Available online at www.sciencedirect.com

SCIENCE DIRECT®

Acta Materialia 52 (2004) 5639–5644

Acta MATERIALIA

www.actamat-journals.com

The order of transition of a ferroelectric thin film on a compliant substrate

Biao Wang [1], C.H. Woo *

Department of Electronic and Information Engineering, The Hong Kong Polytechnic University, Hong Kong SAR, China

Received 24 June 2004; received in revised form 18 August 2004; accepted 23 August 2004
Available online 27 September 2004

Abstract

The characteristics of ferroelectricity depend on a myriad of factors, including boundary conditions, sample dimensions, and misfit epitaxial stresses, etc. For this reason, ferroelectric thin films generally exhibit characteristics that may be substantially different from their bulk counterparts. Existent theoretical studies on ferroelectric thin films consider either free-standing films or films on rigid substrates. In this paper, films on compliant substrates are considered. Treating the para/ferro-electric transition as a point of instability of the time-dependent Ginzburg–Landau equation, the order of the transition is shown to depend sensitively on the relative thickness of the film and substrate. It is interesting that a critical thickness of the substrate can be found, above which the transition of a thin film of first-order bulk materials may become second-order.

Keywords: Order of phase transition; Ferroelectric film; Compliant substrate

1. Introduction

It is well known that the physical properties of ferroelectrc thin films are significantly different from those of bulk ferroelectrics. For example, due to the surface constraint on polarization, the para/ferroelectric transition temperatures of the film may be substantially lowered from the bulk, so much so that the ferroelectric transformation may be totally suppressed in very thin films. Indeed, there are both experimental evidence [1] and theoretical support [2–5] for such phenomena. The effect of the depolarization field on the phase transition has also been investigated extensively [6].

Substrates impart mechanical constraints on the thin films, and may thus affect their phase transition characteristics, through the elastic interaction with the transformation strain. The effect of the substrates comes from two sources. Firstly, there is the epitaxial stress generated during the fabrication process due to the misfit of the two lattices. This stress may assist, or obstruct, the transformation, and raise or lower the Curie temperature of the film, accordingly [4]. Secondly, there is also the constraint on the transformation strain due to the presence of the substrate, which always obstructs the proceedings of the transformation, and affects the phase-transition characteristics, such as the order of the transition, the universal exponents, etc. Considering ferroelectric films with thickness much larger than the ferroelectric correlation length ($h > 50$ nm), and neglecting the gradient terms in free energy expression, Pertsev et al. [7] studied the effect of mechanical boundary conditions on phase diagram of ferroelectric film. Wang and Woo [8] considered the two limiting cases, a film on a rigid substrate, and a free-standing film, respectively. In the first case, the transformation strain is completely

---

* Corresponding author.
E-mail address: enchwoo@polyu.edu.hk (C.H. Woo).

[1] On leave from School of Physics and Engineering, Sun Yat-sen University, Guangzhou, China.

1359-6454/$30.00 © 2004 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.actamat.2004.08.025

constrained by the rigid substrate. In the second case, the constraint due to the substrate is minimized. It is found that varying the substrate conditions may cause a first-order bulk ferroelectric to undergo second-order phase transition when made into a thin film. Furthermore, it is found that near the critical point, the domain pattern along the thickness direction is a cosine function, whose period depends on the film thickness. As for the martensitic thin films on a substrate with finite thickness, Bhattacharya and James [9] developed a theory of deformation to study the behavior of the martensitic films, and Shu [10] proposed a multiscale modeling to study the effective behavior of a heterogeneous martensitic film.

In the present paper, we generalize previous calculations to consider ferroelectric films on a compliant substrate. We study the behavior of the film near the transition temperature. Characteristics, such as the order of the transition and the transition temperature, are determined as a function of the relative thickness of the film and substrate. We are also interested in the critical ratio between the thickness of the film and the substrate, below which thin films of first-order transition materials will undergo a second-order transition.

