Thickness dependence of polarization in ferroelectric perovskite thin films

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Abstract
The dependence of the polarization of ferroelectric perovskite thin films on the film thickness is explicitly calculated by using a generalized Landau–Ginzburg–Devonshire thermodynamic theory. Both residual stress and stress relaxation in the films have a significant effect on the thickness-dependent polarization. Our calculations demonstrate that the coexistence or competition between the surface effect and the constraint effect results in significant size effects at a finite nanoscale. This is especially so for the compressively strained perovskite films, in which there are two characteristic thicknesses, i.e. h_c (a few nanometres), below which the ferroelectricity disappears, and h_m ($\sim 10 h_c$), where the polarization exhibits a maximum. The theoretical results describe the available experimental data quite well.

1. Introduction

Ferroelectric thin films have attracted ever increasing attention due to their potential for technological applications in microelectronics (e.g. nonvolatile memory) and microelectromechanics [1]. In these devices, the trend towards miniaturization and integration with silicon has resulted in an increasing focus on the effect of the film thickness on the film properties, an understanding of which is important. This has stimulated fundamental investigations on size effects in ferroelectric thin films. In experiments, it has been found that the polarization of the ferroelectric films (e.g. $BaTiO_3$ and $Pb(Zr_x Ti_{1-x})O_3$ (PZT)) is nonmonotonically dependent on the thickness [2–7]. For example, the polarization of a compressively strained $BaTiO_3$ film increases first with decreasing film thickness, but then decreases with further decrease in the thickness after a maximum at a characteristic thickness h_m [3]. The polarization of the ultrathin film could decrease rapidly down to zero at a critical thickness h_c, i.e. the ferroelectricity finally disappears [8]. However, there is still a lack of a comprehensive fundamental understanding of such size effects in real ferroelectric thin films.

A few atomistic approaches have recently been developed to understand the size effects in perovskite thin films.

For example, a recent first-principles calculation reveals that a depolarization field due to dipoles at interfaces results in a nonzero critical thickness, i.e. $h_c \approx 2.4$ nm, for the ferroelectric stability in $BaTiO_3$ ultrathin films [9], which is somewhat in contrast to previous atomistic simulation results of the possible absence of a critical thickness for perovskite ferroelectric thin films [10]. However, these simulations are only available for ultrathin films (e.g. less than 15 nm in thickness), and do not explicitly account for the influences of residual stress in real ferroelectric films. Recently, the influence of the residual stress due to the misfits between films and substrates on the dielectric constant as well as phase equilibrium has been theoretically investigated for ferroelectric thick films (e.g. larger than 100 nm), where the surface (or interface) effect due to dipoles [9] and surface/interface chemistry and structure could be neglected [11–13]. However, nanoscale size effects have been missed in these studies. For thin films of the nanoscale size, both the surface effect and residual stress should be considered in order to explicitly reveal the nanoscale size effects due to the coexistence or competition between the constraint effect and the surface effect in thin films.

In most previous work, a uniform residual stress state has been considered in the films [11–13]. The residual stress in the ferroelectric films might gradually attenuate along the eptiaxial growth direction or thickness direction due to the stress relaxation away from the most constrained

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film/substrate interface [14], resulting in a gradient residual stress (GRS) state, not a uniform residual stress state as considered in previous work [11–13]. In this paper, using a generalized Landau–Ginzburg–Devonshire (LGD)-type thermodynamic theory [15], we present a phenomenological model for understanding the nanoscale size effects in real ferroelectric thin films, by incorporating contributions from GRS and the surface effect. As shown in this work, the way in which the residual stress is distributed over the films has a significant effect on the polarization of the films. The conventional view of uniform stress can be considered as a special case of non-uniform stress distribution states.

