Competitive interactions between the surface effect and the depolarization field effect on the critical size of ferroelectric perovskite ultrathin films

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Received 29 October 2006; revised 18 November 2006; accepted 21 November 2006
Available online 18 December 2006

Keywords: Ferroelectric film; Crucial film thickness; Surface effect; Depolarization field effect

A competitive interaction exists between the surface effect and the depolarization field effect on the size effect of ferroelectric films, and there exists a crucial film thickness ($h_s$), where the dominant influencing effect changes from the depolarization field effect at larger thickness to the surface effect at smaller thickness. We estimate $h_s$ to be $\sim 20–40$ nm, varying with the residual strain, for PbTiO$_3$ films by using a generalized Landau–Ginzburg–Devonshire thermodynamic theory. The calculations are in good agreement with measurements.

Ferroelectric thin films have attracted ever-increasing attention due to their significance for technological applications in microelectronics, such as nonvolatile memory [1,2]. In device technologies, the trend towards miniaturization and integration with silicon has resulted in an increasing focus on the effect of thickness on a film’s properties. Experimental results [3–6] have all shown that there are strong size effects on ferroelectric thin films, i.e. the Curie temperature, spontaneous polarization, dielectric constant, and other electric and thermal properties all decrease with decreasing thickness of thin films. The anomalies induced by the finite size effects are attributed mainly to two influences: the surface effect [7,8] and the depolarization field effect [9,10]. Although, it has been well known that the two influences work simultaneously with distinct mechanisms and cause the collective phenomenon of size effect in combination, some fundamental aspects are still not understood, especially about which is the dominant one and how the two influences interact. It is thus of both theoretical interest and technological interest to better understand the separate and combined contributions of the two influences to the size effects in ferroelectric thin films.

Many studies have been carried out on perovskite thin films, a technologically important type of ferroelectric thin film, to theoretically understand the size effects by considering both the surface effect influence and the depolarization field influence [11–13]. However, only the cooperation between the two influences was concerned in these previous studies, with no attention paid to the competition between the two influences. In reality, there is inevitably a competitive issue to the coexistence of the surface effect and the depolarization field effect, with the dominant effect alternating in regions with different conditions, and the two effects interacting not only in combination but also in competition. The combinatorial interaction results in the collective phenomenon of size effect, while the competitive interaction should result in a critical point, where the dominant effect is alternated. So far as we know, no studies have focused on this critical point or this competitive interaction. In this letter, we reveal this competitive interaction clearly by comparing the single influence of the depolarization field effect with the coupled influence of both depolarization field effect and the surface effect on the thickness dependence of ferroelectric–paraelectric transition temperature ($T_C$) in perovskite thin films. The coupled influence was numerically calculated from...
a generalized Landau–Ginzburg–Devonshire (LGD) thermodynamic theory [11], and the single influence of the depolarization field effect was calculated from the same theory too, but is resolved analytically in order to avoid the incorporation of any surface effect. The consideration of the competitive interaction between the two effects can closely mimic the real experimental situations.

In perovskite thin films, 180° stripe multi-domains, in which the polarization forms a transverse wave with alternating signs between adjacent lamella as schematically shown in Figure 1, are usually presented to minimize the energy of the electric field arising from the polarization distribution of the depolarization field. The unit volume depolarization field, \( E_d \), is then suggested [14] to relate with the energy of the 180° stripe multi-domain walls or the stationary equilibrium domain width, \( d \), as \( E_d = 2 \gamma / d \), with the value of \( d \) being experimentally measured [3] as a function of the film thickness \( h \), the unit area domain wall energy \( \gamma \), and the equilibrium \( P \), i.e., \( d = 0.18 P [\gamma_0 \varepsilon_{ex}(1 + \sqrt{\varepsilon_{1}/\varepsilon_{ex}})]^1/2 \), where \( \varepsilon_1 \) and \( \varepsilon_2 \) are the dielectric constants of the film perpendicular and parallel to the polarization direction, respectively, and \( \varepsilon_{ex} \) is that of the substrate. The domain wall energy is temperature dependent and is proportional to the square of the polarization in first approximation with only the lower order of polarization being considered, so that \( \gamma \) can be simply expressed as \( \gamma = \gamma(0)(P/P(0))^2 \), where \( \gamma(0) \) and \( P(0) \) are the unit area domain wall energy and polarization at \( T = 0 \) K, respectively. After incorporating the depolarization field energy, the generalized LGD free energy for the unit area of a \( c \)-phased perovskite film (\( P_1 = P_2 = 0 \), and \( P_3 = P \neq 0 \)) is expressed as

