

# Effect of wall thickness on the ferroelastic domain size of BaTiO<sub>3</sub>

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**Abstract** Extremely regular self-organized patterns of 90° ferroelastic domains have been reported in free-standing single crystal thin films of ferroelectric BaTiO<sub>3</sub>. Lukyanchuk et al. [Phys Rev B 79, 144111 (2009)] have recently shown that the domain size as a function of thickness for such free standing films can be well described assuming that the domains are due to stress caused by a surface tension layer that does not undergo the paraelectric–ferroelectric transition. From the starting point of Lukyanchuk’s model, it is shown here that the “universal” relationship between domain size and domain wall thickness previously observed in ferroelectrics, ferromagnets and multiferroics is also valid for ferroelastic domains. Further analysis of experimental data also shows that the domain wall thickness can vary considerably (an order of magnitude) from sample to sample even for the same material (BaTiO<sub>3</sub>), in spite of which the domain size scaling model is still valid, provided that the correct, sample dependent, domain wall thickness is used.

## Introduction

An important feature of all ferroic materials—including ferroelectrics—is that they can display regions of different polarity (domains) separated by domain walls. The domains often arrange themselves in surprisingly regular patterns in the form of periodic stripes. The period of the domain scales non-linearly with the size of the device: specifically, for thin films, the domain size typically grows proportional to the square root of the film thickness [1–4]. This square root dependence has the consequence that, on approaching the nanoscale, the domain size decreases very rapidly and thus the number density of domains—and domain walls—can rapidly become very large. The practical consequences of these are twofold: first, as emphasized by Scott [5], the switching characteristics of a ferroelectric device are ultimately limited by the ability of domains to nucleate and grow, so the scaling of domain size is closely correlated with the scaling of switching properties such as coercive field [5]. Second, domain walls have functional properties distinct from those of the domains themselves: superconductivity in the ferroelastic walls of non-superconducting WO<sub>3-x</sub> [6], polarization in the twin walls of paraelectric SrTiO<sub>3</sub> [7] and conductivity in the ferroelectric walls of insulating BiFeO<sub>3</sub> [8] are some examples. Given a sufficiently large volume density of domain walls, then, the functional behavior of the sample may be dominated not so much by the properties of the domains as by those of the domain walls.

In this context, recent studies by groups in Belfast, Cambridge, and Amiens have been aimed at studying and rationalizing the formation of regular domain patterns in “ideal” samples of nanoferroelectrics. The experimental study, pioneered by Gregg et al. [9, 10], is based on the idea that ferroelectric thin films need not be grown on a

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substrate, but can instead be “carved out” of a bulk single crystal of, e.g., BaTiO<sub>3</sub> (BTO) using a focussed ion beam. When placed under a transmission electron microscope (TEM), such single crystal lamella display astonishingly regular stripe domain patterns, with the polarization in-plane alternating at 90° between the *x* and *y* axes [11]. The fact that the polarization is entirely in-plane means that depolarization effects do not play a significant role and that the domain configuration and size must respond to elastic constraints instead [4]. Extension of the thin film work to non-planar structures such as nano-wires [12–14] and nano-dots [15] invariably shows the same feature: the appearance of ferroelectric–ferroelastic domains in regular patterns and in a configuration such that the macroscopic shape of the sample tends to be preserved.

Until very recently, however, the shape-preserving aspect of the domains had remained rather intriguing. After all, if there is no external constraint on the shape of the sample (such as that which may be expected, for example, from clamping to a rigid substrate [4, 16, 17]), why should the samples want to keep any specific shape? In theory, the minimum energy configuration for a free-standing film should be one with a single domain (so as to minimize energy from domain walls) and with the polarization pointing in-plane (so as to minimize depolarization). A possible explanation proposed recently by Lukyanchuk et al. [18] is that the domains appear in order to relieve the stress generated by an encapsulating surface layer that does not itself experience the structural phase transition. Thus, when the interior of the films becomes ferroelectric, it automatically experiences the stress imposed by the untransformed surface layer. This model reproduces well the observed dependence of domain size on lamellar thickness. However, it also poses new questions: (i) is this surface layer extrinsic and sample-dependent or intrinsic and therefore unavoidable? (ii) Does the proportionality between domain size and domain wall thickness, previously reported for ferroelectrics and ferromagnets, hold also true for this ferroelastic twinning? And (iii) if the domain walls are extrinsically broadened, does this affect the domain periodicity? The present article looks at these issues.

