External uniform electric field removing the flexoelectric effect in epitaxial ferroelectric thin films

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received 22 July 2012; accepted in final form 30 July 2012

published online 10 August 2012

PACS 77.55.H – Piezoelectric and electrostrictive films

PACS 77.90.+k – Other topics in dielectrics, piezoelectrics, and ferroelectrics and their properties

Abstract – Using the modified Landau-Ginzburg-Devonshire thermodynamic theory, it is found that the coupling between stress gradient and polarization, or flexoelectricity, has a significant effect on ferroelectric properties of epitaxial thin films, such as polarization, free-energy profile and hysteresis loop. However, this effect can be completely eliminated by applying an optimized external, uniform electric field. The role of such uniform electric field is shown to be the same as that of an ideal gradient electric field which can suppress the flexoelectricity effect completely based on the present theory. Since the uniform electric field is more convenient to apply and control than the gradient electric field, it can be potentially used to remove the flexoelectric effect induced by the stress gradient in epitaxial thin films and to enhance the ferroelectric properties.

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Introduction. – It is well known that ferroelectric thin films can be employed as the main components of non-volatile random access memories for their switchable remnant polarization states [1–3]. With the rapid progress of nanoscale synthesis technology, the characteristic dimension of the films has fallen into nanoscale. However, with the thickness decreasing, the anomaly of many functional properties of ferroelectrics arises, such as the collapsed magnitude of the dielectric constant [4], the increased remnant polarization [5] and piezoelectric coefficients [6], the reduced elastic stiffness [6]. One of the possible origins of these size effects is the inhomogeneous stress along the thickness direction of the ultrathin film, due to the lattice mismatch between the ferroelectrics and substrate [7–11]. Actually, such inhomogeneous stress can affect the performances of ferroelectric ultrathin film through two different mechanisms. One is due to the effect of stress itself [9–11], and the other is the influence of the stress gradient.

So far, the knowledge of stress gradient effects (e.g., flexoelectricity, or FxE) is less clear than that of stress effects (e.g., piezoelectricity), because the FxE is not obvious in most bulk dielectrics. The FxE was theoretically described about 50 years ago [12] and then its effect was discovered four years later by Scott [13] and Bursian et al. [14]. However, the FxE effect has been overlooked due to its relatively small effect compared with piezoelectricity. Recently, the FxE effect has received increasing attention because ferroelectric structures may undergo a large stress gradient at the nanoscale, which may have a significant effect on properties [15,16]. In the past decade, FxE has been extensively investigated by experiments [15–22], first-principles [23–26] and macroscopic theory [8,27–30]. Lee et al. reported that FxE in ferroelectric epitaxial nanofilms can be extremely large and, furthermore, can be modulated, which provides a means of tuning the ferroelectric properties such as domain configurations and hysteresis curves [21]. Catalan et al. reviewed the studies on domains nanoelectronics, in which FxE also plays an important role due to the large strain gradient at domain walls [31]. However, to the best of our knowledge, there are still few practical methods to remove the FxE induced by the stress gradient in ferroelectric films, because it is difficult to apply or control a gradient field (such as the electric field). In this paper, by using the generalized Landau-Ginsburg-Devonshire theory, which has repeatedly been found to be useful down to the nanoscale [32,33],
we found that an external uniform electric field can almost eliminate the FxE effect on polarization, free-energy profile and hysteresis loop completely in epitaxial thin films. The role of such uniform electric field is shown to be nearly the same as that of an ideal gradient electric field, while the uniform electric field is much more convenient to apply in practical applications.

**Theory and modeling.** – A c-phased heteroepitaxial, single-domain perovskite thin film \((P = P_3)\) with misfit stress relaxing along the thickness direction is considered. Based on the phenomenological theory, the generalized free-energy density function of the thin film is given by

\[
G = G_0 + G_1 + G_2 + G_3,
\]

(1)

where \(G_0\) is the free-energy density of the paraelectric phase, \(G_1\) the energy density which is the sum of electrostatic energy, elastic energy, depolarization field energy and surface energy, \(G_2\) the FxE energy density, and \(G_3\) external electrostatic energy density. \(G_1, G_2\) and \(G_3\) are given by

\[
G_1 = \frac{1}{h} \int_0^h \left( \frac{1}{2} \alpha_0 (T - T_{0\infty}) P^2 + \frac{1}{4} \beta P^4 + \frac{1}{6} \gamma P^6 - \frac{1}{2} (s_{11} + s_{12}) X^2 - 2QXP^2 + \frac{1}{2} K \left( \frac{dP}{dz} \right)^2 \right) dz + \frac{K}{2} \left( \frac{P^2}{\delta_s} + \frac{P^2}{\delta_i} \right),
\]

(2)

\[
G_2 = \frac{1}{h} \int_0^h \left( -\zeta \frac{dX}{dz} P \right) dz,
\]

