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A theoretical investigation of the influence of the surface effect on the ferroelectric property of strained barium titanate film

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A R T I C L E I N F O

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A B S T R A C T

The influence of the surface effect on the ferroelectric property of strained barium titanate film has been investigated. In this study, based on time-dependent Ginsburg-Landau-Devonshire thermodynamic theory, the surface effects have been simulated by introducing a surface constant, which leads to the strained $BaTiO_3$ film consisting of inner tetragonal core and gradient lattice strain layer. Further, surface effects produce a depolarization field which has a dominant effect on the ferroelectric properties of the films. The spontaneous polarization, dielectric properties and ferroelectric hysteresis loop of $BaTiO_3$ film are calculated under different boundary conditions. Theoretical and experimental results for strained $BaTiO_3$ film are compared and discussed.

1. Introduction

Barium titanate with a perovskite structure have attracted a great deal of attention, in recent years, for its excellent ferroelectric, piezoelectric, pyroelectric, and dielectric properties. $BaTiO_3$ films has been utilized in a wide variety of applications in dynamic random access memories, high density capacitors, piezoelectric sensors and so on [1,2]. As is well known, the structures and electrical behaviors of epitaxial $BaTiO_3$ films can be greatly affected by film thickness [3,4], electrical boundary conditions [5], process parameters [6], crystallographic orientation [7] and so on. The properties of perovskite ferroelectric film are considered to be closely related to its surface effect.

The size effects and ferroelectric behaviors of ferroelectric film have also been studied theoretically, including by the transverse Ising model [8,9], the Landau–Ginzburg–Devonshire (LGD) theory [4,10–31], phase-field method [27–29], and ab initio methods [32–34]. For example, using the transverse Ising model, the phase transition properties of ferroelectric thin films are studied by modifying the exchange strength at the surface [8], and the frequency dispersion of dielectric properties could be investigated with the Monte Carlo simulation [9]. Using a LGD theory, Tilley [10] studied the surface effect on the phase transitions of ferroelectric films. Zhong and coworkers [11] reported that the extrapolation length of a ferroelectric particle should be size dependent, and Shih et al. [12] studied the depolarization effect on the paraelectric to ferroelectric transition of small particles. Tagantsev et al. [13,14] pointed out that the misfit strains between a ferroelectric thin film and its substrate influence the equilibrium polarization states and shift the phase transition temperature. Ong et al. [15] pointed out that the critical temperature of the ferroelectric film is reduced below Curie temperature for positive extrapolation length and increased for negative extrapolation length. Akdogan and Safari [16] studied the first order tetragonal-cubic phase transition in single domain mechanically unconstrained $BaTiO_3$ nanocrystals with no depolarization fields. Zheng et al. [17] calculated the clamped effect on $PbTiO_3$ film, and analysed the critical thickness of the ferroelectricity. Lo and Li [4] simulated numerically the thickness dependence of the susceptibility and paraelectric–ferroelectric phase transition temperature in ferroelectric films. Considering the mismatch of the substrate and film lattice constants, Glinchuk et al. [18–21] introduced the surface tension energy to solve Euler - Lagrange equation, the boundary conditions of which are related to the surface polarization and extrapolation length, and used misfit or epitaxial strain to analyze the effects of built-in electric fields [22]. Morozovska et al. [23] introduced the surface strain field to calculate surface tension energy, and proposed a direct variational method for primary ferroics nanoparticle in phenomenological theory framework, and surface parts of the Gibbs free energy is expanded as a polynomial of multicomponent order parameter [24–26]. To study the film behavior on the level of ferroelectric domains, Hlinka et al. [27,28] used the GLD model for computation of domain-wall properties in ferroelectric materials. Chen et al. [29–31] investigated domain structures in thin films using the phase-field method, which has achieved great success in modeling domain evolution. By means of ab initio calculations,

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Tagantsev et al. [32] demonstrated the short- and long-range contributions to the size effect in metal-ferroelectric-metal heterostructures by combination of first-principles calculations with a version of the GLD theory, and Duan et al. [33,34] calculated the local polarization in a ferroelectric film < 10 nm and obtain the surface polarization and extrapolation length by fitting the polarization distribution curves. In these studies the surface effects are simulated with the extrapolation length. However, it was not explained reasonably why the extrapolation length remains the same at different external electric field and temperature, and the extrapolation length can not explained scientifically surface effects. It is suggested that the surface effect should be caused by the gradient energy which is produced by the lattice mismatch between the film and the substrate.

In this paper, a surface polarization constant is introduced to simulate the surface effect of $BaTiO_3$ films grown on different substrates. Taking depolarization field effect into account, a single-domain two-phase structure model is established on the basis of Ginsburg-Landau-Devonshire thermodynamic theory. By phase filed simulation, the characteristics of polarization, dielectric constant and hysteresis loop under different boundary conditions are studied. The surface effect leads to the existence of a 50-nm-thick gradient layer on the surface of the film, which induces the depolarization field in the film and determines the dielectric and ferroelectric properties of the nano sized films.