\[
G = G_0 + \int_0^h \frac{d}{dz} \left[ \frac{1}{2} \left\{ A(T - T_{C\infty}) P^2 + \frac{1}{4} BP^4 + \frac{1}{6} CP^6 + \frac{1}{2} D \left( \frac{dp}{dz} \right)^2 \right. \right. \\
- 2 \sigma_1 \varepsilon_1 + 0.37 P^2 \varepsilon_{ex}(1 + \sqrt{\varepsilon_1 / \varepsilon_{ex}}) P(0) / \gamma(0) \] \left( \frac{HE}{P} \right) \right \} \\
+ \frac{1}{2} DP^2 / \delta, \tag{1}
\]

where expansion coefficients \( A, B, C \) and \( D \) are independent of temperature \( T \) and position \( z \), \( T_{C\infty} \) is the Curie temperature of the bulk counterpart, \( P_i \) is the polarization at the film surface, \( \delta \) is extrapolation length and \( \sigma_1 \) is the biaxial residual stress in the film. The coupling effect between the mechanical deformation and the spontaneous polarization in the ferroelectric material can be described using the electrostrictive coefficient \( Q \), where \( \varepsilon_r = QP^2 \) [15]. Experiments have shown that the biaxial residual stress in the film decreased exponentially from the film/substrate interface to the interior, i.e. \[ \sigma_r = \sigma_0 \exp(-kz), \tag{2} \]

where \( \sigma_0 \) is the thickness-independent maximum residual stress, which appears at the interface between the film and substrate and is quantitatively related to the lattice misfit \( \delta_{m} \) between the film and substrate as \( \sigma_0 = \delta_{m} / \left( S_{11} + S_{12} \right) = (a_s - a_f) / a_f \left( S_{11} + S_{12} \right) \) [17], where \( a_s \) and \( a_f \) are lattice parameters of the film and substrate materials, respectively, and \( S_{11} \) and \( S_{12} \) are compliance coefficients of the film. The parameter \( k \) is a decline parameter describing stress relaxation with distance and is experimentally evaluated as \( \sim 0.004 \text{ nm}^{-1} \) for perovskite films [16]. According to Roystburd et al. [18], the presence of residual stress should induces a scaled increase in polarization, i.e. \( P(z) = P_0 \exp(-kz) + P_c \), where \( P_c \) is the intrinsic polarization of film and \( P_0 \) is the maximum increase similar to \( \sigma_0 \).

For a second-order transition of \( C = 0 \) and \( B > 0 \), the Euler’s equation of Eq. (1) is given by

\[
D \frac{d^2P}{dz^2} = A(T - T_{C\infty}) P + BP^3 - E_d - 4QP\sigma_0 \exp(-kz) + 0.74P \sqrt{\Omega/\hbar, \tag{3}}
\]

where \( \Omega = \gamma(0)/\varepsilon_{ex}(\varepsilon_1 + \varepsilon_{ex}) \). Submitting the expression of polarization \( P(z) \) into Eq. (3) and neglecting the infinitesimal item containing the third power of \( P_0 \exp(-kz) \), the following identical equations are analytically resolved based on the classification in items containing the same power of \( \exp(-kz) \):

\[
3BP_0P_c - 4Q\sigma_0 = 0, \tag{4.1}
\]

\[
DK^2 - A(T - T_{C\infty}) - 0.74 \sqrt{\Omega/\hbar} = 0, \tag{4.2}
\]

\[
BP_c^2 = A(T_{C\infty} - T) - 0.74 \sqrt{\Omega/\hbar}. \tag{4.3}
\]

From Eq. (4.3), the critical transition temperature, \( T_{C\infty} \), is derived as

\[
T_{C\infty} = T_{C\infty} = 0.74 \sqrt{\Omega / AV} \tag{5}
\]

Although, the above equation indicates that the transition temperature decreases with decreasing thickness of perovskite thin films, it only reveals the singular influence of the depolarization field effect on the size effect in transition temperature. When the surface effect is considered as well, the coupled influence of the two effects on the variation of transition temperature with thickness could be numerically calculated from Eq. (1) by using the finite-difference method and by introducing the boundary conditions of \( dP/dz = \pm P/\delta \) at \( z = 0 \) and \( h \) [19], \( \delta \approx \sqrt{D/|A(T - T_{C\infty}) - 4Q\sigma_0|} \) in order to make the thermodynamic model self-consistent [7].

