Effect of electromechanical boundary conditions on the properties of epitaxial ferroelectric thin films*

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The effects of internal stresses and depolarization fields on the properties of epitaxial ferroelectric perovskite thin films are discussed by employing the dynamic Ginzburg–Landau equation (DGLE). The numerical solution for $BaTiO_3$ film shows that internal stress and the depolarization field have the most effects on ferroelectric properties such as polarization, Curie temperature and susceptibility. With the increase of the thickness of the film, the polarization of epitaxial ferroelectric thin film is enhanced rapidly under high internal compressively stress. With the thickness exceeding the critical thickness for dislocation formation, the polarization increases slowly and even weakens due to relaxed internal stresses and a weak electrical boundary condition. This indicates that the effects of mechanical and electrical boundary conditions both diminish for ferroelectric thick films. Consequently, our thermodynamic method is a full scale model that can predict the properties of ferroelectric perovskite films in a wide range of film thickness.

Keywords: ferroelectric film, internal stresses, thermodynamic equations, polarizations

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1. Introduction

Owing to excellent characteristics such as high integration density, high speed and low energy consumption, ferroelectric thin films have been used in non-volatile memory elements[1] and ultra-miniaturized electronics systems.[2] Size effect in ferroelectric thin film has a strong sensitivity to polarization, Curie temperature and susceptibilities with thickness of the film decreasing. Hence, investigations, both theoretical and experimental, have intensified for the last several decades.

A synchrotron X-ray study for $PbTiO_3$ discovered the ferroelectricity as a function of temperature and film thickness.[3] The critical thickness h_c, below which polarization is zero, was found. High-quality $SrRuO_3/BaTiO_3/SrTiO_3$ capacitors were grown epitaxially by high pressure sputtering.[4] Both polarization and lattice parameters were measured and analysed. It is interesting that the polarization has a peak value in a limited range of film thickness. To account for these experimental results, Landau theories, Ising models and first-principles calculations have been used widely. For ultrathin ferroelectric films, considering the competition between the surface and strain effects, Zembilgotov *et al.*[5] analysed the polarization properties of ferroelectric thin films using the mean-field Landau theory. The numerical result shows that the polarization will increase rapidly with the thickness of the films increasing. Taking into account the depolarization fields and the even internal stress effects, similar results have been obtained.[6−9] For thick epitaxial ferroelectric film, the relaxed internal stress via the formation of dislocations was presented to predict the phase stability,[10] dielectric property,[11] and Curie temperature[12] based on the Landau–Devonshire thermodynamic formalism. Their analytical results indicated that the polarization and the Curie temperature decrease towards the bulk values with film thickness increasing. Liu and Nan[13]

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and Hu *et al.*,[14] by taking into account the uneven stress in the film, demonstrated the significant size effect on polarization in the ferroelectric thin film. Because of the defects between the electrode and the usual ferroelectric film, the perfect screening of the depolarization field is not actually achieved. Hence, the incomplete screening condition[15] has been presented to describe the thickness-dependent ferroelectric properties,[11,12,16] instead of the short-circuit or dielectric conditions.[9] The foregoing researches indicate that the films have the strong thickness-dependent ferroelectric properties subjected to electrical and mechanical boundary conditions.

In this paper, based on the dynamic Ginzburg–Landau equation, a full scale nonlinear model is proposed to analyse the thickness-dependent ferroelectric properties of epitaxial thin film involving the effect of the relaxed stress, the incomplete screening and surface lattice relaxation. Employing the finite difference method, we simulate numerically and describe the process of phase transition, Curie temperature, polarization and susceptibility for $BaTiO_3$. The effects of various electrical and mechanical boundary conditions are discussed in detail.