2. Theoretical framework

It is well known that the LGD free energy for unit area of a constrained perovskite film is composed of the polarization energy, electrostrictive energy and elastic energy [11–13, 15]. In the present consideration of both the GRS and interface contributions, the total generalized free energy of a c-phased perovskite thin film ($P_1 = P_2 = 0$, and $P_3 = P \neq 0$) is given by

$$G = G_0 + \int_0^h \mathrm{d}z \left\{ \frac{1}{2} A(T - T_{\mathrm{C}\infty})P^2 + \frac{1}{4} BP^4 \right.$$
$$+ \frac{1}{6} CP^6 + \frac{1}{2} D \left(\frac{\mathrm{d}P}{\mathrm{d}z} \right)^2 - \frac{1}{2} E_{\mathrm{d}} P - 2\sigma_r \varepsilon_0$$
$$\left. - \frac{1}{2}(S_{11} + S_{12})\sigma_r^2 \right\} + \frac{1}{2} \frac{DP_{\mathrm{i}}^2}{\delta}, \quad (1)$$

where h is the thickness of the film, the expansion coefficients A, B, C and D are independent of temperature T and position z, $T_{\mathrm{C}\infty}$ is the Curie temperature of the bulk counterpart, E_{d} the depolarization field, i.e. $E_{\mathrm{d}} = -(P - (1/h) \int_0^h P(z)\mathrm{d}z)/\kappa$ with κ being the dielectric permittivity, S_{ij} are the elastic compliance constants, P_{i} is the polarization at the interface and δ the extrapolation length [16]. The coupling effect between the mechanical deformation and the spontaneous polarization in the ferroelectric material can be described using the electrostrictive coefficient Q, where $\varepsilon_0 = QP^2$ [13]. Here, the biaxial residual stress σ_r is assumed to exponentially decrease from the film/substrate interface (figure 1), i.e. [14, 17]

$$\sigma_r = \sigma_0 \exp(-kz), \quad (2)$$

where σ_0 is the position-independent maximum residual stress (MRS), which appears at the interface between the film and substrate, and k is a decline parameter describing stress relaxation with distance; $k = 0$ corresponds to a complete uniform stress state. The experimentally calibrated
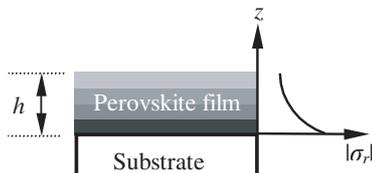

Figure 1. Schematic illustration of a residual-stress-graded perovskite thin film; h is the film thickness and σ_r is the GRS along the thickness direction z.

value of k for ferroelectric films is $\sim$0.004 nm^{-1} [14] and this value is adopted in the present simulations unless specifically mentioned. The value of σ_0 is mainly associated with the lattice misfit u_{m} between the film and substrate and is described as usual, i.e. [11]

$$\sigma_0 = \frac{u_{\mathrm{m}}}{S_{11} + S_{12}} = \frac{a_{\mathrm{s}} - a_{\mathrm{f}}}{a_{\mathrm{s}}(S_{11} + S_{12})}, \quad (3)$$

where a_{s} and a_{f} are, respectively, lattice parameters of the film and substrate materials.

In equation (1), the first five terms in the second part on the right-hand side represent the polarization energy [18], the sixth term corresponds to the electrostrictive energy, and the seventh term is the elastic energy [19]. The present generalized LGD free energy is a function of the film thickness as integrated from 0 to h. In comparison, the recent work by Zembilgotov et al [19], which dealt with the competition between the residual stress and the surface effect as well, treated the residual stress as uniform and so the total free energy was a symmetric function of the thickness as integrated from $-h/2$ to $h/2$. In addition, the depolarization field energy [9, 16] is introduced in this work to take into account the effect of the mean depolarization field.

Due to the two-dimensional clamping effect in films, the ferroelectric transition in the epitaxial thin film may become the second-order transition even if it is the first order in its bulk counterpart [11]. This situation occurs in epitaxial BaTiO$_3$ and PbTiO$_3$ films [11], and, thus, in the present calculations we consider the second-order transition [11], whereas in a recent similar work by Wang et al [17], they simply considered the first-order transition. For the second-order transition of $C = 0$, the Euler's equation of equation (1) is given by

$$D\frac{\mathrm{d}^2 P}{\mathrm{d}z^2} = A(T - T_{\mathrm{C}\infty})P + BP^3 - E_{\mathrm{d}} - 4QP\sigma_0 \exp(-kz), \quad (4)$$

with the following boundary conditions:

$$\frac{\mathrm{d}P}{\mathrm{d}z} = \pm \frac{P}{\delta} \quad \text{at } z = 0 \text{ and } h \text{ with the interface effect}$$
considered,

or

$$\frac{\mathrm{d}P}{\mathrm{d}z} = 0 \quad \text{at } z = 0 \text{ and } h \text{ without the interface effect}$$
considered.