2. Model

Generally speaking, the ferroelectric phase transition is caused by a change of the crystallographic structures associated with a transformation strain. If the polarization P is along one direction, the transverse transformation strain can be expressed as $\varepsilon^{\mathrm{T}} = QP^2$, where Q is the electrostrictive coefficient. Consider a ferroelectric thin film and substrate system (Fig. 1). Both the film and the substrate are treated as cubic elastic body with elastic Modulus $C_{11}, C_{12}; C_{11}^0, C_{12}^0$ and thickness h, H, respectively. The polarization is assumed to be normal to the surface of the film. Due to the constraint of the substrate and the inhomogeneous distribution of the polarizations in the film, characteristics of the phase transition may be affected, such as the transition temperature, or even the order of the transitions, etc. For cubic free-standing film, the transformation strain on the plane of the film is $\varepsilon_{xx}^{\mathrm{T}} = \varepsilon_{yy}^{\mathrm{T}} = QP^2$, the elastic stress can be derived. First fix the square film element to allow the transformation to happen, it will create a normal stress in the film $\sigma_{xx}^{\mathrm{T}} = \sigma_{yy}^{\mathrm{T}} = -GQP^2$, where $G = (C_{11} + C_{12} - 2C_{12}^2/C_{11})$, then, to satisfy the force-free conditions, one must apply the negative axial force $-\frac{1}{h}\int_{-h/2}^{h/2} \sigma_{xx}^{\mathrm{T}}\,\mathrm{d}z$ on the y-boundary and x-boundary of the element. Thus, the total stress in the film becomes $\sigma_{xx} = \sigma_{yy} = -GQP^2 + \frac{GQ}{h}\int_{-h/2}^{h/2} P^2\,\mathrm{d}z$, then the elastic strain energy can be obtained, it is due to the inhomogeneous distribution of P along the thickness direction. For 2D clamping film, the second term in the stress expression is zero.

Fig. 1. Schematic of ferroelectric thin film and substrate system.

The elastic strain energy induced by the transformation strain can then be calculated,

$$\begin{aligned} U_{\mathrm{s}} &= \frac{1}{2}\int_0^{H+h} \frac{\sigma_{xx}^2 + \sigma_{yy}^2}{G}\,\mathrm{d}z \\ &= \frac{1}{G}\int_0^h \sigma^2(z)\,\mathrm{d}z + \frac{1}{G_0}\int_h^{H+h} \sigma^2(z)\,\mathrm{d}z \\ &= GQ^2\int_0^h P^4\,\mathrm{d}z + g_1\left[\int_0^h P^2\,\mathrm{d}z\right]^2 + g_2\left[\int_0^h P^2(z-a)\,\mathrm{d}z\right]^2 \\ &\quad + g_3\int_0^h P^2\,\mathrm{d}z\int_0^h P^2(z-a)\,\mathrm{d}z, \end{aligned} \tag{1}$$

where

$$\begin{aligned} g_1 &= Q^2\left[\frac{Gh + HG^2/G_0}{(H+h)^2} - \frac{2G}{H+h}\right], \\ g_2 &= Q^2\left\{-\frac{2G}{I} + \frac{G}{3I^2}\left[a^3 + (h-a)^3\right]\right. \\ &\quad \left. + \frac{G^2}{3G_0I^2}\left[(H+h-a)^3 - (h-a)^3\right]\right\}, \\ g_3 &= \frac{Q^2}{(H+h)I}\left\{G[-a^2 + (h-a)^2]\right. \\ &\quad \left. + G^2/G_0[(H+h-a)^2 - (h-a)^2]\right\}, \end{aligned} \tag{2}$$

where $I = (H + h)^3/12$ is the area moment of inertia, and the neutral axis can be determine as follows:

$$a = \frac{\int_0^{H+h} G(z)z\,\mathrm{d}z}{\int_0^{H+h} G(z)\,\mathrm{d}z} = \frac{Gh^2 + G_0H^2 + 2G_0Hh}{2(Gh + G_0H)}. \tag{3}$$

