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Effect of the nanopore on ferroelectric domain structures and switching properties

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ABSTRACT

Porous ferroelectrics have some special properties and features for specific promising applications. The nanopores structure have been observed in experiments may have great influence on the ferroelectric domain structures and the switching properties of ferroelectrics. In this study, we proposed a phase field model to predict the domain structures of porous ferroelectrics and their evolution under a switching electric field. The effects of the pores size/shape on domain structure, switching properties, and dielectric/piezoelectric properties are investigated and analyzed. The simulated hysteresis loop is in good agreement with experimental reports. It is shown that the porosity can strongly affect the ferroelectric domain size, and furthermore, will influence the hysteresis loop. Therefore controlling the porosity of ferroelectrics may provide a possible way to adjust the properties of porous ferroelectric materials.

1. Introduction

Porous ferroelectric materials can be tailored to achieve special properties and features for specific applications [1,2]. By controlling ferroelectric porosity with its size/shape/orientation/interconnectivity shows enhanced properties including piezoelectric coefficient [3–8], dielectric constant [5–8], and ferroelectric properties [7–9]. Porous ferroelectrics also show higher pyroelectric harvesting for its potential energy harvesting applications [10–12]. These properties enhancement suggest that porous ferroelectrics have great potential in various applications.

Very recently, nanosized pores formed in nano-thin film or nanowires also have attracted great attentions. Ferreira et al. reported nanoporous piezo- and ferroelectric thin films from sol-gel solutions [13], and noticed ferroelectric properties are enhanced in nanoporous films [14]. Kalinin et al. studied local ferroelectric properties and switching polarization using piezoresponse force spectroscopy and have revealed an enhanced piezoresponse from the nanostructured films [15]. Nanopores with a typical diameter of around 10 nm are discovered in ferroelectric nanowires, nanopores didn't break the monocrystallinity and the negative pressure results in enhancement of tetragonality, Curie temperature, spontaneous polarization and piezoelectric [16]. Please note that nanoporous ferroelectrics/piezoelectrics are highly promising as platforms to construct mechanical/magnetoelectric composites with a designed architecture.

Many experimentalists would like to avoid pores to fetch a perfect crystal. However, the generation of porosity in ferroelectrics can be seen as an avenue to achieve lighter materials with enhanced or optimized ferroelectric properties. Thus, it is important to study the roles played by pores for improving/adjusting ferroelectric properties. Many theoretical works have been developed to expect the properties, e.g., a finite element model (FEM) built by Mitoseriu et al. investigated permittivity and tenability for isotropic/elongated pores in 2D [17] and 3D interconnectivity [18,19]. The switching properties also have been investigated by the multiscale nonlinear finite element simulation [20] or 3D Ginzburg-Landau theory based finite element model [21], and the simulated ferroelectric properties can be compared to experimental observations. The switching properties of Nb-PZT (Lead Zirconate Titanate) ceramics with anisotropic porosity (~40% relative porosity) were investigated by comparison with the dense ceramics (~5% relative porosity) of the same composition by means of the first-order reversal curve analysis [22]. Khachaturyan et al. used FEM simulations of the statistical field-distributions to study switching process of the ferroelectric ceramics with pores of different size, shape, and orientation. Simulation results predicted the roles played by the shape isometric/anisometric, size, distribution of the pores in ferroelectric switching process [23]. Some very early works done by Li et al. [24] and Brown et al. [25] with a finite element model show that the remanent polarization decreases with

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the increase of porosity density. The effect of the shape and displacement was also analyzed in three dimensional [25].

However, above studies didn't include any ferroelectric domain structures, which is strongly affiliated with the ferroelectric properties, and also, domain structure affiliated switching process is less investigated. A significant differences in remanent polarization (P_r) between porous and dense PZT films was observed by Trolier-McKinstry et al. [26], which suggests that the porosity has an impact on domain wall motion and may further contribute to the switching properties [27,28]. Weng et al. used a thermodynamic model to simulate the hysteresis loop of ferroelectric crystal on various porosity [29].

Recently, phase field method have great potential in simulating porous ceramics [30], ferroelectric domain structures [31] and various types of magnetoelectric materials [32–35]. The switching properties also have been simulated using this method [35–38]. In this paper, we would like to solve the following problems: (i) what is the domain structure like when a specific shaped pore (isometric/anisometric) is introduced into the ferroelectrics, (ii) what is the hysteresis loop and the remanent polarization (P_r)/coercive electric field (E_c) like with this porous material. (iii) The relationship between the hysteresis loop and the domain structures, how the pores influence on the switching properties and the P_r/E_c. In this work, the ferroelectric domain structure of $BaTiO_3$ with various shapes/sizes of pores was studied by employing the phase-field dynamical model with solving the time dependent Ginzburg-Landau (TDGL) equations. The switching properties of $BaTiO_3$ with nanopores are also illustrated with its domain structure evolution, and the influence of the porosity on the ferroelectric domains and switching properties have been studied.

