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Scaling of domain periodicity with thickness measured in BaTiO$_3$ single crystal lamellae and comparison with other ferroics

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The focused ion beam microscope has been used to cut parallel-sided {100}-oriented thin lamellae of single crystal barium titanate with controlled thicknesses, ranging from 530 nm to 70 nm. Scanning transmission electron microscopy has been used to examine domain configurations. In all cases, stripe domains were observed with {011}-type domain walls in perovskite unit-cell axes, suggesting 90° domains with polarization in the plane of the lamellae. The domain widths were found to vary as the square root of the lamellar thickness, consistent with Kittel's law, and its later development by Mitsui and Furuichi and by Roytburd. An investigation into the manner in which domain period adapts to thickness gradient was undertaken on both wedge-shaped lamellae and lamellae with discrete terraces. It was found that when the thickness gradient was perpendicular to the domain walls, a continuous change in domain periodicity occurred, but if the thickness gradient was parallel to the domain walls, periodicity changes were accommodated through discrete domain bifurcation. Data were then compared with other work in literature, on both ferroelectric and ferromagnetic systems, from which conclusions on the widespread applicability of Kittel's law in ferroics were made.

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I. INTRODUCTION

It has been known for decades that the functional behavior of thin film ferroelectrics is somewhat different from that of bulk single crystal material.[1] For example, ferroelectric thin films tend to show a dramatic suppression in the dielectric permittivity measured at radio frequencies, with an associated significant broadening of the Curie anomaly (the peak in dielectric constant with respect to temperature);[2–5] the coercive field for ferroelectric switching increases as film thicknesses decrease[6,7] and there are apparent changes in the nature of the paraelectric-ferroelectric phase transition from first to second order.[5,8]

A significant barrier in the consistent rationalization, and full understanding, of such observations is that there are many aspects associated with heterogeneous thin film structures that could contribute to altering functional behavior; film microstructure,[9] defects,[10] strain state and strain clamping to substrates,[11] the electronic structure of the interface between ferroelectric and electrode,[12] and gradients induced by strain, defect concentration profiles, or electrode work functions[13,14] are only examples. With so many possible extrinsic influences, many of which are not readily quantifiable, it has been difficult to ascertain what the fundamental response of thin film ferroelectrics is, and whether or not apparent changes in behavior are due to reduced dimensions, or due to some combination of the extrinsic influences brought to bear. This issue has assumed increased importance with the advent of ferroelectric-based memory technology,[1,15] and has prompted the authors to attempt experiments on a paradigm system of free-standing single crystal thin film ferroelectric, made using a focused ion beam microscope (FIB).[16–18] Previous work[16,17] has shown that permittivity changes, and smearing of the Curie anomaly seen in conventional thin film studies are neither inherent to reduced size, nor to unavoidable physics associated with the electrode-ferroelectric interface.

The work described herein focuses on the domain configurations seen in thin film lamellae of BaTiO$_3$, in a thickness regime relevant to ferroelectric memory cells: Samsung and Matsushita are currently developing commercial computer memories with thicknesses $\sim$120 nm.[19] The present laboratory limit of 280 ps for the switching speed of such memories[20] is fundamentally limited by domain size, and hence establishing the manner in which domain sizes scale with thickness, within this size regime, is a current priority.

II. THEORY

The proportionality between the square of the domain width (w^2) and the thickness of a parallel-sided slab (d) was initially proposed by Kittel for ferromagnetic materials, but it has been proposed as a general property of ferroic domains of any kind: ferromagnetic [Kittel, 1946 (Refs. 21 and 22)], ferroelectric [Mitsui and Furuichi, 1953 (Ref. 23)], and ferroelastic [Roytburd, 1976 (Ref. 24)]. This is because the free energy associated with the domains in a ferroic material has at least two components, one from the energy of the domains themselves, which is proportional to the domain size (w), and another coming from the domain walls. The number of domain walls is inversely proportional to the domain size ($1/w$), while the domain wall energy is proportional to the domain wall area, which itself scales directly with the film thickness (d). Using U and γ as constants of proportionality, this leads to the expression

$$F = Uw + \gamma\frac{d}{w}. \qquad (1)$$

Under equilibrium conditions ($dF/dw=0$)

