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Domains in three-dimensional ferroelectric nanostructures: theory and experiment

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Online at stacks.iop.org/JPhysCM/19/132201**Abstract**

We report the experimental measurement of domains in single-crystal nanocolumns of ferroelectric BaTiO₃, together with a theory of domain size scaling in three-dimensional structures which explains the observations.

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

In the continuing race to decrease the size of electronic devices, the development of thin film technologies and the achievement of ever-decreasing thicknesses have played a central role. Ferroelectrics have not escaped this trend, as the reduction of film thickness has obvious advantages for practical applications in terms of increasing capacitance for capacitor and dynamic random access memory applications (DRAM), and decreasing coercive voltages for non-volatile ferroelectric random access memories (NVFRAM). However, it seems that, at least at the cutting-edge laboratory level, the ultimate limits of ferroelectric film thickness reduction have already been reached for planar devices. Films as thin as three unit cells have been shown to be ferroelectric [1], and ferroelectric/paraelectric superlattices with a stacking periodicity of one unit cell are also ferroelectric [2]. And, while the dielectric constant generally decreases for thin films in the sub-micron region, this decrease is now considered to be mostly extrinsic, with single-crystal films as thin as 70 nm displaying perfectly bulk-like properties [3].

On the other hand, the reduction of lateral size in ferroelectric memories is also approaching its practical limits. Ferroelectric random access memory cells have reached 450 nm × 400 nm production (0.18 μm²) at Samsung with lead zirconate titanate (PZT), 0.13 μm² at Matsushita with strontium bismuth tantalate (SBT), and comparable sizes at Fujitsu with BiFeO₃. The next step in device miniaturization is thus not in the reduction of film thickness or lateral size, but in the achievement of ever-smaller 3D structures. Indeed, the technology roadmap in the capacitor industry actually indicates that 2010 should be the

year in which 3D capacitor structures such as trenches or nanotubes should take over planar structures [4]. In this respect, Wouters' group at IMEC has fabricated commercial capacitors in which both the ferroelectric layer and the top electrode are bent over to produce a 3D mushroom-shaped structure [5], and the group of Ishiwara and Funakubo, in collaboration with Samsung, have produced 3D trenched capacitor electrodes for DRAMs [6]. But research into three-dimensional ferroelectric nanostructures is still, nonetheless, incipient, with relatively few works in the last few years addressing these and other three-dimensional morphologies such as ferroelectric nanorods, nanotubes and nanocolumns [5–10]. Some of these, such as the nanotubes, will find application not just in capacitors and memory devices, but also for microfluidics, such as ink-jet print heads and drug-delivery systems [11, 12].

Here we have turned our attention to the problem of the scaling of ferroelectric domain size as a function of the lateral dimensions of the ferroic material. The interest in this problem is more than purely academic: domain behaviour is essential to rationalize dielectric and electromechanical properties of ferroelectrics, and the scaling of domain size is correlated to the scaling in other domain-related properties such as coercive fields and switching kinetics [12]. It is also worth mentioning that even conventional planar architectures cease to be amenable to 2D analysis as the aspect ratio of the capacitor decreases; the aspect ratio in planar capacitor memories such as Samsung's is already less than 3, so three-dimensional effects are already relevant even for these devices.

The structures analysed in this work are tetragonal columns with the sides parallel to the main crystallographic axes of ferroelectric BaTiO₃ single crystal. These were cut out from a commercially obtained single crystal using focused ion beam milling [13]. The crystals were cut in a two-stage process: first, thin slabs of different thickness were made, and then several columns with different lateral sizes were carved out of each lamella. An example of one such structure is shown in figure 1. The detail and a schematic diagram of the domain symmetry are depicted in figure 2. The 'front' faces (*X*-faces in our notation) have domain walls at 45° with respect to the crystallographic planes, typical of tetragonal in-plane 90° domains (also called *a*₁–*a*₂ domains). The domain structure is the same as observed in the surfaces of the lamellae [14], and it probably propagates from the lamellae into the column via the attachment points. But although the symmetry is the same as in the lamellae, the domain size is different, and it changes as a function of the lateral dimension 'y' [15].