In this paper, only the positive δ value is considered in order to describe the worse case of polarization suppression in the interface layers of the film [20]. For simplification, we rescale variables into dimensionless forms, i.e. $t = T/T_{\mathrm{C}\infty}$, $y = P/P_0$ with $P_0 = \sqrt{AT_{\mathrm{C}\infty}/B}$, $e_{\mathrm{d}} = E_{\mathrm{d}}/E_0$ with $E_0 = P_0/\varepsilon_0$, $\xi = z/\xi_0$ with $\xi_0 = \sqrt{D/\sqrt{AT_{\mathrm{C}\infty}}}$. Then, equation (4) can be rewritten as

$$\frac{\mathrm{d}^2 y}{\mathrm{d}\xi^2} = \left[(t - 1) - 4Q \exp(-kz) \frac{\sigma_0}{AT_{\mathrm{C}\infty}} \right] y + y^3 - \Theta e_{\mathrm{d}}, \quad (5)$$

where $\Theta = (AT_{\mathrm{C}\infty}\varepsilon_0)^{-1}$. By using the finite-difference method, the polarization profile $P(z)$ (not presented here) of the film can be numerically solved and the mean polarization of the film, $\bar{P}$, can be integrated based on $P(z)$.

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Table 1. Properties of BaTiO$_3$ and PZT (20/80) used in the present simulations [11–13, 21, 22].

Properties	BaTiO$_3$	PZT (20/80)
$T_{C\infty}$ (°C)	118.0	459.1
$\varepsilon/\varepsilon_0$	1100	910
Q (m^4 C^{-2})	−0.043	−0.046
A (10^5 Vm C^{-1})	6.65	1.33
B (10^9 Vm^5 C^{-3})	3.56	4.76
D (10^{-9} Vm^5 C^{-3})	4.51	4.46
$S_{11} + S_{12}$ (10^{-12} m^2 N^{-1})	5.62	6.65

3. Numerical results and discussion

For quantitative purposes, two technologically important ferroelectric films, i.e. Pb(Zr$_x$Ti$_{1-x}$)O$_3$ (PZT) and BaTiO$_3$, are taken as examples and some of the properties of the two materials used for the calculation are presented in table 1. According to Zembilgotov *et al* [19], the δ value should be proportional to $\sqrt{D/|A(T - T_\infty) - 4Q\sigma_0|}$ in order to make the thermodynamic model self-consistent. Here, the scale factor is taken as 0.2 and 0.3 for PZT and BaTiO$_3$ thin films by referring to recent experimental [23] and simulated results [10], respectively. This self-consistent treatment makes δ dependent on σ_0 or on the interfacial constraint conditions; this is significantly different from the treatment by Wang *et al* [17], where δ was simply chosen as a constant equal to 1 nm [17]. For comparison, the individual influence of the interface effect (without considering GRS) or GRS (without considering the interface effect) as well as the combined influence from both the interface effect and GRS on polarization behaviour are simulated to understand the competition between GRS and the interface effect in the nanoscale regime.