During fabrication, the misfit between the film and the substrate creates a misfit stress $\sigma^0 = \sigma_{xx} = \sigma_{yy}$ in the film. If the misfit strain is $\varepsilon^0 = (a_{\mathrm{s}} - a_{\mathrm{f}})/a_{\mathrm{f}}$, where a_{s}, a_{f} are the lattice constants of the substrate and the film, respectively, the misfit stress in the film can be derived as,

$$\sigma^0 = G\varepsilon^0\left[\frac{h}{H+h} + \frac{h^2 - 2ah}{2I}(z-a) - 1\right]. \tag{4}$$

For thick substrates, the first two terms in Eq. (4) vanish as $H \to \infty$ and only the last term remains.

The misfit stresses here play the role of an applied load. Their interaction with the transformation strains is given by,

$$U_{\mathrm{e}} = -\int_0^h (\sigma_{xx}\varepsilon^{\mathrm{T}} + \sigma_{yy}\varepsilon^{\mathrm{T}})\,\mathrm{d}z = -2Q\int_0^h \sigma^0 P^2\,\mathrm{d}z. \tag{5}$$

According to the Landau phase transition theory, the free energy associated with the ferroelectric thin film could be written as

$$U_{\mathrm{p}} = \int_0^h \left[\frac{A}{2}(T - T_{\mathrm{c0}})P^2 + \frac{B}{4}P^4 + \frac{C}{6}P^6 + \frac{D}{2}\left(\frac{\partial P}{\partial z}\right)^2 - \frac{1}{2}E_{\mathrm{d}}P\right] \mathrm{d}z + \int\int_S \frac{D\delta^{-1}}{2} p^2 \,\mathrm{d}x\,\mathrm{d}y, \tag{6}$$

where A, B, C, and D are expansion coefficients of the corresponding bulk material. T_{c0} is the transition temperature of the bulk crystal, S represent the upper and lower unit surface planes of the film, δ is the extrapolation length that measures the strength of the surface effect on the polarization [8], and E_{d} is the depolarizing field, which depends on the electric boundary condition, which can be expressed in the following form [7]:

$$E_{\mathrm{d}} = -\frac{1}{\alpha}\left(P - \frac{\phi}{h}\int_0^h P \,\mathrm{d}z\right), \tag{7}$$

where α is the dielectric constant of the film, and ϕ takes on the value of 0 or 1, respectively, when (1) the ferroelectric film is between two metallic electrodes in short-circuit conditions; (2) the ferroelectric film is between two dielectrics.

The evolution equation corresponding to the energy Eqs. (1), (5) and (6) can be established through the following variational derivative,

$$\begin{aligned} -K\frac{\partial P}{\partial t} &= \frac{\delta(U_{\mathrm{s}} + U_{\mathrm{e}} + U_{\mathrm{p}})}{\delta P} \\ &= (\Lambda_1 z + \Lambda_2)P + \Lambda_3 P^3 + CP^5 - D\frac{\mathrm{d}^2 P}{\mathrm{d}z^2} - R, \end{aligned} \tag{8}$$

where K is the kinetic coefficient related to the domain wall mobility, and

$$\begin{aligned} \Lambda_1 &= 4g_2\Delta_2 + 2g_3\Delta_1 - \frac{2QG\varepsilon^0}{I}(h^2 - 2ah), \\ \Lambda_2 &= A(T - T_{\mathrm{c0}}) + \frac{1}{\alpha} - 4QG\varepsilon^0\left(\frac{h}{H+h} - \frac{ah^2 - 2a^2h}{2I} - 1\right) \\ &\quad + (4g_1 - 2ag_3)\Delta_1 + (2g_3 - 4ag_2)\Delta_2, \\ \Lambda_3 &= B + 4GQ^2, \\ R &= \frac{\phi}{\alpha h}\int_0^h P \,\mathrm{d}z, \end{aligned} \tag{9}$$

with

$$\Delta_1 = \int_0^h P^2 \,\mathrm{d}z, \quad \Delta_2 = \int_0^h P^2(z - a) \,\mathrm{d}z \tag{10}$$

and the boundary conditions are

$$\frac{\partial P}{\partial z} = \frac{P}{\delta}, \quad \text{for } z = 0; \quad \frac{\partial P}{\partial z} = -\frac{P}{\delta}, \quad \text{for } z = h. \tag{11}$$

