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Nanodomain Patterns in Ultra-Tetragonal Lead Titanate (PbTiO₃)

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Abstract:

Very recently, the discovery of ultra-tetragonal PbTiO₃ thin films was reported [L. Zhang *et al.*, Science, **361**, 494 (2018)], in which the switchable out-of-plane polarization was seen to be almost twice that of any previously known ferroelectric. To understand more about this system and to explore features that might contribute to these remarkable functional properties, we have mapped the polarisation microstructure on the nanoscale using piezoresponse force microscopy (PFM) (scan sizes less than 700 nm). Our study reveals an extremely fine-scale pattern, with individual domains typically 20-50nm in size, all of which exhibit both out-of-plane and in-plane polarisation components. In-plane vector PFM polarisation maps show strongly charged quadrant-lattice domain arrays with four-fold domain wall junctions (vertices). The existence of four-fold vertices in ferroelectrics is rare but can be explained via the 'Ashkin-Teller' model, in which very large interfacial lattice mismatch strains and local electric fields play a role. This ultra-tetragonal ferroelectric system was expected to contain straightforward c-axis out-of-plane 180° domains, but instead shows an extremely rich nanoscale domain tiling pattern; these unusual nanodomains may be important in facilitating the extremely high switchable polarisation values previously reported.

Domain wall vertices (or meeting points) are established and ubiquitous features in ferroelectric microstructures^{1,2,3,4}, but historically they have not been considered as being particularly important. This view is now changing: from an applied point of view, domain wall vertices have already been seen to act as 1D electrically conducting channels (in BiFeO₃ thin films⁵); in addition, in some rare-earth manganite systems^{6,7,8}, 1D p-n junctions should form at six-fold vertices, where both conducting head-to-head (n-type) and tail-to-tail (p-type) domain walls meet; new forms of domain wall Josephson junctions have even been proposed, in systems such as WO_{3-x} where domain wall superconductivity has already been established.^{9,10} From a fundamental point of view, the energetics associated with domain wall vertex formation, dynamics¹¹ and the underpinning physics associated with their topological form are interesting and relatively unexplored; basic ideas are certainly much less well developed than they would be for domain walls, for example.

A phenomenological description by Srolovitz and Scott¹², based on Potts and clock models, provides some theoretical basis upon which different vertex configurations may be rationalised: it focuses on whether 4-fold “X” vertices or adjacent pairs of 3-fold “Y” vertices are stable and the mechanisms by which vertex coalescence or separation might occur. According to the model, a four-state Potts model is required to describe the domain wall vertices in either of the two cases. However, to explain pairs of adjacent Y-shaped three-fold vertices, the Potts model involves scalars only (a simple extension of an Ising model). In contrast, a vector Potts model (“clock model”) is required to describe the stable existence of four-fold vertices. In general, a given ferroelectric can exhibit three-fold or four-fold vertices, but not both. It is also useful to point out that the general question in nature of whether four-fold or three-fold vertices are stable is rather well examined. In two dimensions, Voronoi partitions (domain walls in the present context) subdivide space into four quarters only when the objects of interest are symmetrically placed on the vertices of a rectangle (nucleation sites at defects in the present example). Otherwise, any other configuration generates closely spaced pairs of three-fold vertices. This is a result of the growth of domains from initial nucleation sites to fill two-dimensional Euclidean space.¹³ The collapse of four-fold vertices into adjacent pairs of three-fold vertices is further considered by Opperman¹⁴, who also emphasizes qualitative changes in dynamics due to axial anisotropy. In general, static experimental observations in ferroelectrics suggest that pairs of separated three-fold vertices are more stable than more compact four-fold “core” vertex geometries.^{15,16,11} However, the converse may become true in thin films where the energetics may be dominated by the presence of a strong internal/external electric field. A very few systems illustrate both cases. This does not violate the Srolovitz-Scott model, but rather implies that the interaction parameter is anisotropic, with out-of-plane polarized domains satisfying a scalar Potts model and in-plane polarized domains satisfying a vector “clock” model. This behaviour has only

been seen in lead strontium titanate (PST),¹⁷ where pairs of three-fold vertices are found and – “very rarely” – a few four-fold vertices, and SrBi₂Ta₂O₉ (SBT) which exhibits both three-fold and four-fold vertex geometries.

