Asymmetric screening of the depolarizing field in a ferroelectric thin film

S. Prosandeev[1,2] and L. Bellaiche[1]
[1]*Physics Department, University of Arkansas, Fayetteville, Arkansas 72701, USA*
[2]*Institute of Physics, Rostov State University, Rostov on Don 344090, Russia*
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A first-principles-based approach is developed to mimic the (asymmetric) screening of the depolarizing field at the top surface of ferroelectric ultrathin films. Varying the magnitude of this one-side screening (i) results in the formation of different kinds of periodic nanostripe domain patterns, including original ones that are highly asymmetric and that can be thought of as connecting (and generalizing) the traditional Landau-Lifshitz and Kittel models of dipolar domains, and (ii) leads to a change in the domain's period, suggesting that the asymmetric screening of the depolarizing field is responsible for the existence of two recently observed nanostripe phases.

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Stripe domains in ferromagnetic and ferroelectric systems are of technological importance because the properties of such systems depend strongly on the dipole arrangement. They are also of great fundamental interest because, among other things, their morphology reveals the balance between competitive interactions. The first theory of stripe domain structures was developed by Landau and Lifshitz in 1935 for magnetic systems.[1] In this model, the dipoles at the surfaces lie in plane, while the dipoles inside the film are parallel or antiparrel to the film's orientation (to be referred to as the z axis). This results in a closure domain pattern (that does not produce any macroscopic field outside the film) with 90° domain walls. The stability of this kind of stripe domain is due to the anisotropy of the lattice, with the easiest axis being along the z axis, overcoming the energetic cost of having domain walls. Later on, Kittel[2] suggested another pattern for stripe domains in magnetic thin films, in which all dipoles (including the ones at the surface) point either along the $+z$ or $-z$ direction. Such pattern produces a (stray) magnetic field outside the film that results in a costly magnetostatic energy. Such a solution is thus only stable for "uniaxial" thin films, i.e., having a very large anisotropy that overcomes the magnetostatic energy. The traditional Landau-Lifshitz and Kittel models both lead to the annihilation of the so-called demagnetizing and/or depolarizing field inside the film, and both predict that the stripe pattern of a given film under a given mechanical boundary condition has a unique domain period (that solely depends on the thickness of the film). Recently, 180° periodic stripe domain structures, with remarkably small periods (of the order of nanometers), were observed in ultrathin ferroelectric films.[3] The morphology of such stripes were not determined because this represents a major experimental challenge. On the other hand, a rather surprising result was found; namely, that these stripes can have two different periods for the same film but for different temperatures. It was then suggested that the existence of these two periods (that roughly differ by a ratio of $\sqrt{2}$) is related to the asymmetry of the experimental setup; namely, that the top (free) surface and the bottom (substrate/film) interface do not provide the same quantitative screening (if any) of the depolarizing field and that this asymmetry is somehow temperature dependent.[3] One may want to know if this suggestion is indeed correct, and one may also wonder if other stripe patterns (that is, deviating from the traditional Landau-Lifshitz and Kittel pictures) can result from this asymmetric screening. (Note that Ref. 4 strongly hints that varying the magnitude of the asymmetric screening of the depolarizing field can indeed affect domain width. However, the authors of Ref. 4 assumed that the Kittel model always applies when describing the domain configuration, which may have prevented them from discovering other stripe patterns.) Obviously, first-principles-based methods constitute a powerful tool to answer such questions because of their accuracy and deep microscopic insight. However, such methods have "only" been developed and/or used so far (to the best of our knowledge) to tackle problems related to a *symmetric* screening of the depolarizing field,[5–9] that is, when both surfaces similarly contribute to the domain's morphology.

The aims of this study are twofold. First, we wish to develop a first-principles-based approach allowing an asymmetric screening of the depolarizing field. Secondly, we want to use such a method to provide answers to the aforementioned questions. As we will see, such asymmetric screening can result in other stripe domain patterns and can indeed explain the experimental observations of Ref. 3.

