Fractal Dimension and Size Scaling of Domains in Thin Films of Multiferroic $BiFeO_3$

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Domains in ferroelectric films are usually smooth, stripelike, very thin compared with magnetic ones, and satisfy the Landau-Lifshitz-Kittel scaling law (width proportional to square root of film thickness). However, the ferroelectric domains in very thin films of multiferroic $BiFeO_3$ have irregular domain walls characterized by a roughness exponent 0.5–0.6 and in-plane fractal Hausdorff dimension $H_{\|} = 1.4 \pm 0.1$, and the domain size scales with an exponent 0.59 ± 0.08 rather than $\frac{1}{2}$. The domains are significantly larger than those of other ferroelectrics of the same thickness, and closer in size to those of magnetic materials, which is consistent with a strong magnetoelectric coupling at the walls. A general model is proposed for ferroelectrics, ferroelastics or ferromagnetic domains which relates the fractal dimension of the walls to domain size scaling.

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Magnetoelectric multiferroics are currently attracting considerable attention on account of their interesting physics and potential applications [1]. Among these materials, one of the most studied is the perovskite $BiFeO_3$ (BFO), a room temperature magnetoelectric multiferroic (ferroelectric and antiferromagnetic) [2,3]. Its lead-free nature and large remanent polarization [4] have already motivated Fujitsu to use it as the active layer in prototype ferroelectric memories [5]; also, sublattice magnetic switching using voltage has been demonstrated [6], which may find its way into spintronic applications via exchange bias [7]. The possible coupling between ferroelectric and antiferromagnetic domains has triggered a flurry of work on the morphology and functional properties of the domains [6,8–11]. Standard BFO films are generally found to have straight-walled domains which follow the well-known scaling law of Landau, Lifshitz, and Kittel (LLK) [12–14], that is, domain width grows proportionally to the square root of film thickness [10].

The room-temperature rhombohedral phase is normally monoclinic for epitaxial thin films, but the monoclinic distortion is either very small or possibly nonexistent (being tetragonal instead) below a critical thickness, which for BFO grown epitaxially on $SrTiO_3$ substrates is of the order of 100 nm [15]. In this Letter the morphology and scaling of the domains in the small-thickness regime has been analyzed in detail, and found to be qualitatively different from that observed at higher thickness: (i) the domains are not straight, but irregular in shape, with a domain wall roughness characterized by a fractal-like Hausdorff dimension; (ii) the ferroelectric domains are bigger than those of "pure" (nonmultiferroic) ferroelectrics and closer in size to those of magnetic materials, suggesting strong magnetoelectric coupling at the domain walls, and (iii) the average domain size appears to depart from the usual LLK square root dependence on film thickness. The anomalous scaling may be directly related to the fractal Hausdorff dimension of the walls according to a simple model.

The thin films of BFO were grown by pulsed laser deposition on $SrTiO_3$ with a conductive buffer layer of (La, Sr)MnO_3 [16], and the ferroelectric domain morphology was studied by way of piezo-response atomic force microscopy (PFM). The shape of the spontaneous domains is highly irregular (Fig. 1). Films of 35 nm thickness or less displayed unit-cell steps in the topography, with the extra surface roughness likely to be due to adsorbates. Adsorbates can substantially modify the depolarization field and affect the out-of-plane domain morphology [17], as ob-

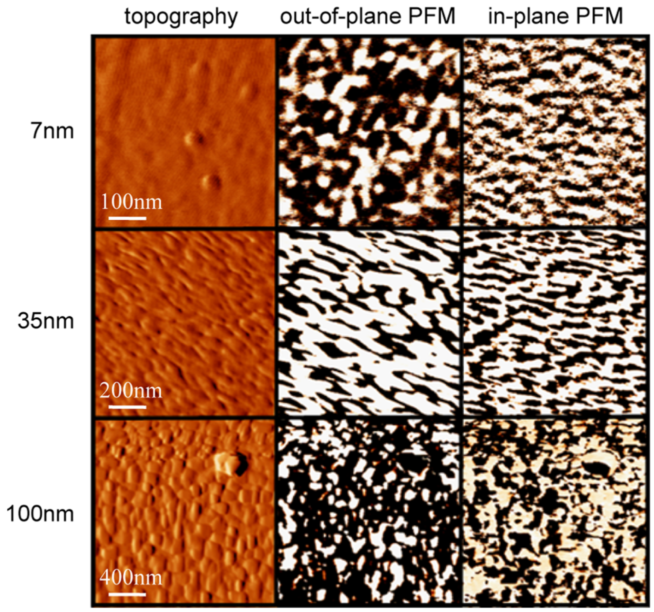

FIG. 1 (color online). Topography and PFM of domains in films of 7 nm, 35 nm and 100 nm. Surface roughnesses were, respectively, 0.2, 0.4, and 3.8 nm. The PFM cantilever was oriented along [100]. The scale bar is the same along each row.

served in several of our samples. Accordingly, only in-plane domains are analyzed here.

