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Unusual domain evolution in semiconducting ferroelectrics: A phase field study

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ABSTRACT

The effect of electrical conductivity on the domain evolution of semiconducting ferroelectrics is investigated using a phase field model which includes the drift of space charges. Phase field simulations show that the tail-to-tail 90° charged domain wall appears during the domain formation in the semiconducting ferroelectrics at zero field, which is prohibited in common insulating ferroelectrics. Due to the screening of polarization charges, the domain switching takes place through the motion of head-to-head 180° charged domain wall in the semiconducting single-domain ferroelectrics subjected to an electric field. Comparing to the insulating ferroelectrics, the semiconducting ferroelectrics have a lower speed of domain evolution due to the decrease of mobility of charged domain walls. The response of semiconducting ferroelectrics to a mechanical load is also found different from that of insulating ferroelectrics.

1. Introduction

Ferroelectric materials have been attracted much attention due to their distinguished dielectric, ferroelectric and electromechanical coupling properties, which are closely related to the domain structures and domain evolution in the materials [1]. The depolarization field plays an important role in the formation of domain structures, and the strength is dependent on the screening of polarization-induced charges in the materials. Ferroelectric materials are generally regarded as insulators which have no free charge. However, a vast majority of the perovskite ferroelectrics are actually wide-band-gap semiconductors [2,3]. The semiconducting ferroelectrics exhibit characteristic properties originated from the drift and diffusion of free carriers. The screening of polarization charges could induce new properties and behaviors that differ from the common insulating ferroelectrics [4–6]. In particular, the charged head-to-head and tail-to-tail domain walls are metastable in the insulating ferroelectrics [7,8] while they can stably exist in the semiconducting one [4].

To understand the effect of free space charges on ferroelectrics, many theoretical investigations have been performed in the framework of Landau–Devonshire theory [9]. For instance, the effect of space charges on the phase transition [10,11], polarization switching [12–14] and fatigue [15] in ferroelectric thin films have been predicted using the phenomenological theory. Most of the investigations make a priori assumption on either the profile of polarization [16–19] or free charges [20,21]. Without such priori assumption, the evolution of polarization and space charges has been investigated using the time-dependent Ginzburg–Landau model [2,22,23]. The model successfully described the coupling between the polarization and space charge, such as the formation of charge double layers at the 90° domain walls [2] and the accumulation of space charges near the superlattice interface [22]. Recently, a time-dependent and thermodynamically consistent theory is proposed to describe the evolution of space charges and polarization in semiconducting ferroelectrics subjected to an external electric field [24]. But the simulation is limited to the one-dimensional and non-deformable ferroelectrics. To study the interactions between the charges and domain structures, two-dimensional phase field simulations have been carried out [25,26]. A phase field study has also been performed to understand the enhanced linear electromechanical response of semiconducting ferroelectrics with fixed head-to-head and tail-to-tail charged domain walls [27]. Although these studies have provided deep insights into the coupling between the space charges and polarization, the three-dimensional study on the temporal evolution of charged domain wall and domain switching in the semiconducting ferroelectrics has not been investigated so far. In this Letter, the effect of electrical conductivity on domain formation and polarization switching of semiconducting ferroelectrics is investigated by using a phase field model.

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2. Phase field model

The electrical conductivity is explicitly included into the present phase field model via Maxwell's equations, which describe the drift of free charges under an electric field in the semiconducting ferroelectrics and have the form as [27]

$$D_{i,i} = q^F, \qquad \frac{\partial q^F}{\partial t} + J_{i,i} = 0, \tag{1}$$

where D_i, q^F and J_i $(i = 1, 2, 3)$ are the electric displacement, free space charges and electric current, respectively. Following Schwaab et al. [28], the diffusion of free charges is ignored in the present study. Therefore, the electric current is given by

$$J_i = \gamma E_i, \tag{2}$$

where γ and E_i are the electrical conductivity and electric field, respectively. In addition to Maxwell's equations, the following mechanical equilibrium equation must be satisfied for the deformable ferroelectrics:

$$\sigma_{ij,j} = 0 \quad (i, j = 1, 2, 3), \tag{3}$$

where σ_{ij} is the elastic stress tensor.

In the phase field model of ferroelectrics, the temporal evolution of the polarization of $\mathbf{P} = (P_1, P_2, P_3)$ is described by the time-dependent Ginzburg–Landau equation

$$\frac{\partial P_i}{\partial t} = -L\left[\frac{\partial h}{\partial P_i} - \frac{\partial}{\partial x_j}\left(\frac{\partial h}{\partial P_{i,j}}\right)\right] \quad (i, j = 1, 2, 3) \tag{4}$$

where L is the kinetic coefficient, h is the electrical enthalpy density of the simulated system, and t is time. The electrical enthalpy h is a function of the polarization P_i, the strain ε_{ij}, the polarization gradient $P_{i,j} = (\partial P_i/\partial x_j)$, and the electric field E_i, which has the form as [29]

$$\begin{aligned} h(P_i, P_{i,j}, \varepsilon_{ij}, E_i) = {} & \alpha_i P_i^2 + \alpha_{ij} P_i^2 P_j^2 + \alpha_{ijk} P_i^2 P_j^2 P_k^2 \\ & + \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} - q_{ijkl} \varepsilon_{ij} P_k P_l \\ & + \frac{1}{2} g_{ijkl} (\partial P_i/\partial x_j)(\partial P_k/\partial x_l) \\ & - \frac{1}{2} \kappa_0 E_i E_i - E_i P_i. \end{aligned} \tag{5}$$