## Theory

According to the model of Lukyanchuk et al. [18], the domain width (*w*) is given by:

$$w = \frac{w_0}{1 - \frac{w_0}{kt_{\text{SL}}}} \quad (1)$$

where *k* = 7.4 is a numerical constant, *t*<sub>SL</sub> is the thickness of the surface layer and *w*<sub>0</sub> is the Roytburd-type

equilibrium domain size of the ferroelastic domains, which is given by

$$w_0 = \sqrt{kDt_{\text{FL}}} = 2.72\sqrt{D(t - 2t_{\text{SL}})} \quad (2)$$

where *t*<sub>FL</sub> is the thickness of the ferroelectric layer of the film, here expressed as the difference between the total film thickness (*t*) and the thickness the two surface layers. *D* is the elastic length-scale parameter of the system, which is given by [18]:

$$D = \frac{\sigma}{Ge_{\text{ac}}^2} \quad (3)$$

where  $\sigma$  is the surface energy density of the domain wall, which is  $\sim 2\text{--}4$  mJ/m<sup>2</sup> for BTO [19], *G* is the shear modulus ( $\sim 50$  GPa for BTO [20]) and  $e_{\text{ac}}^2$  is the tetragonal strain:  $e_{\text{ac}} = \frac{c-a}{b}$ , with *a* and *c* the tetragonal lattice parameters of BTO, and *b* the pseudocubic lattice parameter of the paraelectric phase. Physically, this length-scale parameter coincides with the half-thickness of the ferroelastic domain wall. This can be seen noticing that  $\frac{1}{2}Ge_{\text{ac}}^2$  is the elastic energy density per unit volume of domain wall (as in Hooke's law, where *G* is the elastic constant and *e* is the deformation). Multiplying this volume energy density by the thickness of the domain wall ( $\equiv \delta$ ), one obtains the energy density per unit area of the domain wall:

$$\sigma = \delta \times \frac{1}{2}Ge_{\text{ac}}^2 \quad (4)$$

Comparing Eqs. 3 and 4 it is immediately obvious that the domain wall thickness is  $\delta = 2D$ . The calculated value for the intrinsic thickness of the ferroelastic domain wall is thus estimated to be  $\delta \sim 1$  nm for BTO. It is important to note, however, that this wall thickness is based only on the elastic interactions. If the ferroelectric polarization is incorporated, one obtains instead the classic results for ferroelectric–ferroelastic domain wall thickness of Zhirnov [19] and Cao et al. [21, 22]. The actual experimental values of the domain wall thickness differ for different studies, but our calculated intrinsic value of  $\delta \sim 1$  nm coincides with the lower limit of the range of thicknesses directly measured by Zhang et al. [23] using electron holography.

Equation 2 can be re-written as:

$$\frac{w_0^2}{\delta} = 3.7(t - 2t_{\text{SL}}) \quad (5)$$

where  $\delta = 2D$  is the domain wall thickness. Here we note that Eq. 5 is essentially identical to that previously obtained for domain size scaling in 180° stripe domains in ferromagnets and ferroelectrics [24–26], provided that the surface layer is sufficiently thin in comparison with the total thickness of the film (i.e.,  $2t_{\text{SL}} \ll t$ ). This suggests that, theoretically at least, the proportionality between the square of the spontaneous domain size and the domain wall

thickness is indeed a universal feature of all ferroics, irrespective of the specific forces involved.