Figure 2 shows the typical dependence of $\bar{P}/\bar{P}_\infty$ ($\bar{P}_\infty$ being the mean polarization of the bulk counterpart) on the interface effect and GRS as a function of thickness h for these two thin films. The calculations clearly reveal the whole profiles of the mean polarization as a function of h. For comparison with available experiments, we first consider a stress status as in the experiments, such as a compressively strained BaTiO$_3$ film with $\sigma_0 \approx -2.0$ GPa [3] and a PZT film with $\sigma_0 \approx -1.0$ GPa [5], and a tensely strained BaTiO$_3$ film with $\sigma_0 \approx 0.3$ GPa [6] and a PZT film with $\sigma_0 \approx 0.2$ GPa [7]. When only the surface effect is considered (see dotted lines in figure 2), the ferroelectricity of the films is suppressed at a finite size, and the spontaneous polarization of the ultra-thin films sharply decreases with decreasing thickness around 10 nm and disappears at a critical thickness, which is in agreement with the previous first-principle calculations [9]. At large thickness, the surface effect is minor and the perovskite films exhibit the same ferroelectric behaviour as the bulk. When only the GRS is considered, the compressive GRS (see dashed lines in figure 2) or negative lattice misfit between the substrate and film ($a_s < a_f$) is favourable to enhance and stabilize the ferroelectricity of the perovskite films, especially at small thickness. This is in contrast to the influence of the surface effect above. As the film thickness increases, the influence of the compressive GRS gradually decreases. For real ferroelectric films where both the surface effect and the constraint effect from the compressive GRS coexist, the competition between
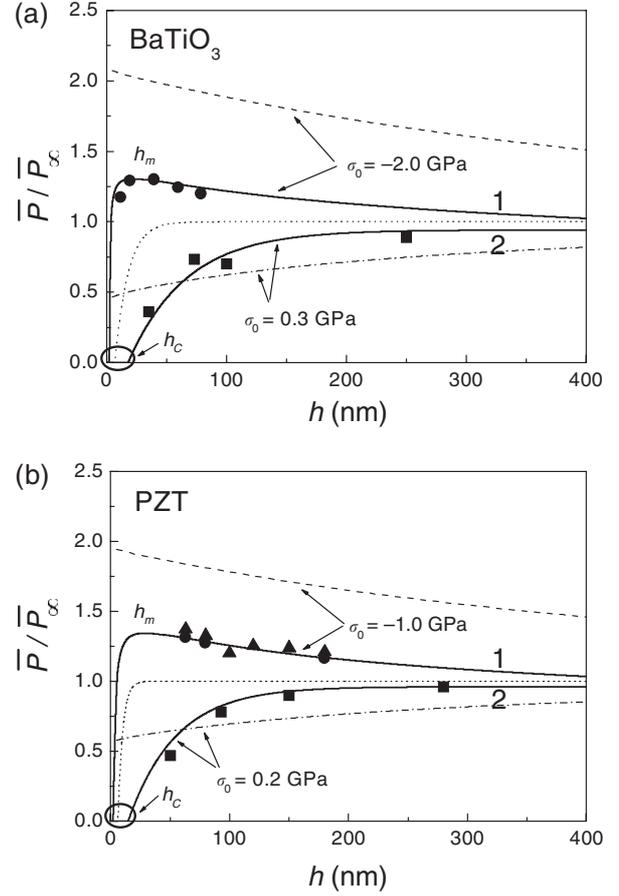

Figure 2. Normalized mean polarization $\bar{P}/\bar{P}_\infty$ calculated from the surface effect alone ($\cdots\cdots$), GRS alone (- - - - for the compressive GRS and — · — for the tensile GRS), and both surface and GRS contributions (——, line 1 is the compressive one and line 2 the tensile, respectively) as a function of the film thickness h for (a) BaTiO$_3$ and (b) Pb(Zr$_{0.2}$, Ti$_{0.8}$)O$_3$ (PZT) film at room temperature. The solid dots and squares in (a) are experimental data for the BaTiO$_3$ films from [3] and [6], respectively. The solid dots and triangles, and squares in (b) are experimental data for the PZT films from [5] and [7], respectively.

both effects occurs in the nanoscale regime. What is of interest here is that the calculations demonstrate that this competition results in the appearance of a maximum polarization ($\bar{P}_m$) at a characteristic thickness h_m, and thereby a saddle-shaped dependence of $\bar{P}/\bar{P}_\infty$ on the film thickness, as shown by the solid lines denoted by 1 in figure 2. Above h_m, the constraint effect due to the compressive GRS dominates over the interface effect, and the polarization of the films decreases with increasing h, as observed in experiments [2–4]. In contrast, below h_m, the surface effect overwhelms the constraint effect, and thus the spontaneous polarization of the thin films sharply decreases from $\bar{P}_m$ to zero with decreasing thickness from h_m down to the critical thickness h_c. The comparison in figure 2 illustrates that the calculations are in quite good agreement with experiments available for the compressively strained BaTiO$_3$ film [3] (figure 2(a)) and PZT film [5] (figure 2(b)), and that the calculated h_m value for the compressively strained BaTiO$_3$ film (figure 2(a)) coincides well with the experimental observation [3].

