order to minimize the energy associated with uncompensated surface charges (thus representing an equilibrium state). While the third model is the preferred one, we note that the second and third models are not mutually exclusive.

Understanding the domain states that form in ferroelectric objects, as their physical dimensions are reduced and the complexity of their external morphology is increased, has recently become an issue of both technological and fundamental importance.

Technologically, for example, the geometries of the capacitors used in ferroelectric nonvolatile random access memories (FeRAM) are changing such that progressive miniaturization will soon be accompanied by a move from two-dimensional planar architectures to more complex three-dimensional trench structures.1,2 Crucially, in this context, the relationship between sample size and domain size is usually nonlinear, such that domain widths are relatively insensitive to changes in size and shape for macroscopic ferroelectric objects, but become highly sensitive to variations at the nanoscale; accordingly, nanoferroelectrics have proportionally considerably more domains, and also more domain walls, per unit volume than seen in bulk. This has at least two practical consequences.

(i) Since the stability and active operation of ferroelectric memory devices is linked to the control of domain states, as well as their dynamic response to electric fields, an understanding of the domain configurations that occur in more phologically complex ferroelectric structures at the meso and nano scale is essential to optimize switching response.

(ii) Since domain walls are known to have their own functional properties different from those of the domains themselves, the number density and type of domain walls in nanoscopic devices are likely to greatly affect their functional behavior. This latter point is well illustrated by the discovery of enhanced conductivity in certain types of domain wall in multiferroic BiFeO3;3 in this material, walls separating adjacent domains with polarization at 180 or 109° conduct, whereas those separating walls at 71° do not. An abundance of the “wrong” domain walls in this material could therefore lead to excessive leakage and prevent its planned use in ferroelectric memories.4

In terms of fundamental science, there has been a surge of activity in nanoscale ferroelectrics fueled by atomistic simulation predictions of new polarization vortex structures,5–11 as well as experimental observations of vortex states in ferromagnetic analogues.12–17 In general, the modeled formation of a polarization vortex develops through the relaxation or broadening of the boundaries between sets of four 90° domains arranged in field-closure quadrant groups. This broadening is predicted to occur as the physical dimensions of the object are reduced and depolarizing fields become dominant in determining local dipole orientations.

A significant amount of experimental work has been done on nanoscale ferroelectric objects, such as planar thin
films, nanowires\textsuperscript{18-21} and nanodots.\textsuperscript{26,27} However, polarization vortices have not yet been unequivocally observed, despite inferred evidence of their transient formation during switching, recently presented by Gruverman et al.,\textsuperscript{28} and noteworthy piezoforce microscopy measurements made by Rodriguez et al.\textsuperscript{29} Surprisingly, even classical 90\degree field-closure quadrant structures, ubiquitous in ferromagnetism, are yet to be clearly seen in ferroelectric nanostructures.

In an attempt to address the shortfall in experimental information, we herein present observations made on the domain patterns that form in novel free-standing single crystal nanodots of the archetypal ferroelectric BaTiO\textsubscript{3}. In general, quadrant packets of relatively fine scale 90\degree stripe domains were consistently observed for dots of different lateral sizes ranging from less than 100 nm to approximately half a micrometer. The physical explanation for the existence of such domain patterns is not entirely clear; however, several possible scenarios have been considered.

The meso/nanoscale isolated dots were directly machined from a starting material of commercially obtained polished single crystal BaTiO\textsubscript{3}, using a single beam focused ion beam (FIB) microscope (FEI 200TEM). A schematic of the process is given in Figure 1. Scanning transmission electron microscopy images of the ferroelectric dots are shown in Figure 2. The majority of the dots, irrespective of their size, show a characteristic domain configuration whereby “stripes” develop within four well-defined quadrants. The boundaries between stripe domains were of \{110\}_\text{pseudocubic} orientation, characteristic of 90\degree domain walls in tetragonal BaTiO\textsubscript{3}, while the boundaries between quadrant packets were consistently found to be approximately parallel to \{100\}_\text{pseudocubic}, irrespective of the crystallographic orientation of the sidewalls of the dots.