Domain periodicity was measured by either Fourier analysis of the PFM image or by simply counting the number of domains of a given polarity across a straight segment. Whenever the two methods could be applied (Fourier analysis is only possible when the periodicity is quite regular), they yielded the same results. The average domain periodicities are plotted in Fig. 2 in a log-log scale as a function of film thickness. For comparison, equivalent data for domains in other ferroic systems (ferroelectric or ferromagnetic) are included. Ferroelectric domains are generally smaller than ferromagnetic domains [18–21], but the ferroelectric domains in BFO are noticeably bigger, and close to the domain size of magnetic Co. This suggests a higher energy cost of the domain walls [21,22], consistent with a strong magnetoelectric coupling at the wall [6]. This contrasts with the apparently low intrinsic magnetoelectric coupling of the bulk material [23], and underlines the interest of domain walls as multiferroic entities in their own right [24].

A least squares fit of the domain period w as a function of film thickness d yields a power law $w = Ad^{\gamma}$, with a scaling exponent $\gamma \simeq 0.59 \pm 0.08$. The data set used for the analysis is small, and the average domain size is not as well defined as in stripe domains, so the empirical value should be treated with caution. Nonetheless, equivalent analyses performed on similar data sets have always yielded exponents closer to the classic value of 0.5 [10,20]. The bigger value of γ in the BFO films may instead be related to the irregularity of the domain walls, as discussed below.

Using the program WSXM [25], the ratio of domain perimeters (P) to areas (A) can be analyzed. The in-plane Hausdorff dimension of the domain walls ($H_{\parallel}$) is extracted using $P \propto A^{H_{\parallel}/2}$; if the domain walls were perfectly smooth, $H_{\parallel} = 1$, otherwise $1 \leq H_{\parallel} \leq 2$. Plotting log($P$) vs log($A$) for the domains in the different films (Fig. 3), values of $1.29 \leq H_{\parallel} \leq 1.52$ were found [26]. These are comparable with $H_{\parallel} \simeq 1.5$ found in written domains of BFO-doped lead zirconium-titanate (PZT) films [27].

The wall roughness of PFM-written linear domains, created by alternate applications of negative and positive voltage (±8 V) to the film surface, was analyzed (Fig. 4) using the pair-correlation method described by Paruch *et al.* [28]. The correlation function of relative displacements essentially measures the local variance of the wall position from an elastically ideal flat configuration as a function of the length L along the wall, and is predicted to show a power-law growth at equilibrium, governed by a characteristic roughness exponent ζ. We observe such a power-law growth at short length scales ($L < 100$ nm) followed by a saturation. The value of the roughness exponent $\zeta \sim 0.5$–0.6 is higher than that observed in PZT [28], and could be an indication of either a lower dimensionality (being close to the theoretically predicted

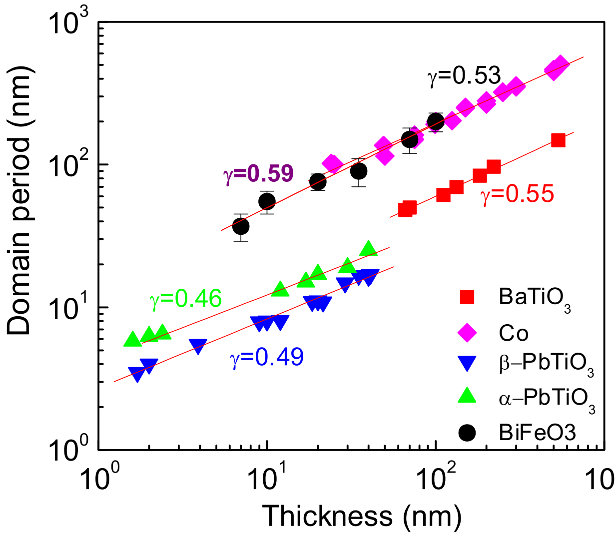

FIG. 2 (color online). Periodicity of in-plane domains as a function of BFO film thickness. The straight line is a least-squares fit giving a scaling exponent of 0.59 ± 0.08. We have also included the domain periodicity of other ferroics found in the literature.