2. Free energy and dynamic equation

Consider an epitaxial (001)-oriented single domain ferroelectric perovskite thin film ($P_1 = P_2 = 0, P_3 = P \neq 0$) grown on a (001)-oriented cubic substrate. We assume that the epitaxial ferroelectric film is sandwiched between two electrodes. The total generalized free energy for unit area, including polarization energy, electrostrictive energy and electroelastic energy, can be described as,[8,10,14,16,17]

$$\begin{aligned} G = & \iiint_V \left\{ \left[\frac{1}{2} a_1 (T - T_{\text{bulk}}) - Q \left(\sigma_{xx} + \sigma_{yy} \right) \right] P^2 \right. \\ & + \left[a_{11} + \frac{Q^2}{(s_{11} + s_{12})} \right] P^4 + a_{111} P^6 \\ & \left. + \frac{1}{2} g \left(\frac{\mathrm{d}P}{\mathrm{d}z} \right)^2 - \frac{1}{2} E_{\text{d}} P \right\} \mathrm{d}V \\ & + \iint_S \left(\frac{1}{2} g \frac{P_{-h/2}^2}{\delta_1} + \frac{1}{2} g \frac{P_{h/2}^2}{\delta_2} \right) \mathrm{d}x \, \mathrm{d}y, \end{aligned} \tag{1}$$

where h is the film thickness; V is the volume of the film; S represents the upper and lower surface planes; P denotes the polarization orthogonal to the surface of the film; T_{bulk} is the Curie temperature of the bulk crystal; a_1, a_{11}, a_{111}, and g are Landau coefficients, respectively; s_{ij} and Q are the elastic compliance coefficients and the electrostrictive coefficient, respectively; δ_1 and δ_2 are the extrapolation lengths representing the extrapolation of polarization beyond the volume of the ferroelectric film, caused by surface eigenstrain relaxation.[8,10]

The incomplete screening of the depolarization field has a great influence on the ferroelectric property, so we adopt $E_{\text{d}} = -\lambda P / \varepsilon_{\text{e}} \varepsilon_0 h$ to represent the depolarization field,[11,15] where λ is the screening length, ε_0 and ε_{e} are the electric permitivities of the vacuum and the electrode, respectively.

The in-plane stresses σ_{xx} and σ_{yy} in the films are induced by lattice mismatch between the film and substrate. In an epitaxial film, internal stress is somewhat high for ultrathin film. With the increase of thickness of film, the formation of misfit dislocations will reduce the internal stress, which is a function of the film thickness. So considering the relaxation of internal stresses, the real internal stresses in the film can be written as

$$\sigma = \sigma_{xx} = \sigma_{yy} = \begin{cases} \varepsilon_{\text{m}} / (s_{11} + s_{12}), & h \leq h_\rho, \\ \varepsilon_{\text{m}} h_\rho / h (s_{11} + s_{12}), & h \geq h_\rho, \end{cases} \tag{2}$$

where $\varepsilon_{\text{m}} = (a_{\text{s}} - a_0) / a_{\text{s}}$ is the misfit strain, a_0 and a_{s} are the lattice parameters of the film and the substrate, respectively. The critical thickness for dislocation formation h_ρ can be obtained by Matthews–Blakeslee model.[18]

According to the dynamic Ginzburg–Landau equation, the time-dependent equation of the polarization $P(z, T, t)$ can be described by

$$\begin{aligned} & \frac{\partial P(z, T, t)}{\partial t} \\ = & -L \frac{\partial G}{\partial P} \\ = & L \left\{ \left[-a_1 (T - T_{\text{bulk}}) + 4 Q \sigma - \frac{\lambda}{\varepsilon_0 \varepsilon_{\text{e}} h} \right] P \right. \\ & \left. - 4 \left[a_{11} + \frac{Q^2}{s_{11} + s_{12}} \right] P^3 - 6 a_{111} P^5 + g \frac{\mathrm{d}^2 P}{\mathrm{d}z^2} \right\}, \end{aligned} \tag{3}$$

where L is the kinetic coefficient.

