Flexoelectricity induced increase of critical thickness in epitaxial ferroelectric thin films

Hao Zhou [a], Jiawang Hong [b], Yihui Zhang [b], Faxin Li [a], Yongmao Pei [a,*], Daining Fang [a,b,**]

[a] State Key Laboratory for Turbulence and Complex Systems, College of Engineering, Peking University, Beijing 100871, China
[b] Department of Engineering Mechanics, Tsinghua University, Beijing 100084, China

A B S T R A C T

Flexoelectricity describes the coupling between polarization and strain/stress gradients in insulating crystals. In this paper, using the Landau–Ginsburg–Devonshire phenomenological approach, we found that flexoelectricity could increase the theoretical critical thickness in epitaxial $BaTiO_3$ thin films, below which the switchable spontaneous polarization vanishes. This increase is remarkable in tensile films while trivial in compressive films due to the electrostriction caused decrease of potential barrier, which can be easily destroyed by the flexoelectricity, between the ferroelectric state and the paraelectric state in tensile films. In addition, the films are still in a uni-polar state even below the critical thickness due to the flexoelectric effect.

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1. Introduction

Flexoelectricity (FxE) describes the coupling between polarization and strain/stress gradients in insulating crystals. Although it has been discovered for more than 40 years [1], FxE did not arouse much attention for a long time, since it is not obvious in bulk materials. With the development of synthesis of ferroelectric films widely used in microelectronic devices, FxE, which can exist in all dielectrics under inhomogeneous deformation, has raised great concern in recent years, because it may significantly affect the functional properties of films, superlattices and nanostructures. For instance, it may be responsible for a variety of anomalous phenomena, such as the imprint behavior of ferroelectric thin films [2–4] and the "dead layer" effects in nanocapacitor systems [5].

The historical development of FxE study has been reviewed by Tagantsev [6] and more recently by Cross [7]. A series of experiments have been done by Ma and Cross [8] and large FxE coefficients in several ferroelectric ceramics have been found. Zubko et al. obtained the full FxE tensor in the single crystals of the paraelectric $SrTiO_3$ [9]. Catalan et al. also found that the FxE coupling played a fundamental role in the dielectric constant of epitaxial ferroelectrics thin films [10,11]. Recently, Shen and Hu

established an extended linear theory on FxE [12]. Maranganti et al. discussed a theoretical framework that can describe the size-dependent electromechanical coupling owing to strain or polarization gradients [13]. In addition, Hong et al. did a first attempt at calculating the longitudinal FxE coefficient for $SrTiO_3$ and $BaTiO_3$ from first-principles [14]. The first-principles theory of froze-ion FxE was developed very recently [15,16], which represents an important step in the direction of a full first-principles theory of FxE.

Despite the great advances in FxE study, there are few theoretical models and calculations addressing the FxE effect on the critical thickness of ferroelectric thin films below which the switchable spontaneous polarization vanishes. For epitaxial-grown thin films, the misfit strain between the film and substrate will relax as the film thickness increases. This will inevitably induce the strain gradient in the film and the FxE may have a significant effect on the properties of ferroelectric films, such as polarization [9–11,17], dielectric constant [9–11], transition temperature [18], hysteresis loops [19] and critical thickness etc. The critical thickness is an important parameter for ferroelectric films below which the ferroelectric phenomena disappear and the films become paraelectric. However, so far very few works address the FxE effect on critical thickness. As the Landau–Ginsburg–Devonshire (LGD) theory has repeatedly been found to be very powerful in studying ferroelectric thin films, nanowires and other heterostructures down to the nanoscale [20–22], in this work, we use the LGD thermodynamic approach to investigate the FxE effect on the critical thickness of epitaxial $BaTiO_3$ ultrathin

films. Our results show that the FxE increases the critical thickness and this effect is especially remarkable in the tension stressed films. In addition, we demonstrate that the film is still in a polar state even below the critical thickness due to the FxE effect, which is quite different from the conventional paraelectric state below the critical thickness without FxE.