Here, we consider a (001) $PbZr_{1-x}Ti_xO_3$ (PZT) thin film sandwiched by a nongrounded metallic plate, from the top side, and by a nonconducting substrate, from the bottom side. The film is PbO terminated. The distance between the top BO layer (where B atoms are either Ti or Zr) of the thin film and the metallic plate is denoted as R_{met}, and is allowed to vary. A "dead layer" (separating the top PbO surface and the metallic plate) can thus exist in our simulation, with its thickness being denoted by D and being equal to $R_{met}-\frac{a}{2}$ (where a is the five-atom unit-cell parameter). Here, this dead layer is assumed to possess a dielectric permittivity equal to unity. Specifically, the Ti composition and the thickness of the film are chosen to be $x=0.6$ and 48 Å, respectively. Such film is mimicked by a $6\times48\times12$ supercell that is periodic along the x and y directions but finite along the z axis. (The x, y, and z axes lie along the [100], [010], and [001] directions, respectively.) Its total energy is written as

$$E_{\text{tot}}(\{\mathbf{p_i}\},\{\mathbf{v_i}\},\{\sigma_i\},\hat{\eta}) = E_{mat}(\{\mathbf{p_i}\},\{\mathbf{v_i}\},\{\sigma_i\},\hat{\eta}) + E_{surf}(\{\mathbf{p_i}\},\{\mathbf{v_i}\}) + E_{scr}(\{\mathbf{p_i}\}), \quad (1)$$

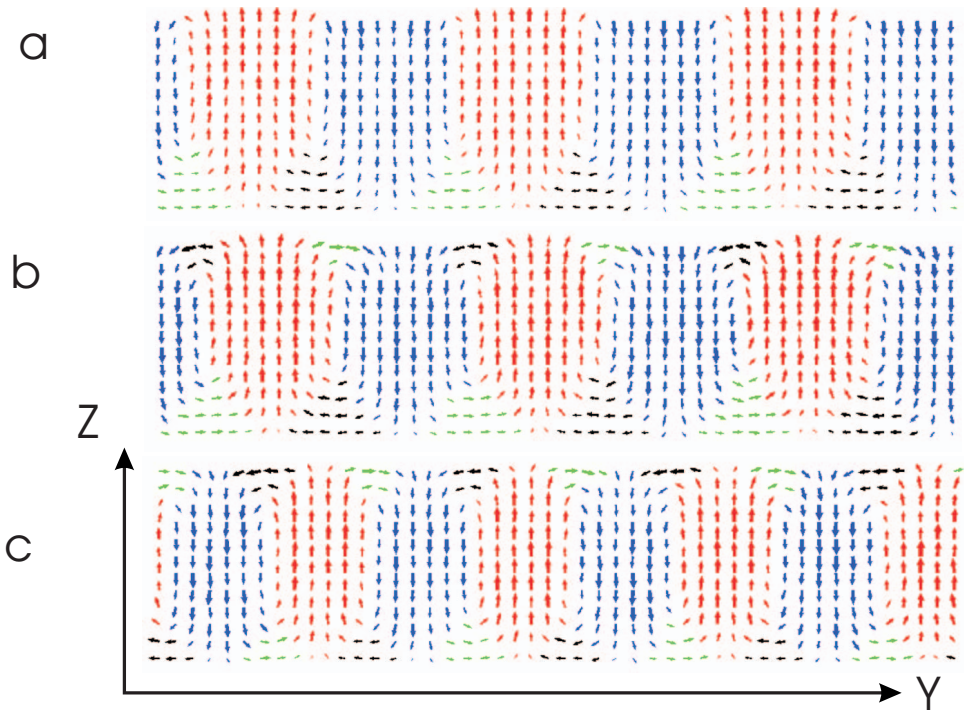

FIG. 1. (Color online) Low-temperature dipole patterns in the studied PZT film, as obtained from our first-principles-based computations. (a), (b), and (c) correspond to dead layer thicknesses of 0, $0.3a$, and $0.5a$, respectively.

where $\mathbf{p}_i$ are the electric dipoles at the i sites and $\mathbf{v}_i$ are dimensionless vectors describing the inhomogeneous strain around these sites. $\{\sigma_i\}$ characterizes the alloy configuration[10,11] that is presently randomly chosen (to mimic a disordered film). $\hat{\eta}$ is the homogeneous strain tensor.[12] Here, we wish to mimic thin films that are compressively strained on a substrate, with a misfit strain of 2.65% as in Ref. 6. Such mechanical boundary conditions are satisfied by freezing three components of $\hat{\eta}$ (namely, $\eta_6=0$ and $\eta_1=\eta_2=-2.65\%$), while the other three components (in Voigt notation) are allowed to relax. The expression and *first-principles-derived* parameters of E_{mat}, the intrinsic effective-Hamiltonian energy of the film, are those given in Ref. 10 for PZT *bulk*, except for the dipole-dipole interactions, for which we use the analytical expressions derived in Refs. 7 and 13 for thin films under ideal open-circuit conditions. Such electrical boundary conditions naturally lead to the existence of a maximum depolarizing field inside the film (denoted by $\mathbf{E}_d$) when dipoles point along the [001] direction. The second energetic term, E_{surf}, of Eq. (1) mimics how the existence of the top surface affects the dipoles and strains near it. Its analytical expression is indicated in Ref. 14, with its parameters having been determined from a *local-density-approximation*[15] computation on a PZT slab surrounded by vacuum. [Note that we do not consider terms analogous to those of E_{surf} at the bottom (substrate/film) surface since we assumed the substrate to be nonferroelectric.] The last term of Eq. (1), E_{scr}, mimics the *one-side* screening of the $\mathbf{E}_d$ maximum depolarizing field inside the film by the metallic plate. This is accomplished using the image method,[16] for which the real dipoles of the films are first mirrored with respect to the metallic plate and then redirected, to provide image dipoles. More precisely, the latter have the same z component as the real dipoles, while having opposite x and y components. Practically, E_{scr} is computed as