The problem of domain scaling was first analysed by Landau and Lifshitz [16] and Kittel [17], who showed that for thin crystals and films the ferromagnetic domain size (*w*) scales as the square root of the crystal thickness (*d*). The proportionality between *w*² and *d* is in fact a universal property of all ferroics [12, 14, 16–22], with the scaling factor being directly proportional to the thickness of the domain walls [12, 14, 22, 23]. To rationalize the results for the nanocolumns, however, it is necessary to extend Kittel's ideas to three-dimensional shapes.

In order to calculate equilibrium domain size, the surface energy and domain wall energy for the entire crystal must be minimized. The surface energy density scales in direct proportion to the domain size *w*. This is true for demagnetization energy in ferromagnets [17], depolarization energy in ferroelectrics [18] and elastic energy in ferroelastics [19, 20]—and, as a matter of fact, also for non-ferroic materials such as martensitic steels [21]. The surface energy density in the two *X*-faces is then

$$F_{\text{domain}}^X = U_x w,$$

where *U_x* is a constant proportional to the energy density. In the *X*-faces, this should only be due to elastic energy, as the in-plane orientation of the polarization means that there is no depolarization. To compute the surface energy of the two *X*-faces we simply multiply the

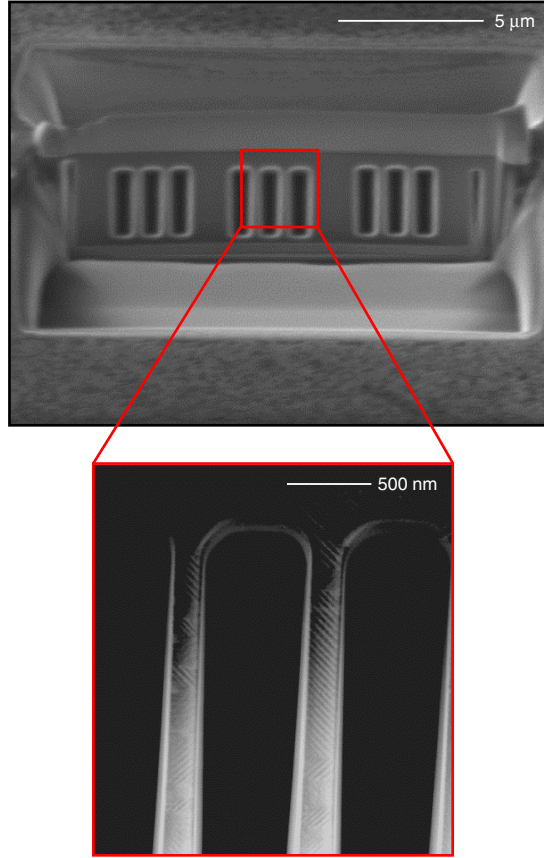


Figure 1. Geometry of BaTiO₃ columnar structures cut with FIB. Ferroelectric 90° domains can be seen inside the columns.

energy density times the area of the two X -faces:

$$E_{\text{domain}}^X = F_{\text{domain}}^X \times 2xy = 2U_x w y z.$$

Likewise, in the Y -faces we have $E_{\text{domain}}^Y = 2U_y w x z$, where U_y contains both elastic and depolarization contributions.

The energy of the domain walls in the crystal is proportional to their size and to their number. The area of each domain wall is $S = \sqrt{2}xy$ and the number of domain walls is $N = \frac{z}{w}$. Let σ be the energy density per unit area of domain wall [23]; the total energy of all the domain walls in the column will then be:

$$E_{\text{walls}} = \sigma S N = \sigma \sqrt{2}xy \frac{z}{w}.$$

Adding the surface and the domain wall terms, the total energy of the crystal is

$$E = \sigma \sqrt{2}xy \frac{z}{w} + 2zw (U_x y + U_y x).$$

Minimizing this energy with respect to the domain size w leads to the final equilibrium condition:

$$w^2 = \frac{\sqrt{2}}{2} \frac{\sigma}{\frac{U_x}{x} + \frac{U_y}{y}}. \quad (1)$$