To avoid unnecessary complexities and elucidate the key factors, we assume that the electrodes are centrally symmetrical alone the thickness of film. Considering the surface lattice relaxation and the symmetrical conditions, equations (1) and (3) need to satisfy

the following symmetrical boundary conditions

$$\left.\frac{\partial P}{\partial z}\right|_{z=\pm h/2} = \mp P/\delta. \tag{4}$$

In contrast to the previous work,[8,11,13,14] the present studies concentrate on the variations of internal stress and depolarization field with thicknesses of the films increasing. For analysing these combined effects on the property of the ferroelectric film, numerical method is necessary.

3. Finite difference method

By using the forward difference method in time and the second order central difference method in space, for each time step the corresponding polarization $P(z_i, T, t)$ at the spatial position z_i can be expressed as

$$\begin{aligned} P(z_i, T, t_{\rm L}) &= P(z_i, T, t + L\Delta t) \\ &= P(z_i, T, t) + L\Delta t \left\{ \begin{array}{l} \left[-a_1(T - T_{\rm bulk}) + 4Q\sigma - \dfrac{\lambda}{\varepsilon_0 \varepsilon_\varepsilon h}\right] P(z_i, T, t) \\ - 4\left[a_{11} + \dfrac{Q^2}{(s_{11} + s_{12})}\right] P(z_i, T, t)^3 - 6a_{111} P(z_i, T, t)^5 \\ + g\left[P(z_{i-1}, T, t) - 2P(z_i, T, t) + P(z_{i+1}, T, t)\right]/\Delta z^2 \end{array} \right\}, \end{aligned} \tag{5}$$

where the film thickness h is separated into N uniform layers with finite spatial step Δz and $i = 1, 2, \ldots, N-1$. In order to satisfy the suitability of the thermodynamics, Δz must be sufficiently large compared with the lattice parameters. Furthermore, the spatial step and the time step should also ensure Eq. (5) constringency.

The approximation of the Neumann boundary conditions of Eq. (4) can be described as

$$\left\{ \begin{array}{l} \left[3P(z_N, T, t_j) - 4P(z_{N-1}, T, t_j) + P(z_{N-2}, T, t_j)\right]/2\Delta z + P(z_N, T, t_j)/\delta = 0 \ , \ \text{at} \ \ z_N = \dfrac{h}{2}, \\ \left[3P(z_0, T, t_j) - 4P(z_1, T, t_j) + P(z_2, T, t_j)\right]/2\Delta z + P(z_0, T, t_j)/\delta = 0 \ , \ \text{at} \ \ z_0 = -\dfrac{h}{2}. \end{array} \right. \tag{6}$$

For improving the convergence rate and stability of the finite different method, the initial polarization at a special temperature is described as cosine distribution

$$P(z_i, T, t = 0) = p_0 \cos(k z_i), \tag{7}$$

where p_0 is a very small value. The eigenvalue k can be obtained by solving the equation $\delta k = \cot(kh/2)$.[16]

The relative susceptibility of the ferroelectric is,[8,19,20]

$$\begin{aligned} \chi &= \frac{1}{\varepsilon_0}\left[\frac{\partial^2 G}{\partial P^2}\right]^{-1} \\ &= \frac{1}{\varepsilon_0}\left[a_1(T - T_{\rm c}) + 12\left[a_{11} + \frac{Q^2}{(s_{11} + s_{12})}\right] P^2 \right. \\ &\quad \left. + 30 a_{111} P^4\right]^{-1}, \end{aligned} \tag{8}$$

where $T_{\rm c}$ is the Curie temperature of ferroelectric thin film and $T_{\rm c} = T_{\rm bulk}$ for ferroelectric bulk.

4. Results and discussions

The present method can predict the properties of epitaxial ferroelectric perovskite film for a wide range of film thickness. As a numerical example, we only calculate the ferroelectric properties of $BaTiO_3$ thin capacitor in this section. The corresponding parameters are listed in Table 1. The electric permittivities of the vacuum and the electrode are assumed to be $\varepsilon_0 = 8.85 \times 10^{-12}$ $(\mathrm{C}^2 \cdot \mathrm{Nm}^{-2})$ and $\varepsilon_{\rm e} = 1$,[10,11] respectively.