At steady state, Eq. (8) satisfies $\partial P/\partial t = 0$, thus giving

$$\begin{aligned} L_{\mathrm{c}}P &\equiv -(\lambda_1 z + \lambda_{2c})P + D\frac{\mathrm{d}^2 P}{\mathrm{d}z^2} + \frac{\phi}{\alpha h}\int_0^h P \,\mathrm{d}z \\ &= A(T - T_{\mathrm{c}})P + \Lambda_3 P^3 + CP^5 + (4g_2\Delta_2 + 2g_3\Delta_1)zP \\ &\quad + [(4g_1 - 2ag_3)\Delta_1 + (2g_3 - 4ag_2)\Delta_2]P \end{aligned} \tag{12}$$

where

$$\begin{aligned} \lambda_1 &= -\frac{2QG\varepsilon^0}{I}(h^2 - 2ah), \\ \lambda_{2c} &= A(T_{\mathrm{c}} - T_{\mathrm{c0}}) + \frac{1}{\alpha} - 4QG\varepsilon^0\left(\frac{h}{H+h} - \frac{ah^2 - 2a^2h}{2I} - 1\right), \end{aligned} \tag{13}$$

where T_{c} is the transition temperature of the film.

We note that $P = 0$ is a trivial solution of Eq. (12), and T_{c} marks a point of instability of that solution. We are interested to find the condition for the existence of a *real*, *stable*, *continuous*, and *non-zero* solution in the neighborhood of the point of instability. We note that this is also the condition for the transition to be second order in nature.

If the solution P exists, continuity guarantees that in a finite neighborhood of T_{c}, it can be assumed small. Following Nicholis and Prigogine [11], both P and $\gamma = T - T_{\mathrm{c}}$ can be expanded in a power series in terms of a small perturbation ε from the critical point:

$$\begin{aligned} P &= \varepsilon P_1 + \varepsilon^2 P_2 + \cdots \\ \gamma &= T - T_{\mathrm{c}} = \varepsilon\gamma_1 + \varepsilon^2\gamma_2 + \cdots \end{aligned} \tag{14}$$

This expansion is more flexible than the seemingly more natural one in which P is expanded in a power series of $(T - T_{\mathrm{c}})$ [11]. More importantly, it allows fractional power dependence of P on $(T - T_{\mathrm{c}})$. By substituting the expansion (14) into Eq. (12), and equating coefficients of equal powers of ε, a set of relations of the following form can be obtained:

$$L_{\mathrm{c}}P_k = a_k, \quad k = 1, 2, \ldots, \tag{15}$$

which have to be satisfied together with the boundary conditions (11). The first several coefficients a_k are:

$$\begin{aligned} a_1 &= 0, \\ a_2 &= A\gamma_1 P_1, \\ a_3 &= A\gamma_1 P_2 + A\gamma_2 P_1 + (B + 4GQ^2)P_1^3 \\ &\quad + (4g_1 - 2ag_3 + 2g_3 z)P_1 \int_0^h P_1^2 \,\mathrm{d}z \\ &\quad + (2g_3 - 4ag_2 + 4g_2 z)P_1 \int_0^h P_1^2 (z - a) \,\mathrm{d}z. \end{aligned} \tag{16}$$

It is easy to check that under the boundary condition (11), the operator L_{c} is self-adjoint, and

$$(L_cP^*, P_k) = \int_{-h/2}^{h/2} P_k L_c P^* \, \mathrm{d}z = (P^*, L_c P_k)$$
$$= (P^*, a_k) = \int_{-h/2}^{h/2} P^* a_k \, \mathrm{d}z = 0, \tag{17}$$

where P^* is the solution of the following homogeneous equation:

$$L_cP^* = 0; \qquad \frac{\mathrm{d}P^*}{\mathrm{d}z} = \mp\frac{P^*}{\delta}, \quad z = \pm\frac{h}{2}. \tag{18}$$

Eq. (17) can be used to determine the coefficients γ_i. Then from the second relation of (14), one can determine ε as a function of $(T - T_c)$. Substituting the resulting ε into the first relation of (14) and solving the inhomogeneous Eq. (15) results in an explicit expression for the solution P.