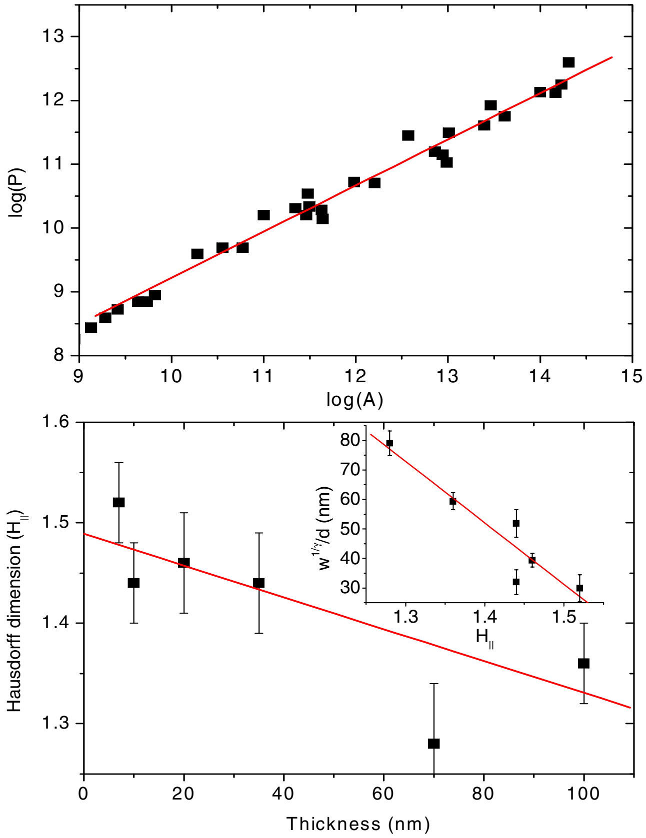

FIG. 3 (color online). Above, perimeter as a function of area for spontaneous domains in the 35 nm sample. The slope of the log-log plot is related to the Hausdorff dimension: $P \propto A^{H_{\parallel}/2}$. Below, Hausdorff dimension as a function of film thickness. (Inset) the domain periodicity renormalized as defined by Eq. (5), yielding a slope $= -208 \pm 40$ and intercept $= 344 \pm 56$.

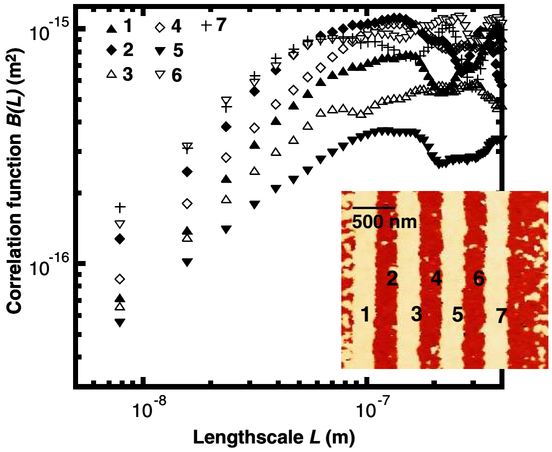

FIG. 4 (color online). Correlation function for the roughness of the written domain walls, measured for a 70 nm thick BFO film. An average value of the roughness exponent $\zeta = 0.56$ was obtained. This higher value of ζ for BFO compared to that for PZT suggests either a lower dimensionality in a random bond pinning scenario, or the presence of stronger individual pinning centers which could also be responsible for the fractal structure of the spontaneous domains in the BFO films.

value of $\zeta = 2/3$ for a one-dimensional elastic domain wall in random bond disorder potential), or possibly a different type of disorder [29]. There are additional self-consistency checks possible for domain dimensionality based on the dynamics of domain growth [28,30] and/or current transients [31,32]. The cause of the domain wall roughness is as yet unknown; it may be intrinsic, or else related to a combination of low in-plane anisotropy and defects -surface texture, vacancies, etc [33]. What interests us, however, is the effect that such roughness may have on the domain size scaling.