Although the nature and crystallography of the quadrants were seen to be insensitive to variations in the size of the nanodots, the periodicity of the 90\degree stripe domains within each quadrant was found to vary. As can be seen in Figure 1, the domain period was found to be proportional to the square root of the sidewall length. Such behavior is consistent with well-established energy models by Landau and Lifshitz\textsuperscript{30} (ferromagnets), Kittel\textsuperscript{31} (ferromagnets), Mitsui and Furuichi\textsuperscript{32} (ferroelectrics), and Roytburd\textsuperscript{33} (ferroelastics), and later models generalized for 3D objects, such as our nanodots, developed by Catalan et al.\textsuperscript{34} All these models assume that the domain period results from tension between the energy associated with the surface of the object and that associated with the existence of domain walls, giving rise to the following relation for nanoscale cuboids: \textsuperscript{34}
where \( x, y, \) and \( z \) are the physical dimensions of the ferroelectric object in a Cartesian space; \( U_x, U_y, \) and \( U_z \) are surface energy densities for surfaces perpendicular to \( x, y, \) and \( z, \) respectively; and \( \sigma \) is the energy density of the domain walls. This scaling relation was also seen to be consistent with previous observations on FIB-milled thin sheets and nanowires, \(^{35-37} \) data from which is also shown in Figure 3 for comparison.

Adherence of the periodicity of the 90° stripe domains to the form of eq 1 implies that surface energy determines their behavior but sheds little light on the origins of the quadrants observed, and hence does not explain the entire domain pattern developed. In an attempt to find a more general model for the domain formation in the dots, three scenarios have been considered, and will be briefly discussed as follows:

Model (i): That the quadrants form to generate a field-closure set, and the resulting disclination stresses then cause the development of the 90° stripe domains within each quadrant.

Model (ii): That bundles of 90° domains nucleate at the sidewalls of the dots and grow inward forming the quadrants as a result of hard impingement (implying the domain patterns are kinetic in origin).

Model (iii): That the quadrant structure of 90° stripe domains simultaneously satisfies the conditions for minimum macroscopic shape change, and minimum electrostatic surface energy in the dots (implying the domain patterns are thermodynamic in origin).

Model (i). It is clearly possible that on cooling through the Curie temperature the system initially attempted to develop polarization into a quadrant field-closure arrangement, as expected by Landau, Lifshitz, and Kittel in ferromagnetic systems \(^{30,31} \) and by atomistic simulations research on nanoscale ferroelectrics. \(^{7,8} \) However, such a simple quadrant arrangement would necessarily give rise to “disclination-type distortions” \(^{38} \) associated with the significant spontaneous strain in BaTiO\(_3\); for dots above a certain critical size, physical fragmentation might be a possibility (see schematic in Figure 4). Much more likely, however, is that alleviation of associated stresses would be provided by the formation of sets of 90° shape-conserving stripe domains within each quadrant. While this is an alluring explanation, there are two key reasons to suspect that it is not correct. First, the boundaries between field-closure quadrants would be expected to be parallel to \( \{110\} \) pseudocubic, whereas experimentally they are always observed to be parallel to \( \{100\} \) pseudocubic; second, the manner in which the 90° stripe domains actually occur (Figures 2 and 6) generates potentially uncompensated surface charge. This would seem a strange outcome if the initial drive for domain formation in the first place was the minimization of the depolarising field through formation of a “closure” structure. On balance then, we would suggest that model (i) is the least likely explanation of the three that were considered.

Model (ii). The possibility that packets of 90° domains nucleate from the sidewalls of the nanodots, grow and meet to form quadrants has been substantiated to a degree by numerical dynamic simulations based on Landau–Lifshitz–Gilbert (LLG) equations, extended from recent work \(^{28} \) (and would also be consistent with the ideas of “perimeter switching” in small-scale ferroelectric structures \(^{39} \). Figure

![Figure 3](image3.png)  
**Figure 3.** Measured periodicity of 90° stripe domains observed in the BaTiO\(_3\) dots as a function of the square root of the length of the sides of the square sections as observed in STEM images (see Figure 2). For comparison, data obtained in previous studies on sheets/lamellae and wires/columns of single crystal BaTiO\(_3\) are also plotted. Note that in all cases a linear relation exists, consistent with Kittel-like energy models, \(^{31} \) and that the gradients decrease as the dimensional constraint increases (from sheets to wires to dots).

![Figure 4](image4.png)  
**Figure 4.** Schematic illustration of the disclination strains that would develop if the spontaneous polarization and strain occurred independently within each quadrant of a ferroelectric nanodot displaying polarization closure.

![Figure 5](image5.png)  
**Figure 5.** Computational simulation of the spatial development of polarization in a ferroelectric nanodot, using software based on the Landau–Lifshitz–Gilbert equations used successfully in nanoferromagnetics research. \( P_r \) and \( P_p \) are the polarization components parallel to the \( x \) and \( y \) axes; red is positive, blue is negative, and green is neutral. Time runs forward from the top to the bottom of the page.
5 illustrates results from the LLG modeling in which a ferroelectric nanodot, initially poled along the z-axis perpendicular to the x-y plane, is allowed to relax under the influence of a small bias field in the negative z direction. Two points should be noted: first, that domains nucleate at the perimeter and spiral into the centers; second, that the geometry of the domains developed after some time is strongly suggestive of the quadrant formations actually observed.