We also draw attention towards the fact that the surface layers of BTO may be harder than the bulk structure. Surface-tension induced hardening is of course not unusual in nature, and Lukyanchuk et al. showed that, if the surface layer of the ferroelastic material is harder than the interior, Eq. 1 should be modified to incorporate the different shear moduli of bulk ( $G_b$ ) and surface ( $G_s$ ), with the resulting equation being

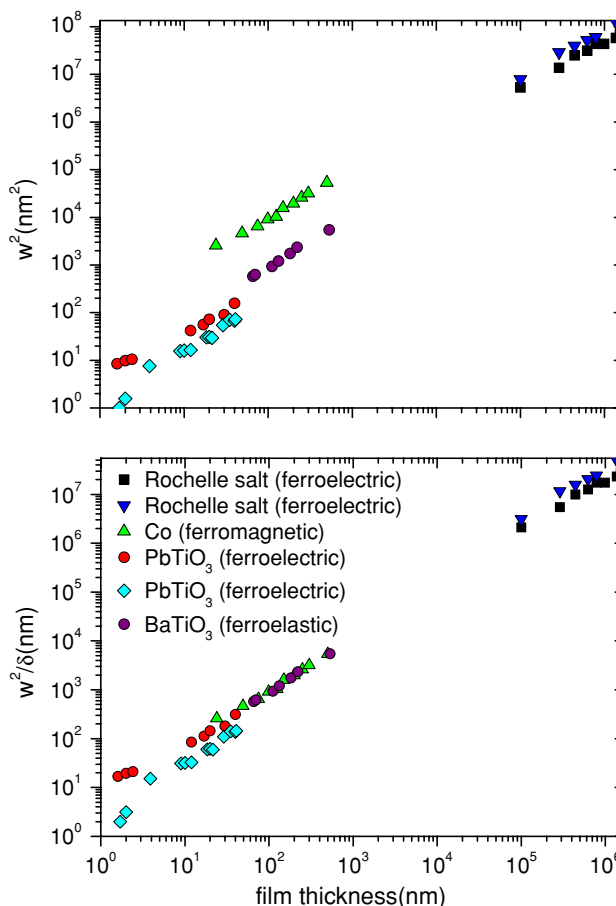
$$w = \frac{w_0}{1 - \frac{w_0 G_b}{k t_{SL} G_s}} \quad (6)$$

Thus, while surface hardening does not affect  $w_0$ , which is the Kittel–Roitburd square root limit for domain size dependence on thickness, it does affect the range of surface layer thicknesses ( $t_{SL}$ ) for which one can assume that  $w \approx w_0$ . Specifically, the harder the surface layer is, the smaller the second term in the denominator and thus the better the square root approximation is. In this context, Gharbi et al. [27] have recently shown that indeed the hardness of BTO increases with decreasing thickness, with the surface being nearly twice as hard as the interior. This result extends range of validity of Eqs. 2 and 5 as reasonable approximations.

### Comparison with experiment

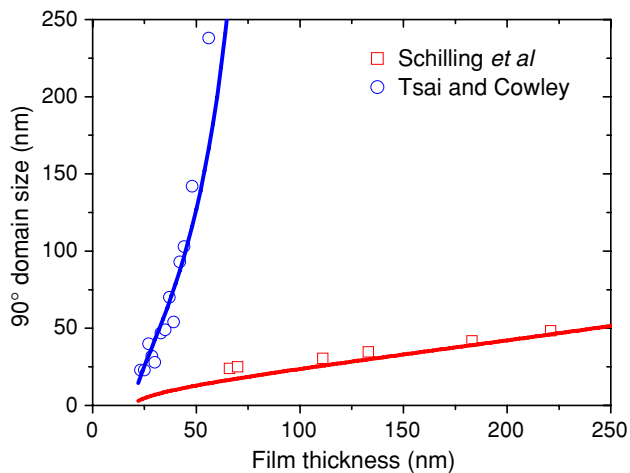
In Fig. 1 we have compared the domain size of the ferroelastic  $90^\circ$  domains of Schilling et al. with the domain size of  $180^\circ$  stripes in ferroelectrics and ferromagnets. The samples in which the ferroelastic domains were studied were thin lamellae that were carved out of bulk BTO single crystals using a focussed ion beam. The lamellae were heated above the Curie temperature and subsequently cooled down so that the domains appeared spontaneously. The comparison between the different types of ferroic domains shows that, while the domain size as a function of thickness is quite different for the different ferroics, once normalized by the domain wall thickness all data fall in the same “universal” curve.