Table 1. Phenomenological parameters of $BaTiO_3$.[21,22]

$T_{\rm bulk}$/K	$a_1/(\mathrm{m/F})$	$a_{11}/(\mathrm{m}^5/\mathrm{C}^2 \cdot \mathrm{F})$	$a_{111}/(\mathrm{m}^9/\mathrm{C}^4)$
383	6.6×10^5	$3.6\,(T - 175) \times 10^6$	6.6×10^9
$g/(\mathrm{J} \cdot \mathrm{m}^3/\mathrm{C}^2)$	$s_{11}/(\mathrm{m}^3 \cdot \mathrm{F}/\mathrm{C}^2)$	$s_{12}/(\mathrm{m}^3 \cdot \mathrm{F}/\mathrm{C}^2)$	$Q(\mathrm{m}^4/\mathrm{C}^2)$
2.7×10^{-9}	8.3×10^{-12}	-2.7×10^{-12}	-0.043

Polarization and susceptibility are generally used to distinguish the ferroelectric state from the paraelectric state. Figure 1 shows that the normalized polarization $P/P_{\rm bulk}$ and reciprocal relative susceptibility $1/\chi$ each are a function of temperature for various electromechanical boundary conditions. In Fig. 1(a), for heat-up and cool-down processes, the Curie temperatures have the same values for epitaxial ferroelectric thin capacitor, which then behave as a typical second-order system. It is obvious that strong surface effect (the large screening length λ and the less extrapolation length δ) will reduce the polarization of the ferroelectric state and the Curie temperature $T_{\rm c}$. In Fig. 1(b), reciprocal relative susceptibility will approach to zero when the temperature is close to Curie temperature. It should be noted that $1/\chi$ increases with temperature decreasing below $T_{\rm c}$ due to the primary effect of the increased polarization and increases with temperature increasing beyond $T_{\rm c}$ because of the temperature effect. From the above analyses, Curie temperature of ferroelectric thin film can be easily obtained by measuring the polarization or susceptibility.

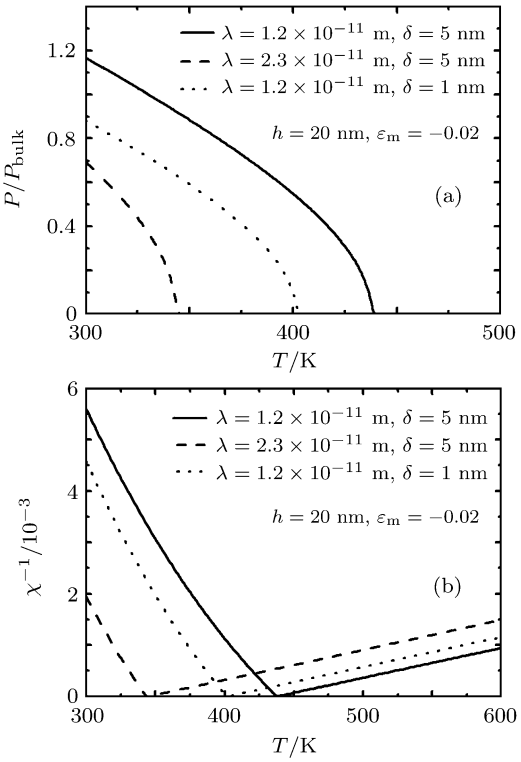


Fig. 1. Normalized polarizations (a) and reciprocal dielectric susceptibilities (b) of ferroelectric films versus temperature for different electromechanical boundary conditions.