$$w^2 = \frac{\gamma}{U} d. \tag{2}$$

When U is magnetostatic this becomes Kittel's law;[21,22] when it is electrostatic, it is Mitsui and Furuichi's law;[23] and when it is elastic, it is Roytburd's law.[24] For ferroelectrics, the formation of antiparallel (180°) c-axis stripe domains is driven by the electrostatic energy of the uncompensated dipoles at the surface. In this case, Eq. (2) becomes, according to Mitsui and Furuichi[23] and Kopal *et al.*[25]

$$w^2 = \frac{\pi^3 \varepsilon_0 \gamma (1 + \sqrt{\varepsilon_a \varepsilon_c})}{8.42 P_0^2} d, \tag{3a}$$

where P_0 is the polarization, ε_0 the permittivity of free space, ε_a and ε_c are the permittivities of the ferroelectric, parallel to the a and c crystallographic axes, respectively. Streiffer *et al.*[26,27] give a very slightly altered expression

$$w^2 = \frac{2\pi^3}{8.42} \frac{\varepsilon_0 \varepsilon_{ext} \gamma \left(1 + \dfrac{\sqrt{\varepsilon_a \varepsilon_c}}{\varepsilon_{ext}}\right)}{P_0^2} d. \tag{3b}$$

Streiffer *et al.*'s equation[26] includes the important factor ε_{ext}, the dielectric constant of the substrate (neglected by previous authors who assumed free-standing crystals), which is 1 for air, but ~300 for $SrTiO_3$ substrates, at room temperature.

The theory of stripe domains was extended by Roytburd,[24] and later by Speck and Pompe,[28,29] and Pertsev and Zambilgotov[30] to ferroelectric-ferroelastic materials, where domains with polarization pointing alternately at 90° are produced so as to minimize the elastic strain energy. In this case the relevant equation is

$$w^2 = \frac{4\pi^3}{8.42} \frac{\gamma d}{G(s_a - s_c)^2}, \tag{3c}$$

where G is the shear strain and s_a, s_c are, respectively, the strains of the short and long lattice parameters of the tetragonal film. Note that this equation is completely analogous to that of the c-axis polar domains, where the dielectric stiffness is substituted by the elastic stiffness, and the polarization is substituted by the strain.

All these equations are predicted to break down at very small thickness. For ferroelectric 180° stripe domains the critical thickness[25] is

$$d_{crit} = 5\pi\gamma\varepsilon_0 \sqrt{\frac{\varepsilon_c{}^2}{\varepsilon_a} \frac{1}{P_0{}^2}}. \tag{4}$$

While for ferroelastic domains the critical thickness[24] is

$$d_{crit} = 10\gamma \frac{1}{G} \frac{1}{(s_a - s_c)^2}. \tag{5}$$

The critical thickness for 180° domains in $BaTiO_3$ and $PbTiO_3$ is of the order of 1 nm, while for ferroelastic domains (assuming s_a and s_c are the spontaneous strains) it is of the order of 5 nm, so that, in theory, ferroelectric/ferroelastic domains should follow Kittel's law[21,22] well into the nanometer regime. The data presented below illustrate the success of the Kittel/Roytburd treatment in single crystal ferroelectric material.

III. EXPERIMENT

Single crystal lamellae of $BaTiO_3$ (15×15 μm^2) were cut to a range of thicknesses between 70 and 530 nm using FIB (FEI 200TEM) as described in previous work.[16,17] All specimens were cut with faces approximately parallel to $\{100\}_\mathrm{cubic}$ in the $BaTiO_3$. Three types of samples were cut: flat, terraced, and wedged in cross-sectional profile. The later two types allowed us to access different thicknesses within the same sample. This removed the intersample variability, but also allowed examination of the manner in which the domain width adapts to thickness gradients. Thickness was measured by secondary electron imaging during and after FIB processing.

For examination of domain structure, the lamellae were cut free from the surrounding bulk $BaTiO_3$ crystal, and were lifted using a fine glass needle and micromanipulator under an optical microscope, and transferred onto a carbon coated 3 mm copper-mesh grid. Imaging was then performed using scanning transmission electron microscopy (STEM) on a 200 kV field-emission transmission electron microscope (FEI Tecnai F20), using a high-angle annular dark-field detector. Specimen imaging was performed with the electron beam parallel to ⟨100⟩-type zone axes (approximately perpendicular to the lamellar face).