It is within this context, where domain wall junctions should be explored more fully, that we report the existence of quadrant lattice domain arrays and four-fold in-plane domain vertices in the rather exotic ultra-tetragonal PbTiO₃ thin-film ferroelectric system. It is well understood that negative pressure, induced by tensile strain, can result in dramatic changes in the structure and functionality of perovskite oxides, particularly in the case of ferroelectrics.¹⁸ One of the novel approaches to achieve this effect in thin epitaxial ferroelectric films is through the realisation of ‘interphase strain’, where two materials with similar crystal structures but different lattice parameters can be grown as a single epitaxial composite film such that their lattice parameters are matched. The isotropic strain generated in the individual phases, as a result of such lattice-matching, can induce negative pressure, thereby generating enhanced polarization, elevated Curie temperatures and large *c/a* ratios. This concept has recently been realised in PbTiO₃ (PTO) - PbO epitaxial composite ferroelectric thin films, where the PTO phase exhibits giant switchable polarisation of approximately 236 $\mu\text{C}/\text{cm}^2$ (nearly twice the record polarisation reported in any ferroelectric).¹⁹ The effect of such enhanced interphase strain on the functional aspects of this film have been examined macroscopically in the previous work.¹⁹ Commensurate with the dramatic enhancement in polarisation, it is expected that the enhanced strain would also influence the nanoscale domain structure of the PbTiO₃ film, both in terms of periodicity as well as complexity of the domain patterns. Previous scanning probe investigations were undertaken on the mesoscale (several μm) and did not reveal domain microstructures clearly. To address this, we investigate the nanoscale domain structure of this material using piezoresponse force microscopy (PFM). Surprisingly, dense domains (with domain diameters 20-50 nm in size) with both out-of-plane as well as in-plane polarisation components are observed. The in-plane polarisation mapping reveals quadrant lattice domain arrays, four-fold in-plane domain vertices and prolific occurrence of apparently charged domain walls in the same region.

The studied films were grown by radio-frequency magnetron sputtering using a PbTiO₃ target, which was sintered at 1100 °C for 2 hours. The samples were 50 nm thick and grown on 0.7 wt% Nb-doped SrTiO₃ substrates. Details of the growth conditions have been reported elsewhere.¹⁹ The PFM measurements were undertaken on an Oxford Instruments MFP-Infinity Atomic force microscope. The crystal structure of the films was investigated using x-ray diffraction (XRD), which was performed on the diffractometer (PW3040/60, PANalytical, Holland) with Cu K α radiation. Single-frequency piezoresponse force microscopy (PFM) has

been employed to investigate the nanometre scale domain structure in the studied strained PTO film. The out-of-plane X-ray investigation on these films, grown on (100) STO substrates, suggests lattice parameters consistent with the PT(I) phase previously reported by Zhang *et al.*, thus indicating large c values and consequently a large c/a ratio (as shown in Fig. 1(a). The reciprocal space map for the 103 Bragg peak of the studied film has been provided in supplementary information (Fig. S1 in supplementary information); it demonstrates that the in-plane lattice parameter is the same as that of the substrate, and that the PTO film is hence demonstrating a super-tetragonal unit cell, commensurate with previous work.¹⁹ In this context, the out-of-plane vertical piezoresponse of the sample was first examined by applying 4V AC to a metal-coated PPP-EFM Nanosensors tip with a tip-surface contact resonance at 330 kHz (the chosen frequency was close to the contact resonance and bias value was chosen for best contrast). As shown in Fig. 1(b), the surface of the film is quite smooth (roughness < 2nm) but shows some contrast in terms of granularity. The vertical phase and amplitude maps (Fig. 1(c) and 1(d)) show evidence of up and down domains on a very fine scale, where the average size of the domains ranges from 50-80 nm.