On the other hand, as only the tensile GRS is considered, the spontaneous polarization of the films decreases with

decreasing film thickness (see the dashed-dotted lines in figure 2). Therefore, in the real tensely strained films with both the tensile GRS and surface effect coexisting, there is no such characteristic thickness h_m, and the tensile GRS accelerates the occurrence of ferroelectric instability in the thin films, i.e. shifts the critical thickness h_c to a large value, as shown by the solid lines denoted by 2 in figure 2. The comparison in figure 2 also demonstrates that the experimental results available for the tensely strained BaTiO$_3$ film (figure 2(a)) [6] and PZT film (figure 2(b)) [7] verify this calculated behaviour.

For comparison, the calculations are also performed by taking into account the uniform residual stress status, as shown in figure 3. The comparison in figure 3 shows that when the uniform residual stress is taken into account, we obtain results different from those obtained by taking into account the GRS. The thickness-dependent polarization calculated, based on the GRS assumption, agrees better with the experiments than that based on the conventional uniform stress assumption. The calculations also demonstrate that the stress status in the films has a significant effect on the polarization.

From the above discussions, we see that the nanoscale size effect in ferroelectric perovskite thin films is strongly dependent on the GRS. Therefore, both the MRS, σ_0, and the decline parameter, k, are important parameters in the nanoscale size effect. For further illustration, figure 4 presents the influence of the MRS on the thickness-dependent
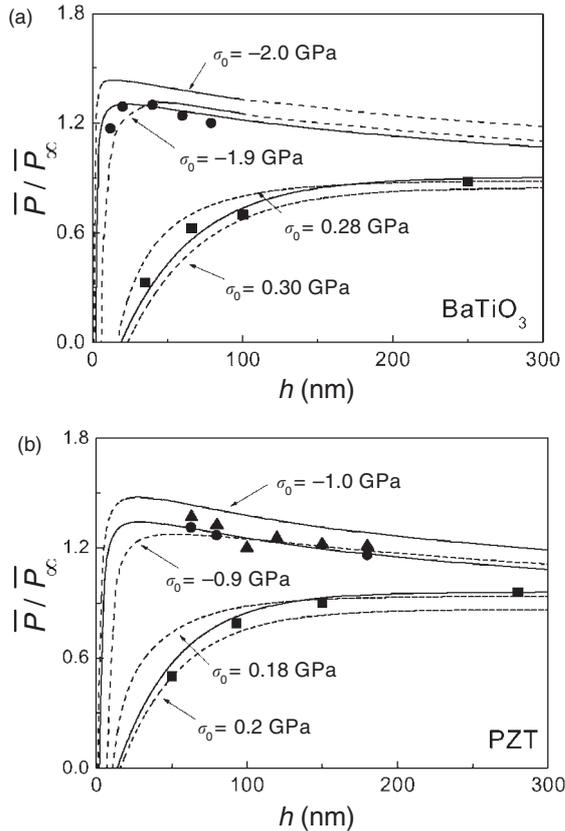
polarization in the nanoscale regime for these two thin films. It is clearly seen that the increase in the compressive MRS leads to an increase in the amplitude of the polarization (figures 4(a) and (b)), and correspondingly to a decrease both in h_c and h_m (figures 5(a) and (b)), while the increase in the tensile MRS leads to a large decrease in the amplitude of the polarization (figure 4(c)) and, therefore, to a large increase in h_c (figure 5(a)). This is mainly attributed to the increase or decrease in the tetragonality c/a caused by axial compression or tension, respectively, which could suppress or stimulate the phase transition from a tetragonal (c-phased) to a cubic one. For the compressively strained thin films $h_m \sim 10 h_c$ (figure 5). The comparison in figures 4(a) and (b) shows that there is good agreement between the calculated h_c values and the available experimental data. For example, for the compressively strained PZT thin film (figure 4(b)), the present calculations show that an ultrathin PZT film of 3.9 nm can still retain ferroelectricity as $\sigma_0 = -0.5$ GPa; in experiments, a critical thickness of
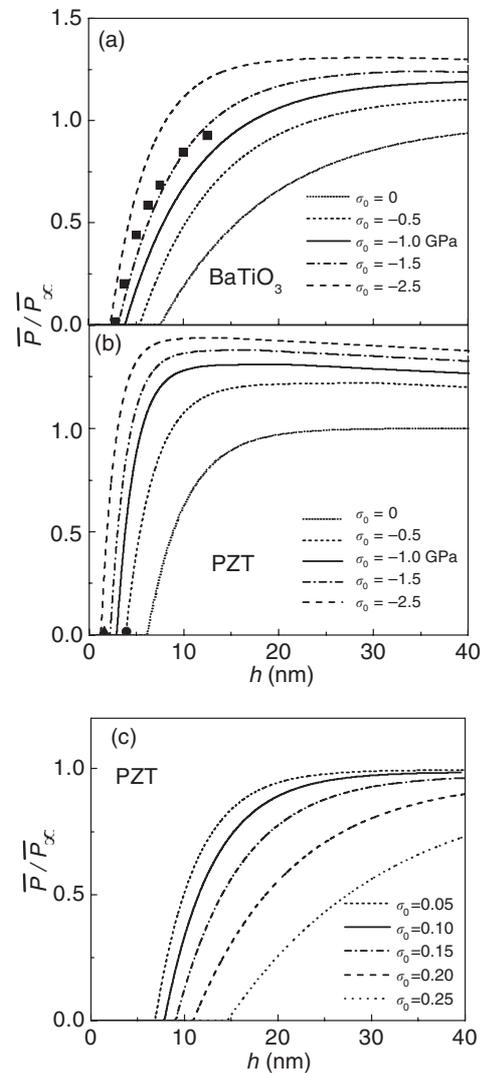