IV. RESULTS AND DISCUSSION

Figure 1 shows a plan-view STEM image of a single crystal lamella of $BaTiO_3$. The image shows clusters of stripe domains with domain walls parallel to $\{110\}_\mathrm{cubic}$, characteristic of 90° domains associated with in-plane oriented polarization. The general diffraction pattern [Fig. 1(b)] and enlarged diffraction spot [Fig. 1(c)] illustrate both the domain wall orientation and periodicity. The domain width could either be measured directly from real-space images, or by measurements of periodicities from diffraction patterns [such as Fig. 1(c)]. In general, for the data presented, real space measurements were used across a series of images for each lamellar thickness, with diffraction information acting as confirmatory evidence.

Figure 2 shows the measured domain period (or wavelength, $2w$) as a function of the square root of the lamellar thickness, demonstrating adherence to the $w^2 \propto d$ relation. The apparent 90° domains, and in-plane polarization, might suggest that the formation of domains is not driven by electrostatic energy at the lamellar surface, but is rather related to an attempt to minimize macroscopic strain in the lamella. It could be that this has arisen because thermal processing above the Curie temperature, and subsequent cooling to room temperature, was initially performed before the lamellae were lifted free from the bulk $BaTiO_3$ crystal (hence they were shape constrained to a degree on passing through T_c). However, to investigate this further, free-standing lamellae which had been lifted out onto the carbon-coated TEM grids were furnace heated to 200 °C, allowed to cool, and their

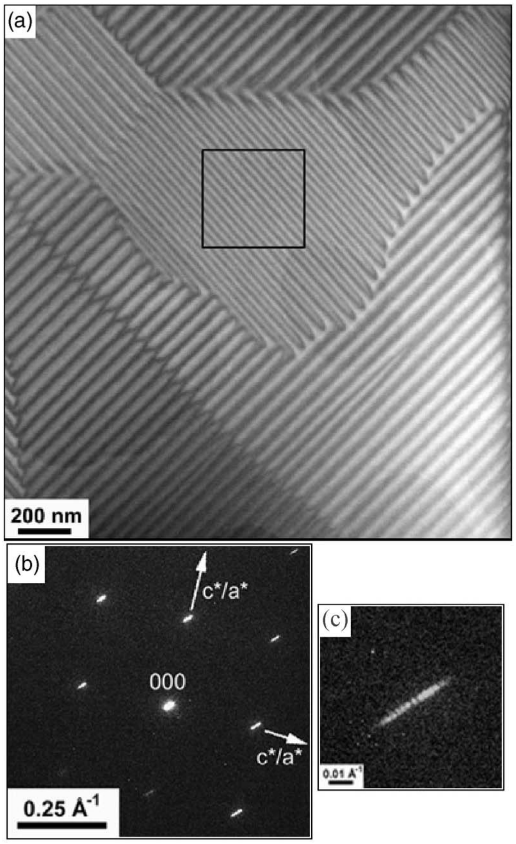

FIG. 1. (a) STEM image of a single crystal lamella which contains areas of parallel domain walls, (b) the diffraction pattern taken from the region above marked by a square, and (c) a detailed view of the intensity around a single Bragg peak showing the domain periodicity.

domain structure reexamined. We found no change in the measured domain periodicity. Perhaps the thin holey carbon support creates enough shape constraint for the development of shape-conserving 90° domains, but this seems somewhat surprising.