Even without this modeling evidence, though, the idea that highly complex patterns can result from the growth and impingement of bundles of 90° domains has been explored some time ago by Forsbergh. In this work, the observation of complex concentric squares seen through birefringence contrast was explained by the existence of distinct tessellating polyhedral regions. Each polyhedron contained only one set of 90° stripe domains. That the domain patterns we observe represent some form of Forsbergh pattern is clearly a distinct possibility. We note, however, that if this is the case, the polyhedra seen in our nanodots (triangular prisms) would be completely new, as they were not specifically observed in bulk by Forsbergh.

Model (iii). In this model, the 90° stripe domains form to minimize the macroscopic shape distortion in the dot as the spontaneous strain develops through the Curie temperature; subsequently, the domains arrange themselves into quadrant packets in order to also minimize the electrostatic surface energy. Thus stress and surface charge related energy terms are simultaneously minimized.

To examine the effect of the domain structure on the minimization of electrostatic energy, three different two-dimensional domain configurations, shown in Figure 6, were analyzed using the finite element package ANSYS. The surface charge distributions along the edge of the dot, responsible for generating depolarizing fields, were assigned as indicated in Figure 6. The total electrostatic energy of the combined system was computed for each of the three configurations in a dot of a fixed size y and varying numbers of domains N. The surface charge in the closed domain configuration of Figure 6a does not depend on N, therefore the energy remains constant and equals

\[ E = A \frac{P_{R}^2 y^2}{\varepsilon_0 \varepsilon_{eff}} \]  

where \( A \) is a scaling factor which depends on the domain configuration, and \( P_R \) is the remanent polarization, and \( \varepsilon_{eff} \) is the effective relative dielectric constant of the collection of domains (taken to be isotropic). It was found that the system energy of the configurations in Figure 6b,c decreased with the number of domains present (N). The scaling factor A for each domain configuration was computed using eq 2, as a function of N, and is shown in Figure 7. As can be seen from the figure, the two configurations that have a surface charge distribution dependent on the number of domains show a decrease in the total system energy as N increases. The quadrant configuration shown in Figure 6a was determined to have a constant scaling factor \( A = 1.33 \); that in Figure 6b asymptotically approached \( A = 0.80 \), while the striped configuration, without the existence of quadrants (Figure 6c) asymptotically approached a value of \( A = 2.00 \). Overall, this finite element analysis revealed a substantial advantage in terms of electrostatic field energies for the formation of quadrant sets of 90° stripe domains, and suggests that if stripe domains form in order to minimize

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Figure 6. Schematic illustrations of two possible dipole arrangements in the single crystal dots (a,b) consistent with the images in Figure 2. Note that within each quadrant boundaries between parallel stripe domains are parallel to \{110\}_{pseudocubic}, implying 90° domain walls. Further, note that boundaries between quadrants were found to be approximately parallel to \{100\}_{pseudocubic}. In (c), a schematic of domains in which no quadrant formation occurs is presented and is used in finite element modeling to compare relative values of the electrostatic energy (see Figure 7).
Figure 7. Finite element modeling demonstrates that the rearrangement of 90° domains into quadrants is favorable in terms of reducing the electrostatic energy. It is therefore plausible that shape-conservation is the primary driving force in the initial creation of 90° domains with specific quadrants forming in order to subsequently minimize the depolarizing field.

strain energy, they should also form into quadrants in order to simultaneously minimize electrostatic energy.

In summary, a methodology has been developed to create almost free-standing meso and nanoscale dots of single crystal ferroelectric BaTiO₃. These dots show domain configurations consisting of quadrant packages of 90° stripe domains. The origin of these domain patterns has been discussed with three viable models being put forward. In the first, the quadrants were considered to form in an attempt to generate a field-closure structure with 90° stripe domains then forming to minimize disclination stresses. In the second, the domain pattern was considered to be the result of impingement of four bundles of 90° stripe domains that had nucleated from the sidewalls of the dots. In the third, the domain patterns were considered to be the optimal solution for simultaneous minimization of macroscopic strain and surface electrostatic charge energies. While it is not entirely clear which model correctly rationalizes the domain configurations present, we consider the second and third ideas to be the most plausible. We also note that the two are not mutually exclusive, as it is possible that the equilibrium domain configuration is reached following nucleation and growth from the side walls of the dots.

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References