Mapping on finer length scales (550 nm x 550 nm), the out-of-plane PFM contrast becomes even clearer, as shown in Fig. 2(a-c). Surprisingly, good in-plane contrast in lateral PFM measurements was also observed for exactly the same region (see matching topographies in Fig. 2(a,d,g)). These lateral PFM measurements were undertaken by applying 4V ac with frequency closer to the lateral tip-surface resonance (650 kHz) and the measurements were conducted in two perpendicular tip-sample orientations (sample rotated with respect to the tip). In both orientations, the amplitude and phase images (Figs. 2(e-f) and 2(h-i)) are well resolved and reveal domain widths on the scale of ~ 50 nm. Overlays of vertical and lateral PFM responses onto the topography of the film are provided in supplementary information (Fig. S2 in supplementary information). Lateral PFM signals (amplitude and phase) show correlations across many grains in strips – perhaps indicative of grain-to-grain polarisation coupling. Vertical PFM response shows correlations with the undulations (~2 nm) in topography. Any concerns about cross-talk were, however, allayed by nearly identical VPFM scans observed at different scan angles (Fig. S3 in supplementary information) as well as observations of tip-induced switching which show domain growth and relaxation, unrelated to the sample topography (Figs. S4 and S5 in supplementary information). Overall, PFM data reveals that the domains in this epitaxial composite film have both in-plane as well as out-of-plane components, prompting a more careful analysis of the domain microstructure. Rcinshi *et al.* have shown that strain can produce in-plane and out of plane domains in the same surface²⁰ depending upon sample thickness and strain. Hence, the observation of both in-plane and out-of-plane polarisation components in this film is not entirely unexpected.

The two in-plane lateral PFM images obtained upon rotating the sample with respect to the tip by 90° were merged to obtain the ‘vector’ map of in-plane polarisation observed in the sample. The phase images were both corrected to remove phase wrapping and binarised before merging them at every pixel (as shown in Fig. 3). The net in-plane polarisation map reveals quadrant lattice domain arrays with periodicities of around 100 nm. In these quadrant arrays, careful analysis of the polar directions reveals alternating convergence and divergence at vertices (centred-type patterns). As a result, the domain configuration suggests surprising but prolific existence of apparently charged walls. It should be noted that such measurements have been made carefully on two different sets of films and found to produce the same form of microstructure. To investigate the electronic properties of the charged walls, conduction mapping was undertaken by applying $\pm 12\text{V}$ to the bottom electrode, but no observable current was obtained across the sample; this does not necessarily imply that the charged domain walls are electrically insulating, as the PbO lenses in the microstructure might prevent conduction pathway percolation through the entire film thickness.

Importantly, most of the vertices observed in this combined in-plane polarisation map are four-fold. These four-fold vertices are expected by Srolovitz and Scott¹² under conditions identified in the Ashkin-Teller model, named after the scientists who first published the relevant equivalent interaction ideas.²¹ It is still studied in the case of a large externally applied field,²² which may be the case here, given the large interfacial lattice mismatch strain and preponderance of charged polarisation patterns. We emphasize that in the absence of such a large field, three-fold vertices are generally dominant. In the composite lateral map shown in Figure 3 however, we observe very few three-fold vertices. Moreover, it is evident from Fig. 2 that the film has co-existing in-plane and out-of-plane polarisation components. By merging the in-plane vector map obtained in Fig. 3 with Fig. 2(c) (phase cleaned and binarised), we obtain a 3D visualisation of the domain microstructure which presents as an even more complex domain pattern shown in Fig. 4. The visualisation suggests that the ‘apparent’ charged walls (discussed in Fig. 3) retain their charged nature even after the inclusion of out-of-plane domain orientation information.

In light of the observation of the dominance of four-fold vertices in the in-plane domain maps, we can discuss another possible physical reason for why the out-of-plane domains satisfy a scalar Potts model and the in-plane domains conform to the vector Potts prediction. It is worth pointing out that these domains are not topologically equivalent, with out-of-plane polarizations allowed to be only up or down while the in-plane domains are allowed to be oriented along four directions. In two dimensions, closely spaced pairs of three-fold vertices is the preferred case (for Voronoi partitions and domain walls) and Weaire and Aste describe this^{23,24} as a two-dimensional law. However, in three dimensions the opposite is true, and four-

fold vertices are stable. Our films (~50 nm thick and roughly equal to the size of lateral domains) represent a pseudo two-dimensional system, and thus could behave like a three-dimensional system. Consequently, the change of vertex geometry from four-fold for in-plane polarisation to three-fold for out-of-plane polarization may derive simply from the effective dimensionality in the two cases. For the studied system, we prefer the strong axial field model²¹ as an explanation (Ashkin-Teller model) for our observed four-fold in-plane vertices, but include the Voronoi discussion for completeness. It is also interesting to note that the observed domain walls are charged, meaning polar discontinuities could create strong electric field which could drive the existence of four-fold vertices as seen in in-plane polarisation maps.