$$E_{scr} = \sum_{i,\alpha} Q_{i,\alpha}^{im} p_{i,\alpha}, \tag{2}$$

where α denotes Cartesian coordinates, and where $\mathbf{Q}_i^{im}$ represents the negative of the electric field produced by the image dipoles at site i of the film. Technically, this field has been computed via a two-dimensional Ewald method, similar to that used for determining the field produced by the real dipoles inside the film.[7,13] Let us emphasize that the possible polarization-induced charges at the *bottom* (substrate/film) interface do not have the possibility of being screened in the present study, unlike those at the top interface and unlike in Ref. 6. As a result, the maximum depolarizing field can never be fully screened, even if the metallic plate is (ideally) placed on the top PbO layer. E_{tot} is used in Monte Carlo simulations[17] that typically run over 40 000 sweeps. The investigated system is cooled down from high temperature to 10 K in small steps.

Figure 1(a) displays the results of our computations for the low-temperature dipole configuration, when no dead layer exists. Figures 1(b) and 1(c) show similar data, but for a dead layer with a thickness of $0.3a$ and $0.5a$, respectively. Figures 2(a)–2(c) schematize the corresponding dipole configurations. One can see that all the studied films exhibit out-of-plane 180° periodic nanostripes that alternate along the [010] direction. (Note that Ref. 6 indicates that a perfect symmetric screening of the depolarizing field at both surfaces leads to a homogeneous pattern, in which the dipoles are all parallel to the z axis, rather than this stripe domain.) Such stripes have recently been experimentally found in (001) $PbTiO_3$ ultrathin films[3] and confirmed theoretically[6] in (001) PZT films. They arise from the competition between the compressive strain (that favors dipoles along the z direction via the well-known dipole-strain coupling[12,18]) and the existence of a large enough depolarizing field (that tends to

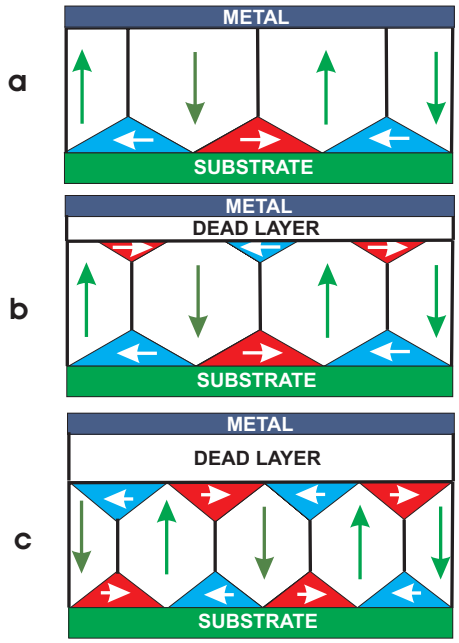

FIG. 2. (Color online) A schematic representation of the domain structures displayed in Fig. 1. The arrows show the direction of the dipoles.

prevent the formation of a spontaneous polarization along the growth direction). Furthermore, all the investigated systems present a similar dipole arrangement near the bottom (substrate/film) interface. Such arrangement consists in dipoles mostly lying in-plane in order to close the flux, in agreement with the Landau-Lifshitz model.[1]