(3)

\[
G_3 = \frac{1}{h} \int_0^h ( -E_d P) dz,
\]

(4)

where \(h\) is the film’s thickness; \(\alpha_0, \beta\) and \(\gamma\) are dielectric stiffness and higher-order dielectric stiffness coefficients; \(T_{0\infty}\) is the Curie-Weiss temperature of the bulk material; \(\zeta\) describes the FxE coupling while \(Q\) describes the electrostrictive coupling; \(s_{11}\) and \(s_{12}\) are the elastic compliance; \(P_s\) and \(P_i\) are the polarization at the surface \((z = 0)\) and the interface \((z = h)\) while \(\delta_s\) and \(\delta_i\) are the corresponding extrapolation length; \(E_d\) is the external electric field, while

\[
E_d = -\frac{1}{\varepsilon} \left( \frac{P}{h} - \frac{1}{h} \int_0^h P dz \right)
\]

(5)

is the internal depolarization field \([9]\), with \(\varepsilon\) the dielectric constant of the film. A widely used model for the stress distribution is adopted as many other works \([9,15,34]\),

\[
X = X_0 e^{-h z},
\]

(6)

which means that the residual stress \(X\) is exponentially relaxing from the film/substrate interface. \(X_0\) is the interface residual stress, and it can be determined by the lattice constants \(a_f\) of the film and \(a_s\) of the substrate \([10]\), as follows:

\[
X_0 = \frac{(a_s - a_f)/a_s}{(s_{11} + s_{12})}.
\]

(7)

The stress profile function, eq. (6), takes into account the relaxation difference among films of different thicknesses through the decline parameter \(k\), given by \([34]\)

\[
k(h) = k_0 - \xi h = 3.925 \times 10^{-3} - 2.325 \times 10^{-6} h,
\]

(8)

which increases as the film thickness decreases, describing a larger stress gradient state in thinner films, while \(k = 0\) represents a uniform stress state.

According to eqs. (1)–(4), if an external electric field \(E_e\) satisfies \(G_2 + G_3 = 0\), then the total free energy \(G = G_0 + G_1\). This provides us a possible way to remove the FxE theoretically by incorporating an external electric field in the energy function. Then we can obtain the following relationship:

\[
\frac{1}{h} \int_0^h \left( -\zeta \frac{dX}{dz} P - E_e P \right) dz = 0.
\]

(9)

Thereby, by applying the following electric field,

\[
E_e(z) = -\zeta \frac{dX(z)}{dz} = k\zeta X_0 e^{-k z},
\]

(10)

the FxE effect can be removed thoroughly in the film. This requires the external electric field to be proportional to the stress gradient in the thickness direction of the thin film.

To obtain the polarization in the film, we carry out the variation of eq. (1) with respect to \(P\), yielding the following Euler’s equation:

\[
K \frac{d^2 P}{dz^2} = \left[ \alpha_0 (T - T_{0\infty}) - 4QX_0 e^{-h z} + \frac{1}{\varepsilon} \right] P + \beta P^3 + \gamma P^5 + k\zeta X_0 e^{-k z} - \frac{1}{he} \int_0^h P \frac{dz}{E_d} - E_e,
\]

(11)

with the boundary conditions at the surface and interface:

\[
\left. \frac{dP}{dz} \right|_{z=h} = -\frac{P}{\delta_s}, \quad \left. \frac{dP}{dz} \right|_{z=0} = \frac{P}{\delta_i}.
\]

(12)

The polarization distribution \(P(z)\) in the thickness direction of the film can be obtained according to eqs. (11), (12) by using the finite-difference method.

**Numerical results and discussion.** – An epitaxial BaTiO\(_3\) thin film is taken as an example in this paper. Parameters of the BaTiO\(_3\) thin film used in the simulations are presented as follows \([9,10,35,36]\):

\[
\alpha_0 = 6.6 \times 10^5 \text{V/m}, \quad \beta = 14.4(T - 448) \times 10^6 \text{V/m}^2, \quad \gamma = 39.6 \times 10^5 \text{V/m}^2, \quad s_{11} + s_{12} = 5.62 \times 10^{-12} \text{m}^2\text{N}^{-1},
\]

\[
K = 0.9 \times 10^{-9} \text{V/m}^2, \quad \zeta = 2.69 \times 10^{-9} \text{m}^3\text{C}^{-1},
\]

