Influence of space charge on domain patterns and susceptibility in a rhombohedral ferroelectric film

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ABSTRACT

The presence of a space charge region induces an internal electric field within the charged region that, in a ferroelectric material, would rotate the polarisations to align with the field. The strength of the induced field would therefore determine the domain patterns and polarisation switching properties of the material. Using a phase-field model, we investigate the effect of charged layers in fully and partially depleted $BiFeO_3$ thin films in the rhombohedral phase. While the domain pattern in a charge-free $BiFeO_3$ film consists of only two polarisation variants, we observe complex patterns with four coexisting variants that form within the charged layers at sufficiently high induced fields. These variants form a head-to-head configuration with an interface that is either wavy or planar depending on the internal field strength, which is determined by the charge density as well as the thickness of the charged layer. For depletion layers with sufficient thickness, there exists a range of charge density values for which the interface is wavy, while at high densities the interface becomes planar. We find that films with wavy interfaces exhibit enhanced susceptibilities with reduced hystereses compared to the charge-free film. The results of our work suggest that introducing space charge regions by careful selection of dopant density and electrode materials can engineer domain patterns that yield a higher response with a smaller hysteresis.

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1. Introduction

When a metal electrode is placed in contact with a semiconductor material, there may be a flow of charge carriers from the semiconductor to the metal, depending on the work function of the metal [1]. An accumulation of charge carriers results at the electrode/semiconductor interface, inducing an electrostatic potential that depletes these carriers in adjacent regions [2,3]. This space charge region, or depletion layer, is typically formed near interfaces such as grain boundaries and interfaces between heterophases, as well as near surfaces. In ferroelectric materials which are regarded as wide band gap semiconductors, the presence of such regions may affect the properties of the material, in many cases detrimental for applications such as non-volatile memory devices and capacitors. It lowers the ferroelectric phase transition temperature and suppresses ferroelectricity in the space charge regions [4]. Furthermore, the domain pattern that forms under the influence of space charge can substantially differ from those without [5–8]. Consequently when such a sample is switched,

the hysteresis loop constricts with a lowering of the coercive field, and depending on the extent of the depletion layer, the remnant polarisation as well [2,8–10]. If the distribution of charges in the sample is asymmetric, the resulting internal electric field leads to a preferred polarisation direction, thereby shifting the hysteresis loop along the electric field axis; this phenomena is called imprint [8,11].

Using a scanning probe microscope (SPM) tip to apply an electric field over a small region in a (100) $BiFeO_3$ film, Vasudevan et al. observed the formation of domains with polarisations that form a closed loop (i.e. head-to-tail configuration of domains) at low applied fields, and domains with polarisations directed towards a central point (head-to-head configuration) at very high fields [12]. Similar patterns may also be formed within space charge regions in ferroelectric films due to the internal electric field induced by the charges. Head-to-tail and 180° domains, whose walls are charge-neutral, are the more stable configurations in a charge-free material, whereas charged walls between head-to-head or tail-to-tail domains may stabilise in the presence of space charge [13–16]. Usually in theoretical investigations concerning the latter type of domains, the models have flat interfaces between the domains [15–18]. Other studies, both experimental [19–21]

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and theoretical [22], report the formation of zigzagged domain walls. It has been suggested that the formation of such interfaces allows the electrostatic energy to be reduced, as locally at the domain walls the polarisations are rotated into head-to-tail configurations [19]. Misirlioglu et al. find a critical thickness of the space charge layer above which this type of domain wall develops in their simulated $BaTiO_3$ films, and below which the film remains as a single domain [22].

It can therefore be deduced that an approach to engineer complex domain structures is to manipulate the space charge regions in ferroelectric materials. The thickness of space charge layers in thin films is determined by the built-in voltage across the layer. For a given dopant concentration, the built-in voltage is a property that depends on the material of the electrode. The layer thickness, which determines whether the film is fully or partially depleted, is thus dependent on the selection of dopant concentration and the electrode in experimental set-ups. When simulating a charged layer within a film, the layer thickness and dopant concentration may be chosen as variables instead; this would be equivalent to specifying the built-in voltage across the layer.

In investigating the properties of ferroelectric materials, the phase-field method has been shown to be a powerful technique and has been widely used [23]. A real-space approach with this technique takes into account long-range elastic and electrostatic interactions in the material of study, and is convenient for nanoscale systems in which free surfaces are important since it is straightforward to apply the boundary conditions [24]. This method has been applied in simulating the domain patterns in free-standing nanostructures of tetragonal lead zirconate-titanate [25].

Most of the studies of space charge effects in ferroelectric materials have been devoted to materials such as $BaTiO_3$ [6,16,17,21,22], $PbTiO_3$ [8,13,15] and $PbZr_{1-x}Ti_xO_3$ (PZT) for $x > 0.47$ [10,11], all of which adopt the tetragonal ferroelectric phase. These systems have 90° and 180° domain walls, with only the former producing a ferroelastic configuration. In these works, the external electric field is usually applied parallel to the polar direction. Few have investigated the effect of space charge on rhombohedral ferroelectric materials [12,19]. Unlike tetragonal ferroelectric materials, the rhombohedral phase has a larger number of ferroelectric variants with two possible ferroelastic domain patterns of 71° and 109° domain walls. Thus it can have more complex domain patterns [26], whose piezoelectric response may be enhanced especially when applying an electric field that is not along one of the polar directions [17,27–32].