On the other hand, varying the thickness of the dead layer dramatically affects the morphology of the domains near the *top* interface. For instance, the film associated with $D=0$ exhibits dipoles in line with the Kittel model[2] near the film/metallic plate interface, i.e., having an out-of-plane orientation [see Figs. 1(a) and 2(a)]. This contrasts with the system corresponding to $D=0.5a$ [see Figs. 1(c) and 2(c)], for which the dipoles at the top surface adopt a pattern that is consistent with the Landau-Lifshitz model (as a direct consequence of the existence of a significantly thick dead layer) and which lead to an overall symmetric configuration with the dipole flux being closed at both surfaces. Unlike this latter case, the dipole configuration shown in Fig. 1(a) [and schematized in Fig. 2(a)] is highly asymmetric between its bottom and top surfaces, and represents a case in which *both* the usually competing, traditional models of Kittel[2] and Landau-Lifshitz[1] apply (depending on which surface one looks at)! [A similar dipole pattern has also been obtained in Ref. 19, where the asymmetric electric boundary conditions without a dead layer ($D=0$) were applied to a lead titanate thin film within a Landau-Ginzburg phenomenological approach.] The intermediate case associated with $D=0.3a$ also exhibits some interesting features, such as the dipoles located in the middle of the stripes, at the top surface, still maintaining a rather large out-of-plane component (showing us that the metallic plate still provides some significant screening), while the other dipoles at the top surface lie in-plane (in order to begin the closing of the dipole flux). Interestingly, this kind of "mixed" dipole arrangement occurring at the top surface is the one predicted by a generalized closure model connecting the Landau-Lifshitz flux-closed domain pattern with the Kittel open structure (see, e.g., p. 319 of Ref. 20). Note that the configuration displayed in Fig. 1(b) [and schematized in Fig. 2(b)] possesses some asymmetry between its top and bottom surfaces. We are not aware that such an asymmetrical configuration has ever been reported before.

Moreover, varying the dead layer's thickness also affects another quantity, that is, the domain period. As a matter of fact, the domain configurations shown in Figs. 1(a) and 1(b) have a period (to be denoted by d_β) of $\simeq 6.4$ nm, while the period associated with the domains depicted in Fig. 1(c) (to be referred to as d_α) is smaller, about 4.8 nm. The transition from domains characterized by d_β to domains associated with d_α is numerically found to occur for a dead layer thickness $D=(0.35-0.4)a$, for our chosen $6\times 48\times 12$ supercell. [Note that the use of this supercell implies that the only possible (commensurate) periods we can numerically obtain are 8, 16, 24, 32, 48, 64, 96, and 192 Å, and that we checked (by comparing the total energy of various supercells) that the period $d_\alpha \simeq 4.8$ nm is the equilibrium period for the largest D values for our 48-Å-thick film.] Reference 4 also predicted that varying the dead layer thickness can affect the domain width of the ferroelectric thin film. However, such previous study assumed that Kittel's model always applies (i.e., independent of the value of D), while our results, displayed in Figs. 1 and 2, show otherwise. Furthermore, one should recall that the experimental work of Ref. 3 reports that decreasing the temperature in *in situ* (001) $PbTiO_3$ ultrathin films epitaxially grown on a $SrTiO_3$ substrate leads to a transition from the so-called α to the β phase, with both of these phases adopting out-of-plane 180° periodic nanostripes that alternate along the [010] direction but where the period of the β phase is larger than the period of the α phase by a ratio of $\simeq\sqrt{2}$. Interestingly, our present numerical results can explain these experimental features, once one realizes that increasing the dead layer thickness in our calculations results in increasing the residual depolarizing field inside the system (or equivalently, in decreasing the magnitude of the one-side screening of the maximum depolarizing field). As a matter of fact, one can easily imagine the scenario that, *at relatively high temperature*, no or very few molecules (that inevitably exist in the experimental setup surrounding the film) are absorbed at the top surface of the (001) $PbTiO_3$ ultrathin films. This leads to a negligible possible screening of the polarization-induced charges at the top surface and thus to the situation depicted in Fig. 1(c), namely, out-of-plane 180° nanostripes having relatively small period. It is also very plausible[21] that more and more molecules are absorbed at the top surface of the (001) $PbTiO_3$ ultrathin films *as the temperature decreases*, yielding a larger screening of the depolarizing field at the top surface and thus corresponding to the results indicated in Figs. 1(a) and 1(b), that is, out-of-plane 180° nanostripes with a larger period. In other words, the suggestion of Ref. 3 is correct: the one-side screening of the depolarizing field at the top surface, with the magnitude of such screening being temperature dependent, *can* explain the observed existence of the α and β phases in the same film.

In summary, a first-principles-based approach was devel-

oped and used to determine the effect of one-side screening of the depolarizing field on domain patterns. It is found that three different kinds of dipole patterns can exist, depending on the magnitude of this screening. Two of such patterns are highly asymmetric between the top and bottom surfaces, and one of them has never been reported (to the best of our knowledge). They both exhibit *coexistence* of features associated with the Landau-Lifshitz flux-closed domain arrangement[1] *and* the Kittel open structure.[2] Moreover, varying the magnitude of this one-side screening also results in changing the domain's width, which provides a successful explanation for the observation of the α and β phases in ultrathin films.[3]

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