\[
Q = -0.043 \text{m}^4\text{C}^{-2}, \quad T_{0\infty} = 383 \text{K}, \quad \delta_i = \delta_s = 1 \text{nm}.
\]
Here we introduce the relative polarization $p(z) = P(z)/P_{\infty}$, where $P(z)$ is the polarization varying along the thickness direction of the film, and $P_{\infty} = \pm 0.27 \text{ Cm}^{-2}$ is the spontaneous polarization value of the bulk BaTiO$_3$ counterpart. The positive and negative polarization corresponds to the polarization orientating towards the surface and interface, respectively. We adopt the misfit stress of $X_0 = 0.3 \text{ GPa}$ and thickness of $h = 20 \text{ nm}$, in accordance with other experimental work [37] and theoretical work [9,30]. Based on our theoretical analysis and calculations, the proposed method to eliminate the flexoelectric effect is applicable for a wide range of the film thickness (from the theoretical critical thickness 15 nm for reversible polarization to 1000 nm). Note that our calculation shows that the polarization due to the flexoelectric effect is less than 2% of the spontaneous polarization as the film thickness increases beyond 1000 nm, and thus the FxE can be ignored.

According to eq. (10), the external electric field to eliminate the FxE of the films is

$$E_e(z) = kX_0 e^{-kz} = 3.130 \times 10^6 e^{-3.879 \times 10^{-3} z}.$$

(13)

The effects of such non-uniform electric field are shown in fig. 1, which indicates that the FxE enhances the polarization all over the film as the black line with filled squares shows in fig. 1(a). However, after applying the external electric field as expressed in eq. (13), the polarization profile (green line with empty triangles) coincides with the original one without FxE and external electric field (blue line with empty circles), which means that the exponentially decreasing electric field can completely dispel the FxE effect on the polarization. However, such non-uniform electric field that is proportional to the stress gradient inside the film is difficult to apply and control in practical applications. As such, we propose to apply a uniform electric field instead, which is more convenient to apply and control, and also have nearly the same effect as the exponentially varying field.

If an external electric field $E_e$ is a uniform field $E_{eu}$, then from eq. (9), we will have

$$E_{eu} = \frac{1}{h} \int_0^h \left(-\frac{dX}{dz}\right) dz = \frac{\zeta X_0}{h} (1 - e^{-kh})$$

$$= 3.0 \times 10^6 \text{ V/m}.$$

(14)

The effect of the uniform electric field on the polarization profile is also shown in fig. 1(a) (red line with filled triangles). As can be seen, it also overlaps with the line without FxE and electric field. The differences between polarizations without and with external exponential electric field (blue line with filled triangles) which means that the exponentially decreasing electric field can completely dispel the FxE effect on the polarization. However, such non-uniform electric field that is proportional to the stress gradient inside the film is difficult to apply and control in practical applications. As such, we propose to apply a uniform electric field instead, which is more convenient to apply and control, and also have nearly the same effect as the exponentially varying field.

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The elimination of FxE by the external electric field can be explained from the energetic point of view. By using the finite-difference method, the energy profiles are obtained and shown in fig. 2. It can be seen that, when there is no FxE coupling and no external electric field, the free energy is a symmetrical double-well profile as indicated by the blue line with empty circles. However, FxE breaks this symmetrical double-well potential and results in an asymmetrical profile with negative polarization (shown by the black line with empty squares). This changes the double-well potential to a single-well potential, and thus causes the increase of the critical thickness of ferroelectric thin films [30]. Such effect resulted from FxE.
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Fig. 2: (Colour on-line) Influence of various external uniform electric fields on the total free energy of the epitaxial thin film at room temperature. The free energy of the paraelectric state \( G_0 \) is set to zero.

Fig. 3: (Colour on-line) Elimination of the shift of the hysteresis loop with an external uniform bias field. A: without FxE and external bias field; B: with FxE but without external bias field; C: with FxE and uniform bias field. \( E_{c1} \) and \( E_{c2} \) are the coercive electric field for A or C and B, respectively.

**Figures**: Figures 2 and 3 illustrate the influence of external uniform electric fields on the free energy and hysteresis loops of epitaxial thin films at room temperature. The free energy of the paraelectric state is set to zero.

**Main Points**:
- The asymmetry in the energy profile due to flexoelectric effects can be removed by an external uniform electric field.
- The coercive field \( E_{c2} \) is significantly affected by the flexoelectric effect, and its change is greater than the change in polarization induced by the flexoelectric effect.
- The asymmetry in the hysteresis loop can be eliminated by applying a uniform electric field.
- The shift of the hysteresis loop due to an external uniform electric field can be measured to estimate the flexoelectric coupling coefficient.

**Conclusions**:
- By applying a proper external uniform electric field, the flexoelectric effects on polarization, free energy, and hysteresis loop can be eliminated, improving the performance of ferroelectric devices.
- The method can avoid dynamic mechanical loads and increase measurement accuracy.

The authors are grateful for the support by the National Natural Science Foundation of China under project 47003-p4.
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grants 11090330, 11090331 and 11072003. Support by the National Basic Research Program of China (G2010CBS832701) is also acknowledged.

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