2. Thermodynamic theory of FxE

We consider a *c*-phased ($P_1=P_2=0$), and ($P_3=P\neq0$) single-domain perovskite ferroelectric thin film epitaxially clamped onto a cubic substrate, with in-plane elastic stress that resulted from lattice mismatch between the film and substrate, as shown in Fig. 1, where h is the film thickness and X the residual stress varied along the thickness direction.

The total free energy density of thin film G can be expressed as follows:

$$G = G_0 + G_1 + G_2, \tag{1}$$

where G_0 is the free energy density of the paraelectric phase, G_1 the sum of electrostatic energy, elastic energy, depolarization field energy and surface energy, and G_2 is the FxE energy density. G_1 and G_2 can be expressed as

$$G_1 = \frac{1}{h}\int_0^h \left\{ \frac{1}{2}\alpha_0(T-T_{0\infty})P^2 + \frac{1}{4}\beta P^4 + \frac{1}{6}rP^6 - \frac{1}{2}(s_{11}+s_{12})X^2 \right.$$
$$\left. -2QXP^2 + \frac{1}{2}K\left(\frac{dP}{dz}\right)^2 - \frac{1}{2}E_dP \right\}dz + \frac{K}{2}\left(\frac{P_i^2}{\delta_i}+\frac{P_s^2}{\delta_s}\right), \tag{2}$$

$$G_2 = \frac{1}{h}\int_0^h \left(-\gamma\frac{dX}{dz}P - \eta X\frac{dP}{dz}\right)dz, \tag{3}$$

where h is the thickness of the film; the expansion coefficient α_0, β and r are material parameters; $T_{0\infty}$ is the Curie–Weiss temperature (i.e. Curie temperature for second-order transition) of the bulk counterpart; γ and η are the FxE and converse FxE coupling coefficients; Q is the electrostrictive coefficient; s_{11} and s_{12} are the elastic compliance coefficients; P_i and P_s are the polarizations of the interface ($z=0$) and the surface ($z=h$) respectively; δ_i and δ_s are the extrapolation lengths of the interface and the surface respectively; ε is the dielectric permittivity, and E_d is the depolarization field [23], i.e.

$$E_d = -1/\varepsilon\left(P - 1/h\int_0^h Pdz\right), \tag{4}$$

the residual stress X is assumed to exponentially decrease from the film/substrate interface [24], i.e.

$$X = X_0\exp(-kz), \tag{5}$$

where X_0 is the maximum residual stress in the interface which is determined by the misfitted lattice constant [25]
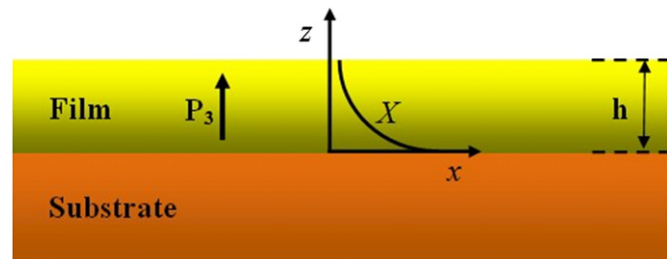
$$X_0 = \frac{a_s-a_f}{a_s(s_{11}+s_{12})}, \tag{6}$$

Fig. 1. Schematic of a film with in-plane mismatched stress in *x*–*z* plane.

where a_s and a_f are lattice parameters of the substrate and film materials. k in Eq. (5) is thickness dependent and it is given by [24] (in nm unit)

$$k(h) = k_0 - \zeta h = 3.925\times10^{-3} - 2.325\times10^{-6}h, \tag{7}$$

It is independent of temperature and has a dimension of (length)$^{-1}$. Eq. (7) indicates that the strain gradient is larger in thinner films.