A rhombohedral ferroelectric material, $BiFeO_3$, has been attracting much interest recently because of its multiferroic [33,34] and photoelectric [35,36] properties. It has potential applications in memory storage, solar energy storage, sensors and telecommunications devices [34,37–39]. Therefore in this work, we select $BiFeO_3$ with polarisations along the $\langle 111 \rangle$ directions (with reference to the pseudocubic lattice) as our material of study and examine the domain structures that form in [001] thin films under the influence of space charge. We also investigate the effective polarisation-electric field behaviour when applying an electric field in the [001] direction. Assuming static charges on the timescale of polarisation switching [6] for the case where the space charge region is generated due to the presence of an electrode/film interface, what we find is a wealth of domain patterns that varies with the strength of the electric field induced by the charges. Calculating the response in the direction parallel to the applied field, we note an optimum charge density with minimum charged layer thickness that produces a domain pattern with a wavy interface whose mobility is higher than the others. Our findings would be useful for applications that require materials with high piezoelectric response and small hystereses.

2. Computational details

The dynamics of the polarisation order parameter components P_x, P_y and P_z evolving with time t is given by the time-dependent Ginzburg–Landau equation as

$$\frac{\partial P_i}{\partial t} = -\Gamma \left[\frac{\delta F}{\delta P_i} - E_i \right] \tag{1}$$

where Γ is a kinetic coefficient related to the domain wall mobility, F is the free energy of the ferroelectric material and E_i is the component i of the electric field $\mathbf{E}$ in the sample. F consists of the Landau free energy F_l, the gradient free energy associated with the domain walls F_g, the elastic free energy F_e and the electrostatic free energy F_{el}:

$$F = F_l + F_g + F_e + F_{el} \tag{2}$$

We express F_l in terms of P_x, P_y, and P_z up to the fourth order:

$$F_l = \int d\mathbf{r}[\alpha_1(P_x^2 + P_y^2 + P_z^2) + \alpha_{11}(P_x^4 + P_y^4 + P_z^4) + \alpha_{12}(P_x^2 P_y^2 + P_x^2 P_z^2 + P_y^2 P_z^2)] \tag{3}$$

where α_1, α_{11} and α_{12} are material parameters. F_g can be expressed as:

$$F_g = \int d\mathbf{r} \left(\frac{K}{2} [(\nabla P_x)^2 + (\nabla P_y)^2 + (\nabla P_z)^2] \right) \tag{4}$$

where K is a gradient coefficient, while the expression for F_e is as below:

$$F_e = \int d\mathbf{r} \left\{ \frac{C_{11}}{2} \left[(\varepsilon_{xx} - \varepsilon_{xx}^0)^2 + (\varepsilon_{yy} - \varepsilon_{yy}^0)^2 + (\varepsilon_{zz} - \varepsilon_{zz}^0)^2 \right] \right.$$
$$+ C_{12} \left[(\varepsilon_{xx} - \varepsilon_{xx}^0)(\varepsilon_{yy} - \varepsilon_{yy}^0) + (\varepsilon_{xx} - \varepsilon_{xx}^0)(\varepsilon_{zz} - \varepsilon_{zz}^0) \right.$$
$$\left. + (\varepsilon_{yy} - \varepsilon_{yy}^0)(\varepsilon_{zz} - \varepsilon_{zz}^0) \right] + 2C_{44} \left[(\varepsilon_{xy} - \varepsilon_{xy}^0)^2 + (\varepsilon_{xz} - \varepsilon_{xz}^0)^2 \right.$$
$$\left. \left. + (\varepsilon_{yz} - \varepsilon_{yz}^0)^2 \right] \right\} \tag{5}$$

C_{11}, C_{12} and C_{44} are material constants. ε_{ij} are the strain tensors having the usual definition in terms of displacements u_i

$$\varepsilon_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) \tag{6}$$

and the electrostrictive strain tensors ε_{ij}^0 have the following expressions:

$$\varepsilon_{ii}^0 = Q_{11}P_i^2 + Q_{12}(P_j^2 + P_k^2) \tag{7}$$

and $\varepsilon_{ij}^0 = Q_{44}P_iP_j$ for $i \neq j$ $\tag{8}$

with Q_{11}, Q_{12} and Q_{44} being material-specific electrostrictive constants.

We determine the electric field $\mathbf{E}$ in the sample from the electrostatic potential ϕ using the relationship

$$\mathbf{E} = -\nabla\phi \tag{9}$$

as well as Gauss's law relating the electric displacement $\mathbf{D}$, $\mathbf{E}$ and polarisation $\mathbf{P}$:

$$\nabla \cdot \mathbf{D} = \nabla \cdot (\epsilon_0 \epsilon_{br} \mathbf{E} + \mathbf{P}) = -\epsilon_0 \epsilon_{br} \nabla^2 \phi + \nabla \cdot \mathbf{P} = \rho(\mathbf{r}) \tag{10}$$

ϵ_0 is the permittivity of free space, $\epsilon_{br} = 10$ is a background permittivity [40] and $\rho(\mathbf{r})$ we have set as

$$\rho(z) = \begin{cases} \rho_0, & L - z < w \\ 0, & \text{otherwise} \end{cases} \tag{11}$$

where L is the thickness of the film and w is the thickness of the space charge layer. We assume $\rho_0 = qN_D$ where q is the charge of