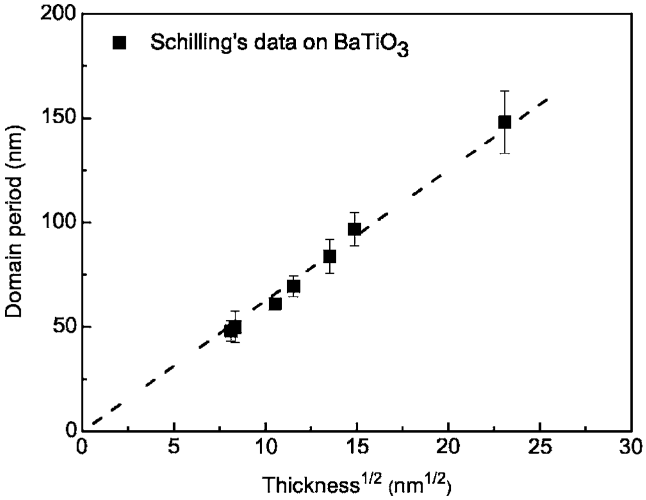

FIG. 2. Thickness dependence of the domain width (expressed as period) in the single crystal BaTiO$_3$ lamellae, measured from STEM images. Data illustrate adherence to the $w^2 \propto d$ relation.

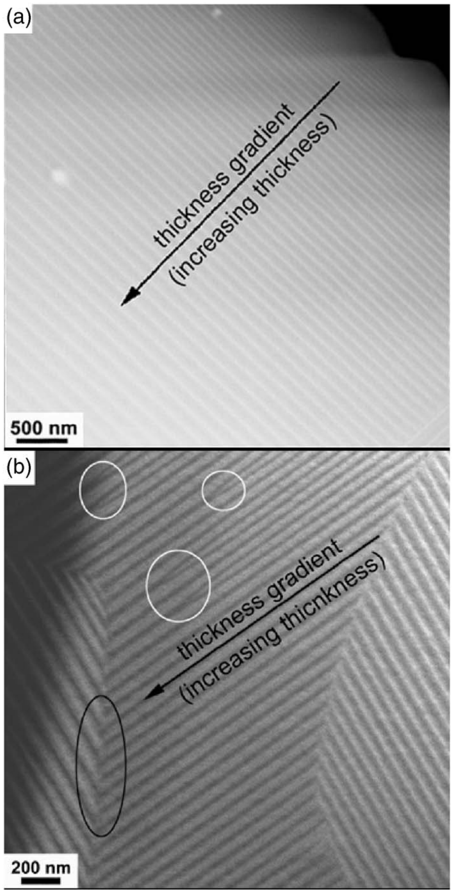

FIG. 3. STEM images of a lamella (with wedge shaped cross-section) showing that: (a) domains perpendicular to the thickness gradient become narrower with decreasing the thickness; (b) domains parallel to the thickness gradient increase their density by bifurcation.

In any case, the orientation of polarization suggests that rationalization of the domain widths should initially be made according to Roytburd's rather than Mitsui and Furuichi's treatment. Using values for the energy density of 90° domain walls (γ) of $\sim 3 \times 10^{-3}$ J m^{-2},[31] a shear modulus (G) of 55 GPa (Refs. 32 and 33) and the spontaneous strains along the a and c axes in BaTiO$_3$ at room temperature for s_a and s_c, one obtains a constant of proportionality in the $w^2 \propto d$ relation (s, where $s = w^2/d$) of 8.5×10^{-9} m. This is in reasonable agreement with our experimentally obtained value of 9.8×10^{-9} m, and thus it appears that the Roytburd treatment is appropriate.

Three mechanisms were found by which the domain periodicity can alter with a thickness change in the same lamellar sample. Figure 3 illustrates domain configurations in a wedge-shaped sample, where the change in gradient was continuous. In Fig. 3(a), the thickness gradient is perpendicular to the domain walls. In this case the domains can continuously get narrower as the thickness decreases. In the second image [Fig. 3(b)], two further adaptive mechanisms were identified: needle-type bifurcation in domains parallel to the thickness gradient [emphasized in Fig. 3(b) by white circles], and discrete period changes at the interface between clusters of stripes perpendicular to each other [emphasized in

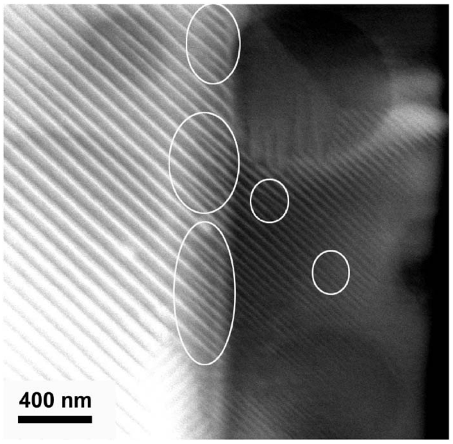

FIG. 4. STEM image across a thickness ledge in a $BaTiO_3$ single crystal lamella that had been FIB patterned with terraces of different thicknesses, and sharp gradient changes between terrace levels. Strong bifurcation around the ledge can be seen.