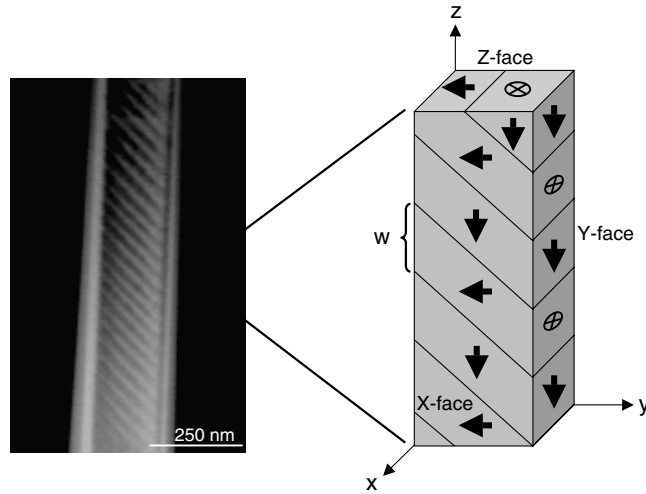


Figure 2. Domain configuration in the tetragonal pillars, and schematic of the domain symmetry.

There are two important limits:

- (1) The thin film lamellae are described by the limit $y \gg x$. In this case we recover $w^2 = \frac{\sqrt{2}\sigma}{2U_x}x$, which is precisely Kittel's result for thin films.
- (2) In the columns, the two length scales are similar ($x \sim y$). The surface energies, however, are not, as the Y-face has an energy contribution from depolarization. Thus, the relevant limit is $U_y \gg U_x$, for which equation (1) becomes $w^2 = \frac{2\sigma}{\sqrt{2}U_y}y$.

This result implies that, in columns where x and y are relatively similar, the lateral size y (the one perpendicular to the face with highest surface energy) will significantly dominate the scaling behaviour, as observed [15]. Furthermore, since the surface energy constant U_y is bigger than the energy constant U_x , the slope of the Kittel plots for the columns will be smaller than for the films, as also observed.

Clearly, though, these are only extreme cases, and in general the experimental results will be best described by equation (1). It is desirable to find a way of representing the results in order to produce a plot that is as visually useful as the Kittel plots (straight lines for w^2 as a function of thickness), but which can be used for columns instead of films. This can be done by rearranging the terms in equation (1):

$$w^{-2} = \frac{2}{\sqrt{2}\sigma} (U_x x^{-1} + U_y y^{-1}). \quad (2)$$

The experimental results for the domain size as a function of lateral dimension have been plotted in figure 3 according to this format (that is, the inverse of w^2 as a function of the inverse of the lateral dimensions). In the figure we have added the least-squares fit of the data to equation (2).

While there is a considerable experimental scatter in the data, the experimental trends are reasonably well reproduced. Furthermore, the parameters of the surface fit can now be compared with other experimental results. In particular, the gradient of the intercept between the surface and the plane $y^{-1} = 0$ of the plot can be compared with that of standard Kittel plots for thin films. In our case, the intercept has a gradient of 0.062 nm^{-1} , the inverse of which is $\sim 16 \text{ nm}$. In the case of BaTiO_3 thin films, the proportionality constant between w^2