2. Phase field model with pores

Consider four types of energy to describe the domain of ferroelectric in phase-field model, where the total free energy of ferroelectric materials includes bulk free energy, domain wall energy, electrostatic energy and elastic deformation energy, i.e.,

$$F_{electric} = F_{land} + F_{wall} + F_{elec} + F_{elas}, \tag{1}$$

where F_{land} can be expressed by an eight-order Landau polynomial:

$$\begin{aligned} F_{land}(P_i) = \int_V & \alpha_1(P_1^2+P_2^2+P_3^2) + \alpha_{11}(P_1^4+P_2^4+P_3^4) \\ & + \alpha_{12}(P_1^2P_2^2+P_2^2P_3^2+P_1^2P_3^2) + \alpha_{111}(P_1^6+P_2^6+P_3^6) \\ & + \alpha_{112}[P_1^2(P_2^4+P_3^4)+P_2^2(P_1^4+P_3^4)+P_3^2(P_1^4+P_2^4)] \\ & + \alpha_{123}P_1^1P_2^2P_3^3 + \alpha_{1111}(P_1^8+P_2^8+P_3^8) + \alpha_{1112}[P_1^6(P_2^2+P_3^2) \\ & + P_2^6(P_1^2+P_3^2)+P_3^6(P_1^2+P_2^2)] + \alpha_{1122}(P_1^4P_2^4+P_2^4P_3^4+P_1^4P_3^4) \\ & + \alpha_{1123}(P_1^4P_2^2P_3^2+P_2^4P_1^2P_3^2+P_3^4P_2^2P_2^2)d^3x, \end{aligned} \tag{2}$$

where a_1, a_{ij}, a_{ijk}, and a_{ijkl} are the phenomenological Landau expression coefficients, P_i (i = 1, 2, 3) is the spontaneous polarization which set as the order parameters, thus the ferroelectric domain structure can be described by the spatial distribution of P_i. V is the volume of the simulated system and $d^3x = dx_1dx_2dx_3$.

The ferroelectric domain wall energy is given by:

$$F_{wall}(\partial P_i/\partial x_j) = \int_V \left[\frac{1}{2}G_{ijkl}\frac{\partial P_i}{\partial x_j}\frac{\partial P_k}{\partial x_l}\right]d^3x, \tag{3}$$

where G_{ijkl} is coefficient of gradient energy and $G_{ijkl} = G_{klij}$.

The electrostatic energy can be written as:

$$F_{elec}(P_i, E_i) = -\int_V \left(\frac{1}{2}\varepsilon_b\varepsilon_0E_i^2 + E_iP_i\right)d^3x, \tag{4}$$

where E_i represents electric field component, which depends on the polarization distribution and the boundary conditions, ε_0 is the vacuum permittivity, and ε_b is the background relative dielectric permittivity.

According to Khachaturyan's elastic theory [39], the elastic energy F_{elas} can be written as:

$$F_{elas}(P_i, \varepsilon_{ij}) = \int_V \left[\frac{1}{2}c_{ijkl}(\varepsilon_{ij} - Q_{ijkl}P_kP_l)(\varepsilon_{kl} - Q_{klij}P_iP_j)\right]d^3x, \tag{5}$$

where ε_{ij} is strain and c_{ijkl} is the elastic stiffness tensor. Q_{ijkl} is the electrostrictive coefficient.

In the current work, we introduce a static phase field $\eta(r)$ to distinguish the ferroelectric phase and the pores phase, as the phase field η do not evolve with time, the position and the size of the pores are fixed. If $\eta(r) = 1$, position r is occupied by the ferroelectric phase, whereas for $\eta(r) = 0$ means position r is occupied by the pore phase. The total free-energy of a ferroelectric material with pores includes the contribution of ferroelectric energy and pore energy, i.e.

$$F_{total} = \eta(r)\cdot F_{electric} + (1-\eta(r))F_{pores}, \tag{6}$$

for simplicity, we set $F_{pores} = 0$, which means the pore phase has no contribution to the total energy of the materials, especially for predicting the domain structures of ferroelectrics.

With all the energetic contributions, the temporal and spatial evolution of the polarization distribution of ferroelectrics can be described by the Time-Dependent Ginzburg-Landau (TDLG) equations,

$$\frac{\partial P_i(r,t)}{\partial t} = -L\frac{\delta F_{total}}{\delta P_i(r,t)}, \quad (i = 1,2,3) \tag{7}$$

where t is time, and L is kinetic coefficient.

All the corresponding coefficients are employed here: $\alpha_1 = 4.124(T-388)\times10^5$, $\alpha_{11} = -2.097\times10^8$, $\alpha_{12} = 7.974\times10^8$, $\alpha_{111} = 1.294\times10^9$, $\alpha_{112} = -1.905\times10^9$, $\alpha_{123} = 2.500\times10^9$, $\alpha_{1111} = 3.863\times10^{10}$, $\alpha_{1112} = 2.529\times10^{10}$, $\alpha_{1122} = 1.637\times10^{10}$, $\alpha_{1123} = 1.367\times10^{10}$, $c_{11} = 1.78\times10^{11}$, $c_{12} = 0.964\times10^{11}$, $c_{44} = 1.22\times10^{11}$, $Q_{11} = 0.10$, $Q_{12} = -0.034$, $Q_{44} = 0.029$, where c_{ij} and Q_{ij} are the Voigt notation for c_{ijkl} and Q_{ijkl}. All the coefficients are in SI unit and T in Kelvin [40].

3. Simulation results

We systematic studied the effects of various shapes/sizes of pores on the domain structure and switching properties. Firstly, we illustrated the simulation of ferroelectric switching process by a hysteresis loop with the evolution of ferroelectric domain structure. Then we assumed the shape of the pores are ideal perfect isometric geography, e.g. square shaped or circle shaped pores. After that, the situation of the anisometric shaped pores were considered, like using a rectangle/ellipse shaped pores with various aspect ratio. Finally we discussed the ferroelectric/dielectric/piezoelectric properties by comparing the P_r, rectangularity factor, dielectric constant and piezoelectric constant with experimental results.

3.1. Hysteresis loop with domain structure for porous $BaTiO_3$

Fig. 1(a, b) illustrates a complete Polarization-Electric field hysteresis loop (PE loop) with the domain evolution of $BaTiO_3$ crystal with a squared shaped single pore under a switching field along the x direction. The simulation size is 256 nm × 256 nm with the pore size of 96 nm × 96 nm. The domain structures A-I in Fig. 1b are corresponding to the points A-I in Fig. 1a, respectively. The microstructure evolution under the