Fig. 3(b) by a black circle]. The later two mechanisms are interesting in that they respond to continuous thickness changes in discrete steps, with the bifurcation mechanism suggesting analogies with misfit dislocations. Figure 4 suggests that such bifurcation is the dominant mechanism for domain periodicity change when the change in thickness is sudden (across a ledge between two flat terraces of differing thickness).

To attempt to put the data obtained in this study into a broader context, Fig. 5 illustrates, on a double-logarithmic scale, the values of domain width w versus d for all our $BaTiO_3$ samples, together with data for $PbTiO_3$ thin films (on $SrTiO_3$) (Ref. 26) and bulk crystals of Rochelle salt (in air).[23] The results show that Kittel's relation remains valid over more than six decades in thickness from the millimeter to the nanometer range (already essentially shown by Streiffer *et al.*[26]). Perhaps more importantly, however, since all three ferroelectric data sets lie on approximately the same line, it suggests that the constant of proportionality s is largely independent of the material under examination. Moreover, it is also largely independent of the boundary conditions at the surface of the ferroelectric and independent of whether or not 90° or 180° domains are being considered (and hence whether it is elastic or electrostatic conditions governing the energetics of domain formation). We currently have no clear rationalization for this observation, but it is certainly intriguing. Parenthetically, we note that, in addition, recent work has shown[34–36] that the Kay-Dunn law of 1962 (Ref. 34) for coercive field versus thickness is also satisfied over the same six decades from $d=2$ nm to 2 mm.

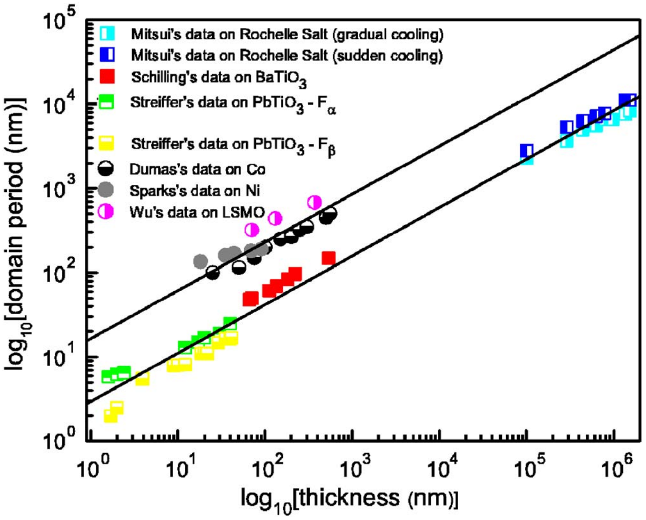

FIG. 5. (Color online) Thickness dependence of domain period for three ferroelectrics and three ferromagnets. The ferroics clearly form into two distinct groups, one ferroelectrics, the other ferromagnets, with similar prefactors in the Kittel-type relation for the members in each group. Datasets other than those obtained in this study were taken from literature (Refs. 23, 26, and 37–39).

The experimental validity of the observation is further illustrated in Table I, where Kittel's relations of the form of Eqs. (3a) and (3b) have been reexpressed as

$$w^2 = kRd \text{ or } w = k^{1/2}R^{1/2}d^{1/2}, \qquad (6)$$

where $R=\varepsilon_0\varepsilon_{ext}\gamma(1+\sqrt{\varepsilon_a\varepsilon_c})/P_0^2$, and k is a geometric factor. Using literature for permittivity and polarization information, the room temperature R and $R^{1/2}$ values have been calculated for $PbTiO_3$ (in vacuum and bounded by $SrTiO_3$), $BaTiO_3$ and Rochelle salt, and all lie within approximately an order of magnitude of each other. Moreover, the value of R calculated for $BaTiO_3$ based on Kittel's expression using electrostatic properties (1.3×10^{-9} m) is relatively close to the

TABLE I. Calculated R values from $R=\varepsilon_0\varepsilon_{ext}\gamma(1+\sqrt{\varepsilon_a\varepsilon_c})/P_0^2$; γ is calculated from $\gamma(T)=\gamma_0(P_0^*(T)/P_0^*(0))^3$. All parameters are expressed in S. I. units.