The normalized polarization and Curie temperature each as a function of film thickness have been plotted in Fig. 2 for various electromechanical boundary conditions. The calculations demonstrate that there is a critical thickness $h_{\rm c}$, below which the ferroelectricity disappears. The critical thickness $h_{\rm c}$ changes into a large value due to tensile stress and strong surface effect. The results in Fig. 2(a) indicate that the normalized polarization rapidly increases with the increase of film thickness at a finite nanoscale (near the critical thickness $h_{\rm c}$) due to strong thickness-dependent effect of the depolarization field and surface lattice relaxation. With thickness of film increasing, the solid line shows that the formation of misfit dislocations will relax the internal stress as $h > h_\rho$ which will weaken the increase in the amplitude of the polarization. It indicates that there is a special thickness $h_{\rm m}$, at which a maximum polarization exists,

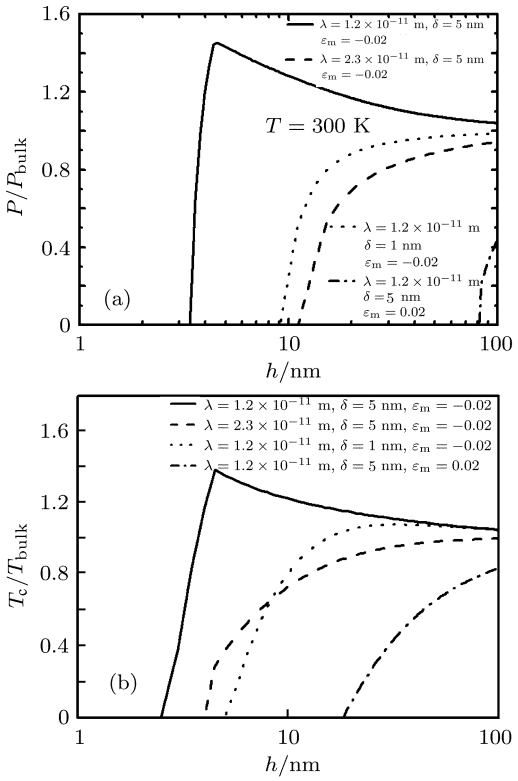


Fig. 2. Thickness dependences of normalized polarization (a) and normalized Curie temperature (b) for different electromechanical boundary conditions.

owing to the competition between the relaxed internal stress and the surface effect. For tensile stress or strong surface effect, the maximum polarization disappears and polarization increases to $P_{\rm bulk}$ monotonically with thickness of film increasing. For the thick film, internal stress and surface effect have a negligible influence on the ferroelectric property and the epitaxial ferroelectric film has the same ferroelectric behaviour as the bulk. So by choosing the appropriate electromechanical boundary conditions, the present method could indicate the different experimental results for ferroelectric perovskite thin films.[4,23] Figure

2(b) shows that Curie temperature has a similar behaviour to the polarization for the full scale ferroelectric film.

Generally, the tensile internal stress will suppress the ferroelectric behaviour and compressive internal stress will enhance the ferroelectric behaviour for the epitaxial (001)-oriented thin film. Figure 3 shows the effects of misfit strain on the normalized polarization for various film thicknesses. Because of thickness-dependence of real strain, all plots have kinks at the special strain points, which vary symmetrically with the origin. The points moves closer to the origin with thickness increasing, which is similar to the behavious of the free-energy plots.[10] For compressive strain film, below these points, the compressive elastic energy is fully converted into the polarization energy and enhances the ferroelectric behaviour. Beyond these special points, the elastic energy is partly converted into the dislocation energy and partly enhances the ferroelectric behaviour. For a tensile strain film, there is a contrary result as the tensile elastic energy suppresses the ferroelectric behaviour. For some ferroelectric films, such as $h = 80$ nm and $h = 100$ nm (dash line and dot line), the normalized polarization will vanish in some range of tensile strains, which indicates that the ferroelectric behaviour in this range is suppressed seriously and the system will still keep in a paraelectric state. This tensile strain range will enlarge with thickness decreasing or temperature increasing. In a high temperature state, this strain range even extends to compressive strain range. From the previous discussion, it is obvious that optimal misfit strain range exists for the ferroelectric thin films with various thicknesses. So the suitable substrates could be selected to design and grow the desired epitaxial ferroelectric films.