2. Model

We consider a single-domain $BaTiO_3$ film. Using the GLD formalism, the Gibbs free energy can be expressed as

$$G = G_{ld} + G_g + G_E \tag{1}$$

where terms G_{ld}, G_g and G_E are the Landau potential, gradient energy term and static electric energy, respectively. G_{ld} is expanded as a polynomial of the polarization components. For convenience, in the $BaTiO_3$ system, we only considered two known stable phases above 300 K. The ferroelectric phase of 4 mm symmetry is stable below Curie temperature. The high temperature phase is paraelectric with cubic symmetry ($Pm3m$). The polarization component parallel to the film surface is assumed to be zero. Therefore, our research object is the polarization component P along the film normal direction. P=0 and P≠0 represent the cubic and tetragonal phases, respectively.

The films are divided into N layers with equal thickness along the normal direction of the films. G_{ld} is expressed as

$$G_{ld} = \frac{1}{N}\sum_{i=1}^{N}[\alpha_1(T-T_0)P_i^2 + \alpha_{11}P_i^4 + \alpha_{111}P_i^6 + \alpha_{1111}P_i^8] \tag{2}$$

Where P_i is the polarization of the ith layer, i=1, 2, ..., N. The gradient energy term can be written as

$$G_g = \frac{c}{N}\sum_{i=0}^{N}\frac{|P_i - P_{i+1}|^2}{d_i^2} \tag{3}$$

Where c are constants. d_i is the distance between the ith layer and the i+1th layer, so we take $d_i=D/N$, i=1, 2, ..., N−1, and $d_0=d_N=D/2N$. Considering that the lattice constant of the substrate material is not consistent with that of the film, the $BaTiO_3$ film will be affected by the surface tension, which can be simulated by taking different boundary conditions.

$$P_0 = P_{N+1} \tag{4}$$

Surface tension energy and gradient energy both arise from electromagnetic interactions. Here, the surface tension energy is equivalent to the gradient energy produced by the mismatch of film lattice constants and the lattice constants of the substrate. Since the substrate is neither ferroelectric material nor thermoelectric material, the lattice constant of the substrate surface is almost independent of the external electric field and temperature, which can be considered as a constant. Based on the results of first principles calculations, Tagantsev et al. [32] found that the spatial scale of variation of the polarization near the interface is about 2 Å, and Duan et al. [33] obtained that extrapolation length is 2–20 Å for $KNbO_3$ ferroelectric films. The extrapolation length is much smaller than the thickness of film, so we consider that the extrapolation length equals to 0, then the boundary conditions of the third kind is simplified as the boundary conditions of the first kind. So it can be assumed that P_0 is a constant. For a film with freestanding surfaces, $P_0=P_1$ and $P_{N+1}=P_N$.

When a normal electric field E is applied, the static electric energy is given by

$$G_E = \frac{1}{N}\sum_{i=1}^{N}(-E_iP_i) \tag{5}$$

Where E_i is the electric field of the ith layer. Due to the inhomogeneous distribution of the polarization in the normal direction, the depolarization field is produced which is [35].

$$E_i = -\frac{P_i}{\varepsilon_r\varepsilon_0} + E + \frac{1}{N}\sum_{i=1}^{N}\frac{P_i}{\varepsilon_r\varepsilon_0} \tag{6}$$

Where E is the external electric field and ε_r is relative dielectric constant.

The temporal evolution of the polarization is governed by the time-dependent Ginzburg–Landau (TDGL) equations as follows [36]:

$$\frac{\partial P_i}{\partial t} = -K\frac{\delta G}{\delta P_i},\ i = 1, 2, 3, \ldots, N \tag{7}$$

where t and K denote time and kinetic coefficients, respectively. We give the initial conditions P_i=0.5 C m^{-2}. Here the polarization at different electric field and temperature under various surface constants is simulated, and further dielectric constant and hysteresis loop are calculated.

3. Results and discussion

We choose α_1=4.124×10^5 Jm/C^{2}K, α_{11}=−2.097×10^8 Jm^5/C^4, α_{111}=1.294×10^9 Jm^9/C^6, α_{1111}=3.863×10^{10} Jm^{13}/C^8, T_0=388 K [37], N=200, ε_r=1000, D=100 nm, T=300 K. There are obvious size effects (Remanent polarization decreases [38–40], dielectric peak becomes smaller and diffuse [6]) when the thickness of $BaTiO_3$ films is smaller than 400 nm. Huang et al. [41] reported that the $BaTiO_3$ films with a thickness of 108 nm have a weak ferroelectric behavior, very slim, and nearly linear polarization hysteresis loops. Based on these experimental data, we choose c=5×10^{-8} Jm^3/C^2, which is consistent with the data in literature [33], and leads to the size effects when the film thickness is reduced to below 400 nm.

Fig. 1 shows the distribution of polarization with different film thickness under different boundary conditions. We can see that the polarization vary continuously based on the minimum gradient energy. The $BaTiO_3$ film can be consist of inner tetragonal core and the surface gradient layer when the thickness is more than 100 nm. The polarization of the tetragonal layer is constant and close to 0.26 C m^{-2} in coarse grain at room temperature, and surface polarization equals to P_0. The gradient layer thickness is about 50 nm, so the surface gradient layer is the only layer in the film when the thickness $D < 100$ nm. As the film thickness decreases further, the polarization is close to P_0. According to (6), the depolarization effects are caused by a non-uniform distribution of the polarization, so the polarization of tetragonal layer is affected by depolarization field because of the non-uniform distribution of the polarization in the surface gradient layer. Then the gradient layer with an increase of surface polarization produces a positive depolarization field in tetragonal layer, and the gradient layer with a decrease of surface polarization produces a negative depolarization field in tetragonal layer. Therefore, with the increase of P_0 both the depolarization