Effect of gradient stress on the formation of heterophase structure in lead titanate films

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Domain formation in ferroelectric films is particularly important since it can have a profound influence on the dielectric/ferroelectric properties of the films. A number of theoretical studies have been done regarding the formation of domains or twins in epitaxial ferroelectric and ferroelastic films. However, some studies neglected either deviations of the polarization in thin film from their equilibrium values in bulk crystals or the changes of the polarization and strain fields within each domain [1–3]. Actually, the mechanical interaction between the film and the substrate may drastically change the polarization in the thin film from their equilibrium values in bulk [4, 5]. The interaction also results in inhomogeneous polarization and strain field within each domain [6, 7]. The theoretical model was based on the assumption that a strain-distribution function of periodic step is imposed on the substrate at the interface [8]. However, the inner cause to form the strain-distribution is still not clear.

This paper intends to investigate the strain-distribution of periodic step and the domain structure in ferroelectric films. We have incorporated a set of gradient stresses into modified Landau–Devonshire theory [7]. The thin-film system we have chosen is epitaxial $PbTiO_3$ (PTO) films, since the films have potential applications in various fields of sensor technology and microelectronic devices [8], and the visible domain structures were observed in the films epitaxially grown on various substrates [9, 10].

Considering a cubic ferroelectric film with lattice constant b_f and thickness $2D$ epitaxially grown on a cubic substrate which is modeled as a semi-infinite elastic continuum and has lattice constant b_s, we can treat the system as a $2D$ symmetric one with the orthogonal coordinate system such that x and z axes are parallel to and perpendicular to the interface between the film and substrate, respectively. There are tractions from the substrate acting on the two surfaces of the film at $z = \pm D$. The interface is assumed to be strained in the case of incommensurate [11], in which there exists a periodic array of misfit dislocations on the interface along the x direction. The length of a periodic array L_s is

$$L_s = b_f b_s / |b_s - b_f| = b_f / |u_m| \tag{1}$$

where $u_m = b_s / |b_s - b_f|$ is the misfit strain at the interface. The entire film can be constructed by the repeat of the periodic array. Assuming that u_m is very small, we can derive the stresses in the film from the elastic mechanical equations [12]

$$\begin{aligned}\sigma_{xx} &= -\frac{\sigma_0}{\sinh\left(\frac{2\pi D}{L_s}\right)} \cos\left(\frac{2\pi x}{L_s}\right) \cosh\left(\frac{2\pi z}{L_s}\right) \\ &= \sigma_1 = -\sigma_{zz}.\end{aligned} \tag{2}$$

The elastic field in the substrate can be neglected when the thickness of the substrate is by far greater than that of the film [1]. For the thick films ($2D > 100$ nm), the contribution of the self-energies of domain walls can also be ignored [3]. Hence, the elastic Gibbs free energy decides the equilibrium thermodynamic state of the film. In the application of the above stresses into the modified Landau–Devonshire phenomenological thermodynamic theory [7], the elastic Gibbs free energy in the film can be expanded in powers of polarizations $P_i (i = x, z)$ and stresses

$$\begin{aligned}G = {} & [\alpha_1 - (Q_{11} - Q_{12})\sigma_1] P_x^2 + \alpha_{11} P_x^4 + \alpha_{111} P_x^6 \\ & + [\alpha_1 + (Q_{11} - Q_{12})\sigma_1] P_z^2 + \alpha_{11} P_z^4 + \alpha_{111} P_z^6 \\ & + \alpha_{12} P_x^2 P_z^2 + \alpha_{112}\left(P_x^4 P_z^2 + P_x^2 P_z^4\right) \\ & - Q_{44} \tau_{zx} P_x P_z + G_0\end{aligned} \tag{3}$$

where

$$G_0 = (s_{12} - s_{11})\sigma_1^2 - \frac{1}{2} s_{44} \tau_{zx}^2$$

and α_1 is the dielectric stiffness, α_{ij}, α_{ijk} the high-order stiffness coefficients at a constant stress, s_{ij} the elastic compliances of the film measured at a constant polarization, Q_{ij} the electrostrictive coupling between the stress and polarization. The dielectric stiffness constant, $\alpha_1 = \alpha_0(T - T_0)$, is assumed to be linearly dependent on temperature T near the Curie point [7].

The stresses lower the symmetry of the paraelectric phase from cubic to tetragonal. As a result, two low-temperature phases are possibly present in the film. The following notation is used to describe the two phases: c-phase for $P_z \neq 0$ and $P_x = 0$; a-phase for $P_x \neq 0$ and $P_z = 0$. The expressions for the spontaneous polarization can be derived from the elastic Gibbs function

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in terms of the stability criterion of the first derivative ($\partial G/\partial P_{\mathrm{i}} = 0$, $i = x, z$). The transition temperature can be obtained from the criterion $G = G_0$

$$T_{\mathrm{ca}} = T_0 + \frac{\alpha_{11}^2}{4\alpha_0\alpha_{111}} + \frac{(Q_{11} - Q_{12})}{\alpha_0}\sigma_1 = T_{\mathrm{c}} + \frac{(Q_{11} - Q_{12})}{\alpha_0}\sigma_1 \quad (4)$$

for the a-phase, and

$$T_{\mathrm{cc}} = T_{\mathrm{c}} - \frac{(Q_{11} - Q_{12})}{\alpha_0}\sigma_1 \quad (5)$$

for the c-phase.