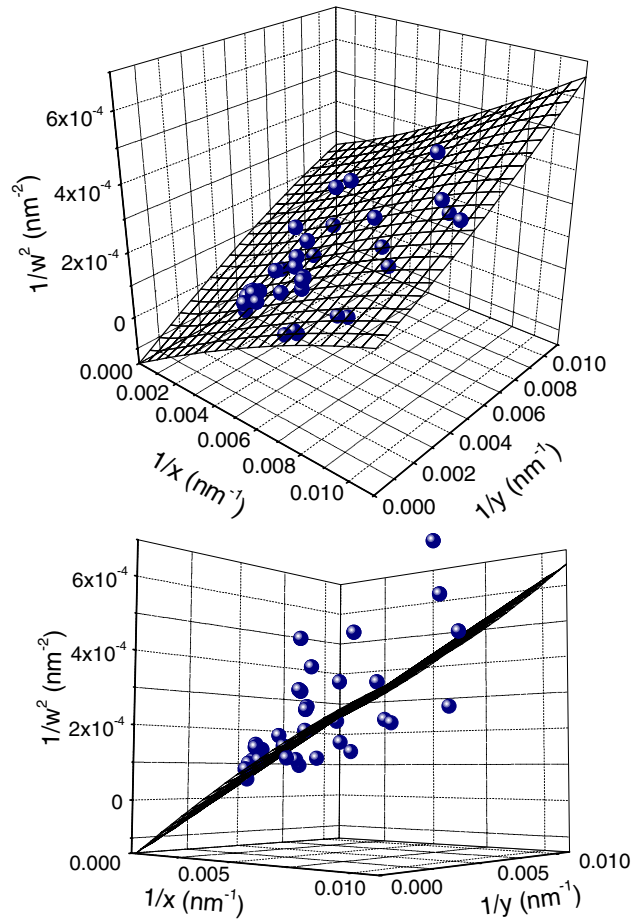


Figure 3. Plot of domain size as a function of lateral dimensions for the pillars. The flat surface is the least-squares fit to the 3D scaling law (equation (2)).

and thickness d was found to be ~ 10 nm [14], but the periodicity in that case was measured perpendicular to the domain walls, whereas in our work we have measured it parallel to the sides of the column and hence at 45° to the domain walls. Thus, a $\sqrt{2}$ correction factor has to be included in the comparison. With this correction, we obtain a proportionality constant of ~ 11 nm for the columns, very close indeed to that measured in the films.

There are some limitations to the applicability of the above calculations. First, we have neglected the surface contribution from the Z -face, $E_{\text{domain}}^z = 2U_z wxy$. Adding this leads to the generalized expression for a tetragonal grain of any size:

$$w^2 = \frac{\sqrt{2}}{2} \frac{\sigma}{\frac{U_x}{x} + \frac{U_y}{y} + \frac{U_z}{z}}. \quad (3)$$

Since in the pillars z is much larger than x and y , the Z -face contribution to equation (3) can be neglected. For nanocrystals of smaller aspect ratios, however, it must be included. Incidentally, equation (3) shows that the domain size in a 3D structure with a depth z and finite lateral dimensions x and y is always smaller than the domain size in a film of thickness z .

A second caution is that we have assumed that the domain structure consists of parallel 90° domains. If, for example, the domain structure was not parallel but a zigzag, such as the column on the left of figure 1, then the energy constant U_y may be different due to the lower depolarization energy, and thus the optimum domain size would also be different. This difference in the value U_y for parallel and zigzag configurations probably accounts for at least some of the scatter in the experimental data.

Our model also neglects the energy contributions from the edges and corners of the columns, which are different from the contributions in the middle of the faces. These will become more important as the columns become narrower. The narrowest columns examined were $\sim 100 \text{ nm} \times 100 \text{ nm}$. Although the experimental results show no obvious departure from equation (1) down to the smallest size, the scatter in the data is too large to establish subtle changes in the trends; future work focusing specifically on edge effects is clearly desirable.

It is also worth noticing that, without external stress, the most stable domain configuration in a free-standing column should in fact be one in which the polarization lies along the z -direction (long axis), because in this way both the depolarization energy and the domain wall energy are minimized. That this is not the case in our ferroelectric columns is surprising, but it is consistent with previous results for free-standing lamellae, where a monodomain configuration with in-plane polarization would also have been the minimum energy state, yet a_1 - a_2 domains were seen instead. The most likely explanation is that, at the phase transition, polarization nucleates in different sites of the lamellae, and the domains then grow laterally until they meet through hard-impingement. Adjacent domains with orthogonal polarization impose elastic stress on each other, providing the driving force for the splitting into smaller twins.

In summary, we have studied the scaling of periodic domain structures in ferroelectric single-crystal pillars as a function of their lateral dimensions. The experimental results for BaTiO_3 were rationalized in terms of minimization of the total free energy of the crystal, including the contributions from domains and domain walls. The proposed equations extend the range of applicability of Kittel's law to ferroic domains in 3D shapes. An important result is that the two in-plane directions are not equivalent in the modelling, with dominance determined by depolarization effects. Importantly too, domain size is smaller in three-dimensional structures than in thin films of comparable thickness, which suggests an enhanced role for domains and domain walls in the new 3D architectures.

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