The Eq. (18) is simplified with the changed variable $\eta = \left(\frac{D}{\lambda_1}\right)^{2/3} \frac{1}{D}(\lambda_1 z + \lambda_{2c})$,

$$\frac{\mathrm{d}^2P^*}{\mathrm{d}\eta^2} - \eta P^* = -R\lambda_1^{-2/3}D^{-1/3}. \tag{19}$$

The general solution of Eq. (19) is a linear combination of the two Airy functions $Ai(\eta)$, $Bi(\eta)$, therefore,

$$P^*(\eta) = C_1P_1(\eta) + C_2P_2(\eta), \tag{20}$$

where

$$P_1(\eta) = Ai(\eta) + R_0, \qquad P_2(\eta) = Bi(\eta) + R_0, \tag{21}$$

and R_0 is a constant, give by

$$R_0 = \frac{\pi}{\alpha h}\left(\frac{\lambda_1}{D}\right)^{-1/3} \int_{\eta_1}^{\eta_2} Ai(\eta)\,\mathrm{d}\eta \times \left[Ai(\eta)\int_{\eta_1}^{\eta_2} Bi(\xi)\,\mathrm{d}\xi - Bi(\eta)\int_{\eta_1}^{\eta_2} Ai(\xi)\,\mathrm{d}\xi\right], \tag{22}$$

where $\eta_1 = (D/\lambda_1)^{2/3} \cdot \frac{1}{D}\lambda_{2c}$, $\eta_2 = (D/\lambda_1)^{2/3} \cdot \frac{1}{D}(\lambda_{2c} + \lambda_1 h)$.

Substitution of Eq. (20) into the boundary conditions (18) yields a relation between the constant C_1 and C_2

$$C_2 = \gamma C_1, \tag{23}$$

where

$$\gamma = \left[\frac{1}{\delta}P_2(\eta_1) - \left(\frac{A_1}{D}\right)^{1/3} P_2'(\eta_1)\right]^{-1} \left[\left(\frac{A_1}{D}\right)^{1/3} P_1'(\eta_1) - \frac{1}{\delta}P_1(\eta_1)\right]. \tag{24}$$

Here, $P_1'(\eta_1), P_2'(\eta_1)$ are derivatives with respect to η at $\eta = \eta_1$, respectively.

By using the orthogonal condition (17), we obtain

$$\gamma_1 = 0, \tag{25}$$

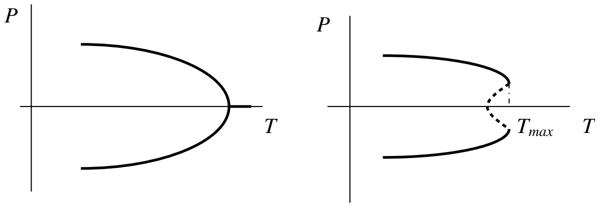

Fig. 2. Schematic of bifurcation diagrams for ferroelectric thin films.

$$\gamma_2 = -\frac{1}{A}\frac{\int_{-h/2}^{h/2} P_1^4\,\mathrm{d}z}{\int_{-h/2}^{h/2} P_1^2\,\mathrm{d}z}(B + 4GQ^2) - \frac{1}{A\int_{-h/2}^{h/2} P_1^2\,\mathrm{d}z}\left[\int_0^h (4g_1 - 2ag_3 + 2g_3z)P_1^2\,\mathrm{d}z \int_0^h P_1^2\,\mathrm{d}z + \int_0^h (2g_3 - 4ag_2 + 4g_2z)P_1^2\,\mathrm{d}z \int_0^h P_1^2(z-a)\,\mathrm{d}z\right]. \tag{26}$$