Figure 3. Comparison of the normalized mean polarization $\bar{P}/\bar{P}_\infty$ calculated by considering a uniform residual stress status (see the - - - -) and GRS (see the ——) for (a) BaTiO$_3$ and (b) Pb(Zr$_{0.2}$, Ti$_{0.8}$)O$_3$ (PZT) films. The solid lines for the GRS case and the dots for the experimental results are re-plotted from figure 2.

Figure 4. Dependence of the normalized mean polarization $\bar{P}/\bar{P}_\infty$ on the MRS, σ_0, as a function of film thickness h for (a) constrained BaTiO$_3$ film; (b) constrained PZT film; and (c) PZT film in tension, respectively, at room temperature. The solid squares in (a) are the first-principles-based calculation results from [9]. The solid dot and triangle in (b) are experimental data from [8] and [23], respectively.
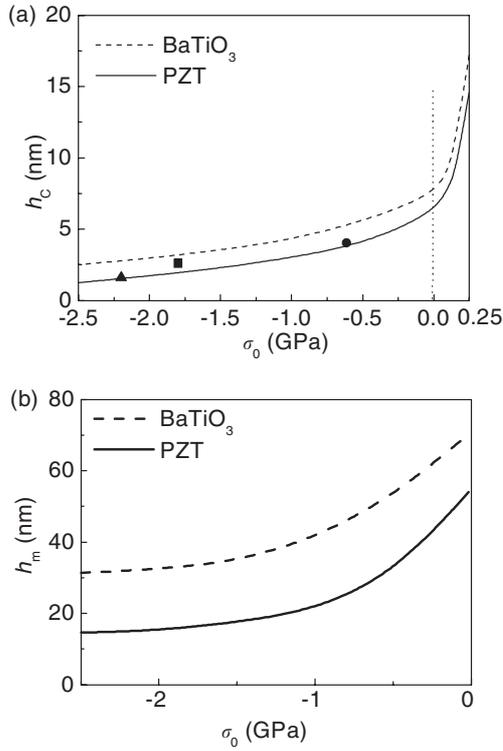
Figure 5. The dependence of (*a*) critical thickness h_c and (*b*) characteristic thickness h_m on σ_0 for PZT and BaTiO$_3$ thin films, respectively. The square, solid dot and triangle in (*a*) are first-principles-based calculation results and experimental data from [8, 9] and [23], respectively.

Figure 6. (*a*) Dependence of the normalized mean polarization $\bar{P}/\bar{P}_\infty$ on the decline parameter k as a function of film thickness h for a BaTiO$_3$ film with $\sigma_0 = -1.8$ GPa. (*b*) Variation of h_m with the decline parameter k for both BaTiO$_3$ and PZT thin films.