Variation of Eq. (1) yields the following Euler's equation:

$$K\frac{d^2P}{dz^2} = \left[\alpha_0(T-T_{0\infty}) - 4QX_0\exp(-kz) + \frac{1}{\varepsilon}\right]P + \beta P^3$$
$$+ rP^5 - k(\eta-\gamma)X_0\exp(-kz) - \frac{1}{h\varepsilon}\int_0^h Pdz, \tag{8}$$

with the following boundary conditions:

$$\begin{cases} \frac{dP}{dz} = \frac{P}{\delta_i} & \text{when } z=0 \\ \frac{dP}{dz} = -\frac{P}{\delta_s} & \text{when } z=h \end{cases} \tag{9}$$

By using the finite-difference method, the polarization profile and the mean polarization of the film can be obtained.

3. Numerical calculation and discussion

In this paper, a BaTiO$_3$ nanofilm is taken as an example to show the effect of FxE on the critical thickness of ferroelectric films. According to recent experimental results by Ma and Cross [26], the value of FxE coefficient is about $\mu=10\,\mu C/m$ at room temperature, and the value of the dielectric permittivity is $\varepsilon_r=2360$. Then by using the relational expression obtained by Catalan et al. [11]

$$\gamma - \eta = (s_{11}+s_{12})\varepsilon_0^{-1}\chi^{-1}\mu, \tag{10}$$

we have $\gamma-\eta=2.69\times10^{-9}\,\text{m}^3\,\text{C}^{-1}$, which is in agreement with the order of magnitude presented by Catalan et al. The properties of the BaTiO$_3$ thin films used in the simulations are presented as follows [23,27–29]: $T_{0\infty}=383\,\text{K}$, $\alpha_0=6.6\times10^5\,\text{V m C}^{-1}$, $\beta=14.4$ $(T-448)\times10^6\,\text{V m}^5\,\text{C}^{-3}$, $r=39.6\times10^9\,\text{V m}^9\,\text{C}^{-5}$, $K=0.9\times10^{-9}$ $\text{V m}^3\,\text{C}^{-1}$, $Q=-0.043\,\text{m}^4\,\text{C}^{-2}$, $\delta_i=\delta_s=\delta=1\,\text{nm}$, $s_{11}+s_{12}=5.62\times10^{-12}\,\text{m}^2\,\text{N}^{-1}$, $\gamma=3.69\times10^{-9}\,\text{m}^3\,\text{C}^{-1}$, $\eta=1\times10^{-9}\,\text{m}^3\,\text{C}^{-1}$.

For the convenience of comparison, we introduce the relative mean polarization $\bar{p}=\bar{P}/P_\infty$, where $\bar{P}$ is the mean value of polarization along the thickness direction of the film, $P_\infty=0.27\,\text{Cm}^{-2}$ is the polarization value of the bulk BaTiO$_3$ material. The size effect of BaTiO$_3$ films from this model agrees well with available experimental results, showing that the approach is effective and accurate at nanoscale (see Appendix A). The positive and negative polarization represents the polarization orientating towards the surface and interface, respectively. Furthermore, we consider the interface stresses $X_0=-2.0\,\text{GPa}$ and $X_0=0.3\,\text{GPa}$ in the calculation which is the same as that in the experiments [30,31].

Fig. 2 shows the free energy profile for different thickness films under compressive and tensile stresses. Taking the compressively strained films (Fig. 2a–c) for an example, we can see that the $G_1-\bar{p}$ profile (blue curves) is the well-known ferroelectric double-well potential for thick film and the potential barrier decreases as thickness becomes thinner (Fig. 2a–b), and then $G_1-\bar{p}$ profile turns to a single-well potential with energy minimum at $\bar{p}=0$ (Fig. 2c). We call this critical thickness as h_{c1} below which the ferroelectric disappears without considering FxE. The FxE energy G_2 (red curves) decreases as polarization increases from negative to positive value for films with different thickness.

However, the total free energy $G=G_1+G_2$ (G_0 is set to zero) shows some interesting features. The $G-\bar{p}$ profile (black curve)