Material	γ ($J\ m^{-2}$) (Refs. 40–44 and 23)	ε_a (Refs. 44, 45, and 23)	ε_c (Refs. 42, 45, and 23)	P_0 ($C\ m^{-2}$) (Refs. 42, 46, and 23)	R (m)	$R^{1/2}$ ($m^{1/2}$)
$PbTiO_3$	9.00×10^{-2}	124	66	0.75	1.3×10^{-10}	1.1×10^{-5}
$PbTiO_3$ (on $SrTiO_3$)	9.00×10^{-2}	124	66	0.75	5.5×10^{-10}	2.4×10^{-5}
$BaTiO_3$	1.00×10^{-2}	4000	200	0.25	1.3×10^{-9}	3.6×10^{-5}
Rochelle salt	1.00×10^{-5}	445	9.8	1.40×10^{-3}	3.0×10^{-9}	5.5×10^{-5}

equivalent calculated parameter in Roytburd's expression [Eq. (3c)] based on elastic properties (5.8×10^{-10} m).

Figure 5 also illustrates data corresponding to three magnetic materials: Co data from Dumas *et al.*,[37] Ni data from Sparks *et al.*[38] and the colossal magnetoresistive material (La,Sr)MnO_3 data from Wu *et al.*[39] First, broad adherence to a Kittel's relation is noted; second, these data suggest that there is clearly a different coefficient of proportionality in the Kittel's relation for ferromagnets than for ferroelectrics. Thus by inspection of literature data alone, it would appear that ferroelectrics adhere to one universal Kittel's relation, and ferromagnets to another.

Some insight might be gained by consulting the work of Zhirnov[31] and rewriting Eq. (6) as

$$\frac{w^2}{\delta d} = M, \tag{7}$$

where δ is the wall width separating domains. In this expression, M is a dimensionless ratio of order 1–10 that depends upon independently determined parameters. It is then the widths of domain walls that determine any gross differences in constants of proportionality in the relations such as those proposed by Kittel. Since ferroelectric domain walls are considerably thinner than ferromagnetic ones,[21,22,31] the distinct difference in their relative positions in Fig. 5 can then be rationalized. Using Kittel's analysis for ferromagnets,[21,22] the domain wall width is determined by the square root of the ratio of the exchange energy integral (A) to anisotropy energy (K) in the particular ferroic system of interest. Hence Eq. (7) may be more fundamentally expressed as

$$\frac{w^2}{d}\left(\frac{A}{K}\right)^{-1/2} = M \tag{8}$$

and it may be then obvious that each kind of ferroic will have characteristic exchange and anisotropy characteristics irrespective of minor material or surface boundary specific variations.

There is no doubt, however, that further addition of experimental data for domain widths, and work on understanding the behavior of the constants of proportionality in the Kittel relations is needed.

V. CONCLUSIONS

The domain widths in single crystal $BaTiO_3$ lamellae, of controlled thickness between 530 and 70 nm (made using focused ion beam milling) were found to vary as the square root of the lamellar thickness, consistent with Kittel's law, and its later development by Mitsui and Furuichi and by Roytburd. Adaptation of domain periodicity to accommodate changes in thickness within the same lamella were observed, with interesting domain bifurcation occurring whenever domain walls were parallel with thickness gradients.

When the data obtained on the single crystal $BaTiO_3$ lamellae were then compared with other work in the literature, on both ferroelectric and ferromagnetic systems, the following observations were made:

(i) Kittel's law holds across six orders of magnitude in thickness for ferroelectrics;

(ii) despite differences in the materials, the surface boundary conditions, and the controlling influence in domain formation being either electrostatic or elastic, the constant of proportionality in Kittel's law is similar for all ferroelectrics plotted;

(iii) there is a distinct difference between the constant of proportionality in Kittel's law for ferroelectrics and for ferromagnets, but this may be accounted for by consideration of differences in exchange and anisotropy energies.

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