

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

Gang Liu, Rui-Hong Wang and Jun Sun*

State Key Laboratory for Mechanical Behavior of Materials, School of Material Science and Engineering, Xi'an Jiaotong University, Xi'an 710049, China

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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 ~ 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.

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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

* Corresponding author. Tel.: +86 29 82667143; fax: +86 29 82663453; e-mail: junsun@mail.xjtu.edu.cn

a generalized Landau–Ginzberg–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 γ , and the equilibrium P , i.e. $d = 0.18P[\varepsilon_0\varepsilon_{\text{ex}}(1 + \sqrt{\varepsilon_1\varepsilon_3/\varepsilon_{\text{ex}}})\gamma h]^{1/2}$, where ε_1 and ε_3 are the dielectric constants of the film perpendicular and parallel to the polarization direction, respectively, and ε_{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 γ 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

$$G = G_0 + \int_0^h dz \left\{ \frac{1}{2}A(T - T_{C\infty})P^2 + \frac{1}{4}BP^4 + \frac{1}{6}CP^6 + \frac{1}{2}D\left(\frac{dP}{dz}\right)^2 - 2\sigma_r\varepsilon_r + 0.37P^2[\varepsilon_0\varepsilon_{\text{ex}}(1 + \sqrt{\varepsilon_1\varepsilon_3/\varepsilon_{\text{ex}}})P(0)h/\gamma(0)]^{-1/2} + \frac{1}{2}DP_i^2/\delta, \right\} \quad (1)$$

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, δ is extrapolation length and σ_r 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

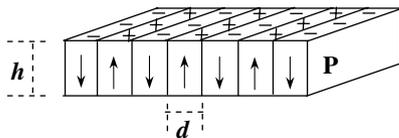


Figure 1. Schematic of a ferroelectric thin film with domains of alternating polarization separated by 180° stripe domain walls. h is the film thickness and d is the domain width.

biaxial residual stress in the film decreased exponentially from the film/substrate interface to the interior, i.e. [16]

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

where σ_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 u_m between the film and substrate as $\sigma_0 = u_m/(S_{11} + S_{12}) = (a_s - a_f)/[a_s(S_{11} + S_{12})]$ [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 Roytburd et al. [18], the presence of residual stress should induce 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 σ_0 .

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

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

where $\Omega = \gamma(0)/\varepsilon_0 P_0(\varepsilon_{\text{ex}} + \sqrt{\varepsilon_1\varepsilon_3})$. 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 $\exp(-kz)$:

$$3BP_0P_C - 4Q\sigma_0 = 0, \quad (4.1)$$

$$Dk^2 - A(T - T_{C\infty}) - 0.74\sqrt{\Omega/h} = 0, \quad (4.2)$$

$$BP_C^2 = A(T_{C\infty} - T) - 0.74\sqrt{\Omega/h}. \quad (4.3)$$

From Eq. (4.3), the critical transition temperature, T_C , is derived as

$$T_C = T_{C\infty} - \frac{0.74\sqrt{\Omega}}{A\sqrt{h}}. \quad (5)$$

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 $^\circ\text{C}$) are from Refs. [3,17] and [20]: $T_{C\infty} = 752$, $A = 3.8 \times 10^5$, $B = 6.3 \times 10^8$, $Q = -0.046$, $S_{11} + S_{12} = 5.5 \times 10^{-12}$, $\varepsilon_1 = 150$, $\varepsilon_3 = 80$, $\varepsilon_{\text{ex}} = 300$, $P(0) = \sqrt{(AT_{C\infty} + 2Q\sigma_0)/B}$, $\gamma(0) = 0.132$.) The experimentally measured decrease in transition

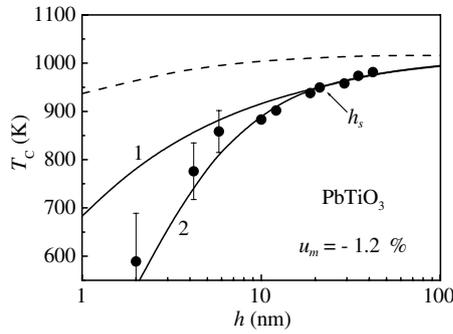


Figure 2. Size effect of the suppression in transition temperature (T_C) with decreasing the thickness (h) for PbTiO_3 thin film. The solid lines numbered 1 and 2 are the predicted singular influence from the depolarization field effect and coupled influence from both the depolarization field effect and the surface effect on the size effect, respectively. h_s is the crucial thickness, where the dominant influencing effect is changes from the depolarization field effect at higher thickness to the surface effect at lower thickness. The dots are experimentally measured values from Ref. [3] and the dashed line is the modeled curve in Ref. [3].

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 $\sim -1.2\%$. 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 sup-

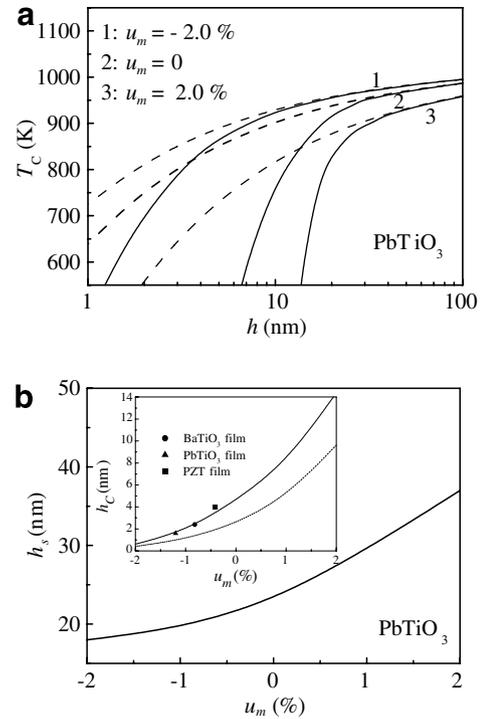


Figure 3. (a) Influence of the residual strain on the size effect of T_C vs. h for PbTiO_3 thin film. The dashed curves are considered with only the depolarization field effect while the solid curves are considered with both the depolarization field effect and the surface effect. (b) Dependence of h_s on the residual strain. The inset shows the dependence of critical size thickness (h_c) on the coupled influence of the two effects (solid curve) and the single influence of the surface effect (dash curve) as a function of thickness. The solid dot, triangle dot and square dot are experimentally measured or first-principle-calculated values from Refs. [22,3], and [5], respectively.

pression 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, where its influence cannot be neglected, 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

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 BaTiO₃ film on SrRuO₃ substrate with a u_m of $\sim -0.8\%$ [22], 1.6 nm for PbTiO₃ film on SrTiO₃ substrate with a u_m of $\sim -1.2\%$ [3] and 4.0 nm for PZT film on SrTiO₃ 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 ~ 20 – 40 nm provides a more fundamental understanding of the size effects in technologically important ferroelectric perovskite ultrathin films.

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