4 nm for the ferroelectric PZT film was recently observed [8] as epitaxially grown on Nb-doped (001)-oriented SrTiO$_3$, i.e. as $\sigma_0 = -0.61$ GPa. In addition, a PbTiO$_3$ film, another perovskite material very similar to PZT, was observed to have stable ferroelectricity even down to 1.6 nm in thickness as the maximum residual compressive strain is about 1.2% or $\sigma_0 = -2.18$ GPa [23], which also falls into the predicted range of 1.25–1.73 nm, as $\sigma_0 = -2.5$ to -2.0 GPa (figure 5(*a*)). As shown in figure 2(*a*) or 4(*a*), for the BaTiO$_3$ thin film, the present calculated results with $\sigma_0 = -2.0$ to -1.5 GPa are in good agreement with the first-principle calculations [9] for the BaTiO$_3$ thin films grown on (001)-oriented SrRuO$_3$ with a MRS of -1.8 GPa. Figure 5(*a*) further indicates that ultrathin films, down to 1–2 nm in thickness, can retain ferroelectricity when bearing a large compressive residual stresses, in accordance with recently measured values [23] and atomistic simulations [9, 10].

In addition to the MRS σ_0, the stress relaxation along the thickness direction (represented by the parameter k) also has an important effect on the polarization behaviour of the films. As shown from figure 6, for compressively strained perovskite thin films grown on substrates such as SrRuO$_3$ and SrTiO$_3$, an increase in k makes the residual stress relax easily, which results in a decrease in the amplitude of the polarization (figure 6(*a*)) and an increase in h_m (figure 6(*b*)). However, the variation in k (i.e. variation in the stress profiles) has less influence on the critical thickness h_c, since the stress relaxation is negligible when the thickness goes down to several nanometres ($\sim h_c$). When there occurs no gradient
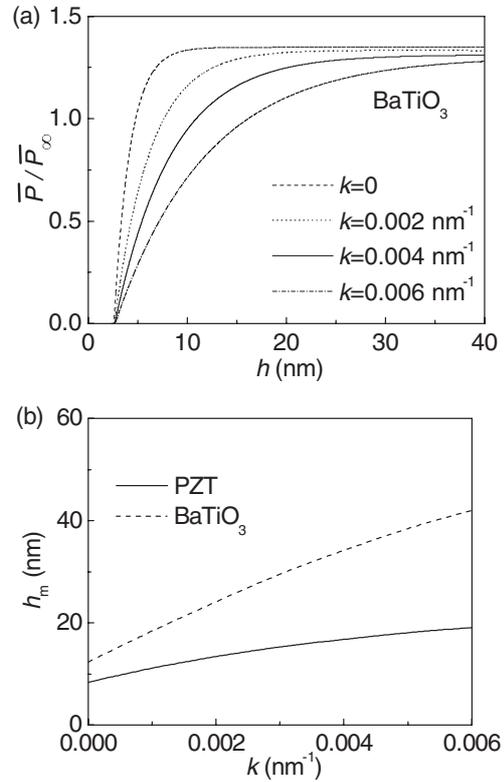
stress relaxation, i.e. $k = 0$, which is the complete uniform stress status, very thin perovskite films having thicknesses close to h_c (i.e. several nanometres) could maintain the same spontaneous polarization as the bulk. This variation in the polarization with k is also a reflection of the competition between the interface effect and the constraint effect from GRS.

4. Conclusions

A generalized LGD thermodynamic theory has been presented to treat the nanoscale size effects in ferroelectric thin films, and the theoretical calculations describe the available experimental data quite well. Significant size effects at a finite nanoscale observed in the perovskite thin films result from the coexistence with or competition between the surface effect and the constraint effect, especially from compressive residual stress. For the compressively strained perovskite films, the competition between two contributions leads to two characteristic thicknesses; i.e. the critical thickness h_c (a few nanometres) below which the ferroelectricity disappears, and h_m ($\sim 10 h_c$), where the polarization exhibits a maximum. For the tensely strained perovskite films, the critical thickness h_c shifts to a large value but there is no h_m. Both residual stress and stress relaxation along the thickness direction have a significant effect on the polarization behaviour of the films. The calculations provide insights not only into how thin perovskite films can retain their ferroelectric stability but also into practical applications, such as how to select suitable substrates for growing desired ferroelectric thin films.

Acknowledgments

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