A second aspect worth considering is the fact that the wall half-thickness given by (3) is a lower limit and is not necessarily the same as the experimentally measured value in real ferroelectrics. For example, defects are known to be attracted to domain walls, and this can considerably broaden them. The domain wall thickness is thus sample-specific and should either be directly measured for the samples being analyzed or else treated as a fitting parameter. This has been verified here by comparing the size of ferroelastic  $90^\circ$  domains in single crystal BTO films made in two different laboratories, as shown in Fig. 2.



**Fig. 1** (Above) Square of the domain size as a function of thickness for different types of ferroic domains found in the literature:  $180^\circ$  ferroelectric domains in  $\text{PbTiO}_3$  [30] (the red and blue sets correspond to different configurations of the stripe domains), and Rochelle salt [3] (rapidly cooled (black) and slowly cooled (blue)),  $180^\circ$  ferromagnetic domains in ferromagnetic Co [31] and  $90^\circ$  ferroelastic domains in  $\text{BaTiO}_3$  [11]. (Below) When the square of the domain size is normalized by the domain wall thickness, all ferroic domains, including the ferroelastic ones, fall into approximately the same “universal” curve

The domain size as a function of thickness is strikingly different between the two sets of samples, even though both the ferroelectric material (BTO) and the type of domain ( $90^\circ$  in-plane) are purportedly the same. And yet, in spite of their very different quantitative and even qualitative trends, both sets of data can be well fitted using Eq. 1. In the modeling of Tsai’s data, we have used their experimentally measured surface layer thickness,  $t_{SL} = 10 \text{ nm}$  [28], and a domain wall half-thickness of  $D = 10 \text{ nm}$  instead of the intrinsic  $D = 0.5 \text{ nm}$  of Schilling’s data. The domain wall half-thickness used for modeling Tsai and Cowley’s data, though apparently thick, is not an arbitrary fitting parameter: it is the value measured in their work for the half-thickness of the boundaries between their domains; though they associated such boundaries to needle domains, we believe that they were in



**Fig. 2** Domain size ( $w$ ) as a function of thickness ( $t$ ) for the BTO films of refs. [11] (Schilling et al.) and [28] (Tsai and Cowley). The symbols are the experimental results and the solid lines are the theoretical fits using Eq. 1. The only difference between the two fits is the domain wall thickness: 1 nm for the data of Schilling et al. and 20 nm for Tsai and Cowley's. The qualitative difference between the two curves is due to the denominator in Eq. 1, which is negligible for small domains but approaches a singularity as domain size increases

fact the domain walls, and our results here are consistent with that view. This wall thickness is also the same as directly measured by Franck et al. [29] using piezo-response atomic force microscopy.

Finally, in the experiments of Schilling et al., the encapsulating layer could be associated with extrinsic surface damage caused by Ga ion implantation during focussed ion milling process. However, samples annealed to remove the extrinsic surface damage still showed regular ferroelastic domain patterns [18]. Likewise, the samples of Tsai and Cowley [28] were made by conventional TEM preparation techniques and so they were, in principle, free from ion implantation damage, in spite of which they also showed a surface relaxation layer. All these observations suggest that the existence of non-ferroelectric layers around ferroelectrics may be an intrinsic feature, and that the influence of surface tension on domain formation should therefore be generally taken into account when modeling nanoscale ferroelectrics.

## Conclusions

In summary, comparison between the surface tension model for ferroelastic domain size in free-standing ferroelectrics and experimental data from different sources allows establishing three principal conclusions:

- (i) The square of the domain size is linearly proportional to domain wall thickness in all ferroic materials

- (ii) The proportionality holds true even for extrinsically broadened domain walls. The equations are based on thermodynamic stability; hence it is the experimental value of sample-dependent wall thickness,  $\delta$ , that is involved, whatever its origin, and not the ideal defect-free, strain-free value of one or two unit cells, and
- (iii) Ferroelastic domains appear even in the absence of extrinsic surface layers, suggesting an intrinsic origin, such as surface tension, for the strain relaxation layer. There are indications that the intrinsic surface layer is harder than the interior [27], and this reinforces its effect on twinning.

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