An unusual feature of the maps presented in Fig. 4 is that eight domain orientations are implied (Fig. 4(c)), as opposed to the six expected for the tetragonal and supertetragonal states. While there may be a possibility that the PTO has adopted another symmetry (a pseudo-rhombohedral state for example), we suspect a more mundane origin: eight apparent domain variants would appear under vector PFM analysis if the microstructure were composed of finescale 180° domains (with polar axes pointing into and out of the plane of the film), as long as the physical orientations of unit cells could meander slightly across the film surface. Such mosaicity, due to a range of very slight crystallographic misorientations or lattice bending, could readily result from coherent cloaking of the subsurface PbO lens structures, which are such a characteristic microstructural feature in these supertetragonal films. Moreover, mosaicity would be consistent with the slight curvature of the 103 Bragg reflection seen in reciprocal space maps (Fig. S1 of the supplementary information) and the absence of multiple diffraction spots and Bragg splitting normally seen in conventional ferroelastic domain microstructures.

In summary, detailed nanoscale mapping of polarisation variants in an ‘interphase-strain’ mediated composite epitaxial film of PbTiO₃ reveals surprising co-existence of out-of-plane and in-plane polarisation components. The in-plane polarisation maps reveal the existence of four-fold vertices and quadrant lattice domain arrays on remarkably small scales (a few tens of nanometers). The existence of four-fold vertices in ferroelectrics is relatively rare and can be explained via the ‘Ashkin-Teller’ model, applicable due to very large interfacial lattice mismatch strain and electric fields from charged dipole configurations.

See supplementary material for additional information regarding XRD studies, overlays of PFM images on topography and results of attempts to switch the ferroelectric domains in limited voltage range.

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Figures

Figure 1: Ultra fine domain structure in super-tetragonal thin films (a) X-ray diffraction (XRD) data illustrating the out-of-plane (00l) peaks for the PT(1) film as described in reference [19]. (b) Nanoscale topography of a representative region of this film shows reasonably smooth contrast overall (RMS roughness < 1nm) but fine-scale granular features are obvious. Vertical piezoresponse force microscopy (VPFM) amplitude (c) and phase (d) for the same region show distinct polarisation states (up and down). It is notable that the domain structure is very fine: the typical domain width is around 50-70 nm. The scale bar shown in (b) measures 390 nm.

Figure 2: Out-of-plane and in-plane piezoresponse force microscopy (PFM) in super-tetragonal thin film (a-c) Topography (a), vertical PFM amplitude (b) and vertical PFM phase (c) from a region of the film surface; (d-f) Topography (d), lateral PFM amplitude (e) and lateral PFM phase (f) for the same region as that shown in (a-c) (key topographic features are maintained); the cantilever orientation with respect to the sample is shown in panel (f) (as are the associated senses of the in-plane polar components); (g-i) Topography (g), lateral PFM amplitude (h) and phase (i) in the same region (again key topographic features remain the same) for the cantilever oriented perpendicular to that associated with panels (d-f). The scale bar measures 110 nm.

Figure 3: Collated lateral piezoresponse force microscopy (PFM) information shows in-plane quadrant lattice domain arrays and the prolific existence of charged domain walls. Information from binarised in-plane domain maps (a) and (b) (from lateral PFM taken with the cantilever in two perpendicular orientations) is combined to create the vector map shown in (c). The colours in (c) indicate the direction of the in-plane components of the polar vector at each location. The scale bars in (a-c) measure 110 nm.

Figure 4: Inclusion of out-of-plane domain orientation information suggests an even more complex domain pattern. The merged in-plane map obtained in figure 3 is further merged with a binarized out-of-plane piezoresponse force microscopy (VPFM) map to obtain a three-dimensional visualisation of the polar variants at each pixel. The manner in which the colours map onto the sense of the resolved 3-D polar vector are made clear in the right-hand schematic. The scale bars in (a,c) measure 110 nm.