Substituting into Eq. (14) and neglecting the higher order terms, we obtain $\varepsilon \simeq \pm\sqrt{\frac{T-T_c}{\gamma_2}}$. From Eq. (14a), for P to be real and physical, γ_2 and $T - T_c$ must have the same sign. Thus, in the ferroelectric regime ($T < T_c$), a continuous solution exists only if $\gamma_2 < 0$. Equivalently, if $\gamma_2 > 0$, a real and physical solution cannot be continuous in the ferroelectric regime.

In the case $\gamma_2 = 0$, one has to consider the higher order terms of the expansions, and thus the critical exponents will differ from their bulk counterpart. Indeed, the critical system behavior obtained from the foregoing analysis can also be understood in another way. When $\gamma_2 < 0$, a real and continuous solution exists only if $T < T_c$, and bifurcation analysis [12] shows that both branches of the solutions are asymptotically stable. The corresponding phase diagram is shown schematically in Fig. 2(a). When, $\gamma_2 > 0$ real and continuous solutions only exist in the $T > T_c$ regime, but both branches of the solution are found to be *unstable*, and are therefore physically unimportant. Nevertheless, it is reasonable to argue, from physical considerations, that away from the neighborhood of the critical point, there should be a maximum value of T_{max} above which only one solution (the trivial $P = 0$ solution) is admissible. Therefore, the subcritical branches should turn in the direction of decreasing temperature at some value T_{max} (Fig. 2(b)), and join the discontinuous solution in the $T < T_c$ regime. This behavior is also consistent with the predictions of [8], obtained via stability analysis.

3. Results

The foregoing shows that the critical system behavior of a thin film is determined by the sign of γ_2, and is therefore not necessarily the same as that of the bulk material, which is completely governed by the sign of

Table 1
Materials' constant of the film and substrate (SI) [7,13–15]

T_{c0} (K)	$A(10^5)$ (J m C^{-2} K^{-1})	D (10^{-9}) (J m^5 C^{-2})	δ (nm)	α/α_0	G $(10^{11}$ Pa)	G_0 10^{11} Pa	Q (SI)	ε_0
763	7.6	2.7	0.5	210	1.82	3.5	−0.026	0.012

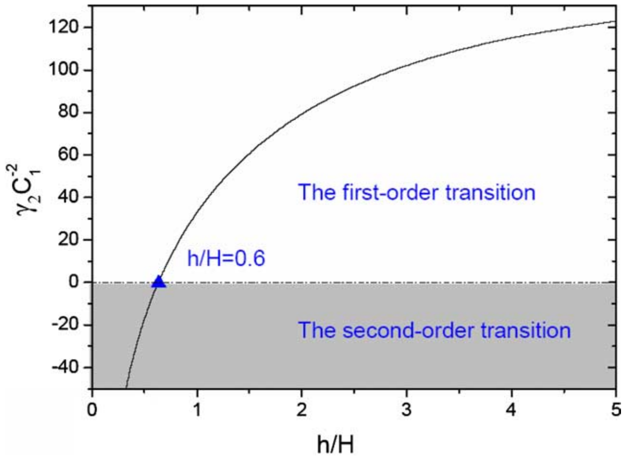

Fig. 3. γ_2/C_1^2 vs the ratio of the film thickness over the substrate thickness of $PbTiO_3/SrTiO_3$ system.

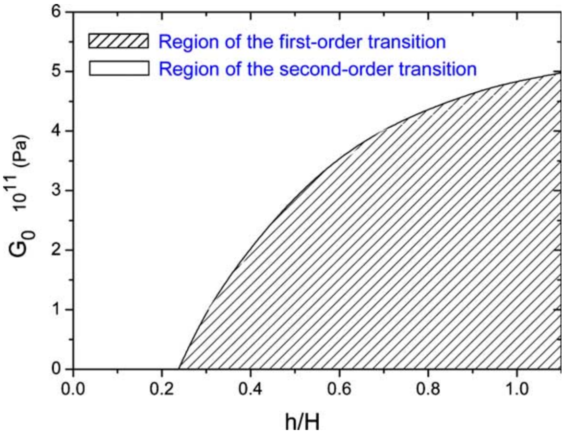

Fig. 4. Phase diagram of a ferroelectric film on a compliant substrate.