Smooth-walled domains, whether mosaic-type [14] or stripe-type (even when they have prefractal size distributions [34]) scale with the conventional $\gamma = 1/2$. On the other hand, the LLK law arises from the need to minimize the energy of the domains against that of the domain walls, so changing the ratio of one over the other (according the Hausdorff dimension) must necessarily affect size scaling. The energy density of the *domains* is proportional to their periodicity w, irrespective of whether they are stripe-type or mosaic-type [14]:

$$E_{\mathrm{domain}} = Uw, \tag{1}$$

where U is a constant arising from either depolarization, demagnetization, strain, or a combination of them. The energy of each wall is equal to its energy density σ times its surface (S), and S is equal to the domain perimeter P times the domain depth, assumed to be equal to the film thickness d; therefore $E = \sigma P d$. Since the domain perimeter scales fractally with the domain size ($P = w^{H_\parallel}$), the energy is $E = \sigma w^{H_\parallel} d$. The energy density (per unit area of film) is found multiplying the energy E of each wall by the number density of domains, which is inversely proportional to the domain area, i.e., $N \propto 1/w^2$. Therefore,

$$E_{\mathrm{walls}} = \sigma w^{H_\parallel} \frac{d}{w^2}. \tag{2}$$

Adding (1) and (2) and minimizing with respect to w, leads to the optimum domain size

$$w = \left[(2 - H_\parallel)\frac{\sigma}{U}\right]^{1/(3-H_\parallel)} d^{1/(3-H_\parallel)} = k d^{1/(3-H_\parallel)}. \tag{3}$$

It is implicitly assumed that the walls are like "folded curtains", irregular in the horizontal direction and straight in the vertical one [28], due to anisotropy in the strength of the dipole-dipole and elastic interactions. If the walls were also rough in the vertical direction, they would scale as $d^{H_\perp}$, and Eq. (3) would become instead

$$w = k d^{H_\perp/(3-H_\parallel)}. \tag{4}$$

The case $H_\perp = H_\parallel = 1$ (flat walls) restores the standard Kittel result $\gamma = 1/2$.

For the measured values $1.3 \le H_\parallel \le 1.5$, and assuming $H_\perp = 1$, Eq. (3) would predict a scaling exponent $0.59 \le \gamma \le 0.67$, which is bigger than the classic Kittel value of 0.5 and compatible with our experimental exponent γ. Also, since $H_\parallel$ was not the same for all films (Fig. 3), there is another test of self-consistency: Eq. (3) predicts that

$$\frac{w^{1/\gamma}}{d} = 2C - CH_\parallel, \tag{5}$$

where C is a constant. This means that a plot of $\frac{w^{1/\gamma}}{d}$ as a function of $H_\parallel$ should be linear, with the slope half the value of the intercept at the origin, as approximately observed (inset of Fig. 3).

The present model is in theory valid for any ferroic (ferroelectric, ferromagnetic or ferroelastic) with fractal walls, as it relies only on the geometrical scaling of the domain wall. However, although it is consistent with our empirical results, we want to emphasize that the robustness of these is limited by several constraints: (i) strain relaxation at one end and instrumental precision at the other limit the range of thickness in which the analysis can be performed, (ii) there is an electronic noise contribution to the PFM signal which, while we have tried to minimize, may still add to the apparent roughness of the walls, (iii) there is a substantial error bar associated with the periodicity of irregular domains. So, while the model is consistent with the experimental results, these should be verified by other techniques (looking at domain dynamics, for example).

It is also worth mentioning that the LLK theory was originally conceived for thick films. In very thin films the interaction between the two opposite surfaces [35], dead layers [36,37] or ferroelastic effects [38–40] can induce a departure from LLK, often in the form of a divergence in domain size for very small thickness. On the other hand, experimentally, for perovskite ferroelectrics the LLK holds down to smaller thickness than those studied here (Fig. 2);

nor does the domain size in the BFO films tend to diverge, which also argues against finite thickness effects.

In summary, we have analyzed the domain periodicity and domain morphology of very thin films of BFO and found: (i) the spontaneous ferroelectric domains in BFO are bigger than those in other ferroelectrics of similar thickness, and close to those of magnetic materials, which is consistent with a strong magnetoelectric coupling at the walls; (ii) the domains are irregularly shaped and their walls can be characterized by a fractal dimension; (iii) the domain scaling appears to depart from the conventional LLK law; and (iv) since the Hausdorff dimension affects the scaling between domain area and perimeter, it should affect domain scaling according to the model presented. The predictions of the model are consistent with the experimental results. Specific further tests on the nature and origin of the inferred fractal dimensionality are suggested, particularly the use of switching current transients and the study of domain growth dynamics. We hope that these findings will motivate more research into the physics of domain walls in ferroic and multiferroic systems.

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