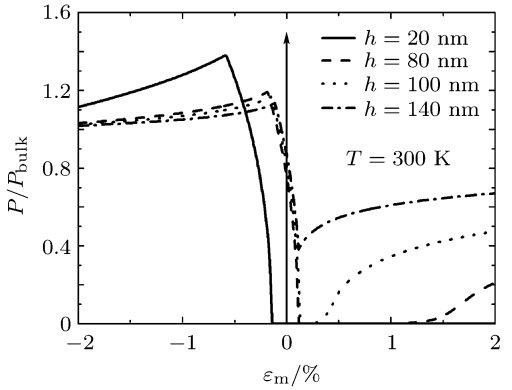


Fig. 3. Normalized polarizations versus misfit strain with some values of h ($\lambda = 1.2 \times 10^{-11}$ m, $\delta = 5$ nm).

Furthermore, we discuss the effects of surface lattice relaxation and the depolarization on the ferroelectric behaviour as shown in Fig. 4. Figure 4(a) shows the variations of normalized polarization with extrapolation length δ for different thicknesses at 300 K. For various thicknesses, polarization value increases with δ increasing and large δ (about $\delta > 10$ nm) can no longer enhance the ferroelectric behaviours. Figure 4(b) shows the relationships between normalized polarization and screening length λ for different temperatures. The screening length λ has great effects on polarization value for different temperatures. At high temperature, polarization will disappear for large λ due to the strong depolarization field.

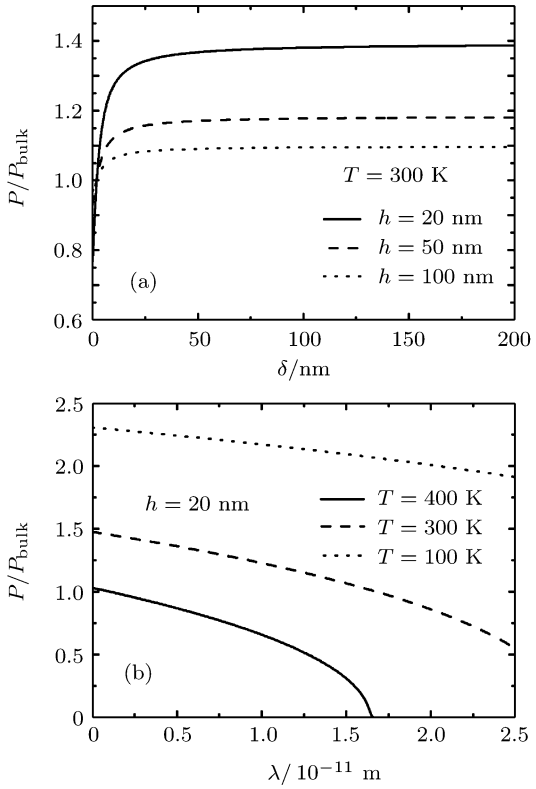


Fig. 4. (a) Normalized polarizations versus extrapolation length with some values of h ($T = 300$ K, $\varepsilon_{\rm m} = -0.02$ and $\lambda = 1.2 \times 10^{-11}$ m) and (b) normalized polarizations versus screening length with some temperatures ($h = 20$ nm, $\varepsilon_{\rm m} = -0.02$ and $\delta = 5$ nm).

5. Conclusions

Based on the dynamic Ginzburg–Landau equation, we present a full scale nonlinear model to describe the ferroelectric properties of the epitaxial ferroelectric perovskite thin films. Taking into account the electromechanical boundary conditions, including the relaxed internal stresses, depolarization field and surface lattice relaxation, thickness-dependent ferroelectric properties are discussed. The numerical re-

sults show that ferroelectric property has a significant size effect for an ultrathin film due to the competition between the relaxed internal stress and surface effect. For the compressively strained film with a weak surface effect, there are a small critical thickness h_c and a special thickness h_m. For the strong surface effect or tensile strained film, the critical thickness h_c changes into a large value and h_m will disappear. In practice, the suitable substrates and buffer layers will be selected to design and produce the desired ferroelectric memories.

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