B. The sign of γ_2 depends, in a complicated way, on the bulk material parameters B, G, Q, film thickness h, substrate thickness, and the surface conditions, through Eq. (26). Some general observations can be made. The condition $B > 0$ also implies $\gamma_2 < 0$, and hence the transition of a thin film is always second order with a critical exponent of 1/2, if the bulk material is second-order. This is independent of the film thickness, substrate thickness and surface conditions considered here.

The interesting case is when $B < 0$, γ_2 may then take either signs for different film and substrate thicknesses and surface conditions. Thus, if γ_2 is negative, the ferroelectric transition of the film is second-order and continuous, despite being first-order and discontinuous in the bulk. An example can be found in a well-known first-order ferroelectric material $PbTiO_3$, the materials parameters of which are listed in Table 1. Plotted in Fig. 3 is γ_2/C_1^2 vs the ratio of the film thickness over the substrate thickness. It can be seen that if one can control the ratio $h/H < 0.6$, one can change the first-order transition into second-order. To graphically show the effect of the substrate, a phase diagram is constructed (Fig. 4), where the vertical axis is the elastic modulus G_0 of the substrate, the horizontal axis is h/H, and the properties of the film remain the same.

4. Summary

In summary, the effect of the mechanical constraint of the substrate on ferroelectric phase transition was investigated. By considering ferroelectric thin films on a compliant substrate, we found that the characteristics of the phase transition, such as, the transition temperature, the order of the phase transition, etc., can be tuned simply by changing the relative thickness of the film and substrate. We emphasize that the conclusions obtained in this paper need experimental verification.

Acknowledgement

This project was supported by grants from the Research Grants Council of the Hong Kong Special Administrative Region (PolyU 5173/01E, 5309/03E, 5312/03E), and the National Science Foundation of China (50232030, 10172030).

References

[1] Streiffer SK, Eastman JA, Fong DD, Thompson C, Munkholm A, Ramana Murty MV, et al. Phys Rev Lett 2002;89:067601.
[2] Zhong WL, Wang YG, Zhang PL, Qu BD. Phys Rev B 1994;50:698.
[3] Junquera J, Ghosez Ph. Nature 2003;422:506.
[4] Zembilgotov AG, Pertsev NA, Kohlstedt H, Waser R. J Appl Phys 2002;91:2247.
[5] Tilley DR. In: Carlos Paz de Araujo, Scott JF, Taylor GW, editors. Ferroelectric thin films: synthesis and basic properties; 1996. p. 11.
[6] Kretschmer R, Binder K. Phys Rev B 1979;20:1065.
[7] Pertsev NA, Zembilgotov AG, Tagantsev AK. Phys Rev Lett 1998;80:1988.
[8] Wang B, Woo CH. J Appl Phys, 2004 [submitted].
[9] Bhattacharya K, James RD. J Mech Phys Solids 1999;47:531.

[10] Shu YC. Arch Ration Mech Anal 2000;153:39.
[11] Nicolis G, Prigogine I. Self-organization in nonequilibrium systems, vol. 85. New York: Wiley; 1977.
[12] Chow SN, Hale JK. Methods of bifurcation theory. New York: Springer-Verlag; 1982. p. 168.
[13] Kwak BS, Erbil A, Budai JD, Chisholm MF, Boatner LA. Phys Rev B 1994;49:14865.
[14] Speck JS, Pompe W. J Appl Phys 1994;76:466.
[15] Li S, Eastman JA, Vetrone JM, Foster CH, Newnham RE, Cross LE. Jpn J Appl Phys 1997;36:5169.