The first three terms represent the Landau energy, where α_i is the dielectric stiffness, α_{ij} and α_{ijk} are higher order dielectric stiffnesses. The fourth term denotes the elastic energy of the system, where c_{ijkl} are the elastic constants. The fifth term denotes the coupling energy between the polarizations and the strains, where q_{ijkl} are the electrostrictive coefficients. The sixth term is the gradient energy, where g_{ijkl} are the gradient coefficients. The gradient energy gives the energy penalty for spatially inhomogeneous polarization. The last terms are the electric energy density due to the presence of electric field. It should be noted that the electric field in Eq. (5) includes the external field and depolarization field. The total electric field can be obtained through the electrical equilibrium equation (1). The external electric field is applied by setting different electrical potentials to the surfaces of ferroelectrics. The electric displacement and stress in Eq. (1) and Eq. (3) are related to the electrical enthalpy as $D_i = -\partial h/\partial E_i$ and $\sigma_{ij} = \partial h/\partial \varepsilon_{ij}$, respectively. A nonlinear finite element method is employed to solve Eqs. (1)–(4). The finite element method is based on the following weak form of governing equations

$$\begin{aligned} & \int_V \left\{ \frac{\partial}{\partial x_j}\left(\frac{\partial h}{\partial \varepsilon_{ij}}\right)\delta u_i - \frac{\partial}{\partial x_i}\left(\frac{\partial D_i}{\partial t} + J_i\right)\delta\phi \right. \\ & \quad \left. + \left[\frac{\partial P_i}{\partial t} + L\left(\frac{\partial h}{\partial P_i} - \frac{\partial}{\partial x_j}\left(\frac{\partial h}{\partial P_{i,j}}\right)\right)\right]\delta P_i \right\} dV \\ & = 0 \quad (i, j = 1, 2, 3). \end{aligned} \tag{6}$$

Using the Gauss theorem, Eq. (6) can be expressed as

$$\begin{aligned} & \int_V \left\{ \frac{\partial h}{\partial \varepsilon_{ij}} \partial \frac{\partial u_i}{\partial x_j} + \left(\frac{\partial D_i}{\partial t} + J_i\right)\partial \frac{\partial \phi}{\partial x_j} \right. \\ & \quad \left. + \left[\left(\frac{\partial P_i}{\partial t} + L\frac{\partial h}{\partial P_i}\right) + L\frac{\partial h}{\partial P_{i,j}}\delta\frac{\partial P_i}{\partial x_j}\right]\delta P_i \right\} dV \\ & = \int_S \left[\left(\frac{\partial h}{\partial \varepsilon_{ij}} n_j\right)\delta u_i + \left(\left(\frac{\partial D_i}{\partial t} + J_i\right) n_i\right)\delta\phi \right. \\ & \quad \left. + L\left(\frac{\partial h}{\partial P_{i,j}} n_j\right)\delta P_i \right] dA. \end{aligned} \tag{7}$$

Based on the constitute equation of $D_i = k_0 E_i + P_i$ and Eq. (2), Eq. (7) can be expressed as

$$\begin{aligned} & \int_V \left\{ \frac{\partial h}{\partial \varepsilon_{ij}}\delta\varepsilon_{ij} - \left(k_0\frac{\partial E_i}{\partial t} + \frac{\partial P_i}{\partial t} + \gamma E_i\right)\delta E_i \right. \\ & \quad \left. + \left(\frac{\partial P_i}{\partial t} + L\frac{\partial h}{\partial P_i}\right)\delta P_i + L\frac{\partial h}{\partial \xi_{ij}}\delta\xi_{ij} \right\} dV \\ & = \int_S (t_i \delta u_i - J_{Sq}\delta\phi + L\pi_i \delta P_i)\, dA \end{aligned} \tag{8}$$

in which $\varepsilon_{ij} = \frac{\partial u_i}{\partial x_j}$, $E_i = -\frac{\partial \phi}{\partial x_i}$, $\xi_{ij} = \frac{\partial P_i}{\partial x_j}$, $t_i = \frac{\partial h}{\partial \varepsilon_{ij}} n_j$, $J_{Sq} = -(\frac{\partial D_i}{\partial t} + J_i)n_i$, and $\pi_i = \frac{\partial h}{\partial P_{i,j}} n_j$, are the strain, electric field, polarization gradient, surface traction, surface current density and the gradient flux of polarization. To solve the governing equations with finite element method, the eight-node brick elements are employed for space discretization. The detailed formulation of the finite element method is given in Ref. [30]. The backward Euler scheme and Newton iteration method are employed for the time integration and nonlinear iteration, respectively.

3. Simulation results and discussions

In the present study, we investigate the effect of electrical conductivity on the domain evolution in the $PbTiO_3$ single crystal tetragonal nanodot. The electrical conductivity is set to 2.5×10^{-8} $(\mathrm{m}\Omega)^{-1}$, which has the same order as that in Ref. [28]. All other material constants used in the simulation are the same as those of Ref. [31] at room temperature. The material parameters and variables are normalized using the same formula as that used in the literature [31]. Based on the normalized formula, the normalized time is $t^* = t|\alpha_1|L$, in which t, $|\alpha_1|$ and L are the real time, the absolute value of α_1 at room temperature, and the kinetic coefficient of Eq. (4), respectively. Accordingly, the normalized electrical conductivity is $\gamma^* = \gamma/L$. It is assumed that the semiconducting ferroelectric nanodot is freestanding and open-circuited, and has the tetragonal shape of $8 \times 8 \times 2$ nm^3. The corresponding mechanical and electrical boundary conditions are $\sigma_{ji} n_i = 0$ and $(\partial D_i/\partial t + J_i)n_i = 0$, respectively, where n_i denote the component of unit vector normal to the surfaces. The free boundary condition of $\partial P_i/\partial n = 0$ is used for the polarizations on the surfaces [32]. In the simulations, we employ $20 \times 20 \times 5$ discrete brick elements to model the tetragonal nanodots.