For quantitative purposes, PbTiO\(_3\) thin film grown on SrTiO\(_3\) substrate is taken as an example. (The values of the relevant parameters used in calculations (in SI units and temperature in °C) are from Refs. [3,17] and [20]: \( T_{C\infty} \) = 752, \( A = 3.8 \times 10^5 \), \( B = 6.3 \times 10^8 \), \( Q = -0.046 \), \( S_{11} + S_{12} = 5.5 \times 10^{-12} \), \( \varepsilon_1 = 150 \), \( \varepsilon_2 = 80 \), \( \varepsilon_{ex} = 300 \), \( P(0) = \sqrt{(AT_{C\infty} + 2Q\sigma_0)/B} \), \( \gamma(0) = 0.132 \).) The experimentally measured decrease in transition temperature

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**Figure 1.** Schematic of a ferroelectric thin film with domains of alternating polarization separated by 180° stripe domain walls. \( h \) is the film thickness and \( d \) is the domain width.
temperature with decreasing thickness \([3]\) is plotted in Figure 2 and the calculated solid curves of the two present models are depicted in the same figure. The solid curve numbered 1 is the analytically resolved one from Eq. (5), which indicates the separate influence of the depolarization field effect on the size effect in transition temperature. The solid curve numbered 2 is the numerically calculated one indicating the coupled influence of the depolarization field effect and the surface effect on the transition temperature. Explicitly, revealed from Figure 2, when the film is thicker than the crucial thickness, \(h_s\), curve 1 is almost coincided with curve 2, both in good agreement with the measured values. When the film is thinner than \(h_s\), curve 2 is progressively lower than curve 1, but is in broad agreement with the measured values. In contrast, curve 1 is far larger than the experimental values, especially at a thickness of several nanometers. A crucial conclusion can thus be drawn that the depolarization field effect makes the overwhelmingly dominant contribution to the size effect, when the film is thicker than \(h_s\), while the surface effect is the more dominant one, when the film is thinner than \(h_s\). However, the size effect is a collective phenomenon resulting from the coupled interaction between the two contributors in cooperation. For comparison, the predicted curve in Ref. [3] is also drawn in Figure 2 as a dashed line. This line deviates greatly from the measured values, which means the present model is more applicable.

As shown in Figure 2, the \(h_s\) is evaluated as about 19 nm for the PbTiO\(_3\) thin films grown on SrTiO\(_3\) substrate, with the \(u_m\) being \(-1.2\%\). When the \(u_m\) is varied, the size effect as well as its contributor should be modulated by the constraint influence from the compressive residual strain or by the consolidated influence from the tensile residual strain, as shown in Figure 3a. The compressive residual strain depresses the size effect and decreases the difference between the depolarization effect and the coupled effect on transition temperature. Hence, the greater the compressive residual strain or the lattice misfit, the lower the \(h_s\) (Fig. 3b). In other words, the suppression of the compressive residual strain on the surface effect is more intense than on the depolarization field effect. In contrast, the tensile residual strain induces an increase in the surface effect, which in turn causes an increase in the \(h_s\). Here, we should mention the core and shell model developed by Glinchuk et al. [21] to calculate the radiospectroscopy spectra for nanoparticles, where the shell is the region near the surface, while the properties of the core is close to the bulk properties. From this point of view, the present crucial thickness \(h_s\) should have a similar physical importance as that of the shell thickness.

The inset in Figure 3b shows the numerically calculated influence of residual strain on another crucial thickness, i.e. the critical thickness for ferroelectric stability, \(h_C\), with and without considering the depolarization field effect or the last item in Eq. (3). The dashed curve is the case without consideration of the depolarization field effect, which means the size effect in this case is exclusively contributed by the surface effect, while the solid curve is the other case considering the coupled interaction of both the surface effect and the depolarization field effect. As a practical situation, the coupling of the depolarization field is clearly found to increase the \(h_C\) or to decrease the ferroelectric stability of ultrathin films.
perovskite films. Some of the experimentally measured or first-principle-calculated values of $h_C$ of perovskite thin films, i.e. 2.4 nm for BaTiO$_3$ film on SrRuO$_3$ substrate with a $u_m$ of $\sim$0.8\% [22], 1.6 nm for PbTiO$_3$ film on SrTiO$_3$ substrate with a $u_m$ of $\sim$1.2\% [3] and 4.0 nm for PZT film on SrTiO$_3$ substrate with a $u_m$ of $\sim$0.4\% [5], agree well with the predictions. However, when the constraint of the compressive residual strain is large enough, the $h_C$ under the coupled effect is close to that under the single surface effect, and both are in good agreement with recently simulated results [23].

In summary, both the cooperative interaction and the competitive interaction between the surface effect and the depolarization field effect in ferroelectric perovskite thin films are studied by using the generalized LGD thermodynamic theory numerically and analytically, respectively. The cooperative interaction between the two effects results in the collective phenomenon of size effect, while the competitive interaction between the two effects results in a crucial thickness of $h_s$, above which the depolarization field is the overwhelming dominant contributor to the size effect and below which the surface effect is the more dominant one. The definition and estimation of the crucial thickness as $\sim$20–40 nm provides a more fundamental understanding of the size effects in technologically important ferroelectric perovskite ultrathin films.

This work was supported by the National Basic Research Program of China (Grant No. 2004CB619303). The authors express their special thanks for the support from the National Natural Science Foundation of China and the National Outstanding Young Investigator Grant of China. This work was supported by Program for Changjiang Scholars and Innovative Research Team in University and the 111 program of China under Grant No. B06025.