We apply the above-developed model to PTO films to discuss their phase structure and ferroelectric/dielectric properties. The parameters are taken from Ref. [4]. The stress–position–temperature phase diagram is shown in Fig. 1. Compressive ($\sigma_1 < 0$) and tensile stresses ($\sigma_1 > 0$) coexist in a periodic array. The region of the tensile stress is in favor of forming a-phase, and the region of compressive stress is in favor of forming c-phase. The tensile and compressive stresses elongate the unit cells in the film along the z and x directions, respectively. Under the action of the stresses, the transition temperature of the PTO film from ferroelectric to paraelectric phase increases linearly with the increase of $|\sigma_1|$ for both a-phase and c-phase and is always higher than that of bulk PTO (see Equation 4 and 5), which agrees with the results from Ref. [4]. When the film cools from growth temperature to $T_{\mathrm{c\,max}}$ ($= T_{\mathrm{c}} + (Q_{11} - Q_{12})\sigma_0$ cth $(2\pi D/L_{\mathrm{s}})/\alpha_0$), c-phase appears at position (0, D) and a-phase appears at ($0.5\,L_{\mathrm{s}}$, D). The region at ferroelectric state extends as the temperature decreases. Hence the ferroelectric and paraelectric states coexist in the film when $T_{\mathrm{c\,max}} > T > T_{\mathrm{c}}$. Fig. 2 shows the spontaneous polarization of a-phase vs. x and z at 500 °C. The region with $P_{\mathrm{x}} \neq 0$ near the interface corresponds to the region at ferroelectric state, which was detected by Raman spectroscopy in (Ba, Sr)TiO$_3$ film [13]. The region with $P_{\mathrm{x}} = 0$ near the center of the film corresponds to the paraelectric state. Phase transition occurs on the boundary between the two regions. The distribution of the spontaneous polarization for the c-phase is the same as that of the a-phase.

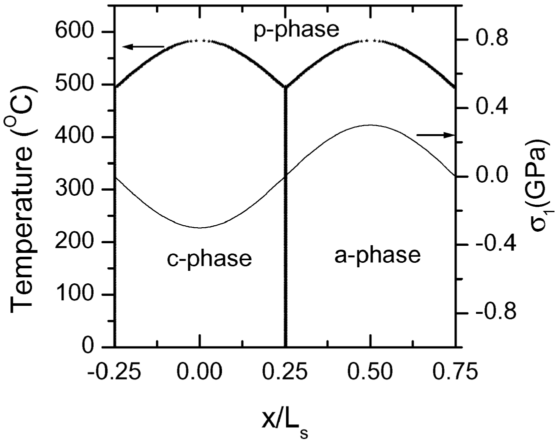

Figure 1 Position-stress-temperature phase diagram. Compressive stress is in favor of forming c-phase and tensile stress in favor of forming a-phase.

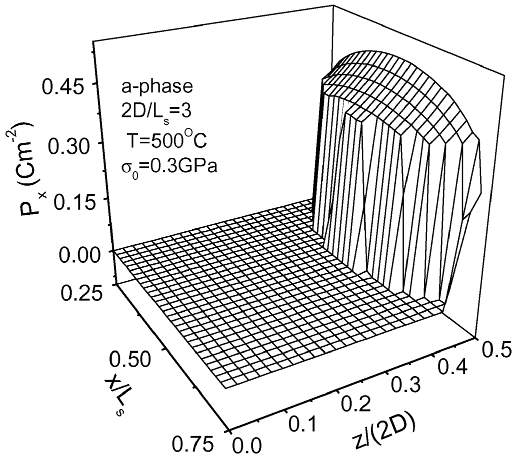

Figure 2 The distribution of the spontaneous polarization for a-phase as the function of x and z. Ferroelectric phase exists near the interface. $T = 500\,^{\circ}\mathrm{C}$, $\sigma_0 = 0.3$ GPa, $2D/L_{\mathrm{s}} = 3$.

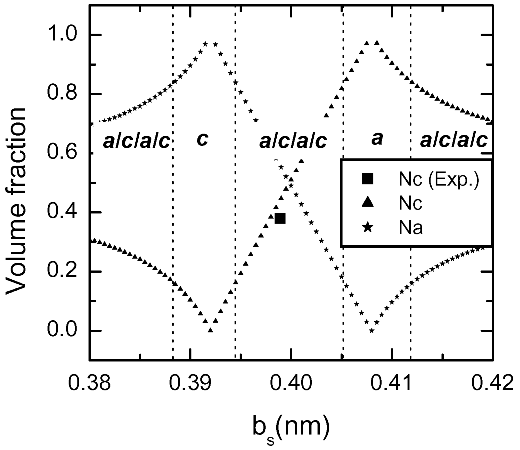

Figure 3 Dependence of volume fraction on the lattice constant of the substrate b_{s} for a-phase (star line) and c-phase (triangle line) at room temperature. Square shows the volume fraction of c-phase, which was observed in PTO film with 250 nm thickness grown on KTaO$_3$ substrate ($b_{\mathrm{s}} = 0.3989$ nm) at room temperature [8]. $b_{\mathrm{fa}} = 0.408$ nm, $b_{\mathrm{fc}} = 0.392$ nm.

At ferroelectric state, the lattice constant of the PTO film b_{f} splits into two terms b_{fa} and b_{fc}, which is for the a-phase and c-phase ($b_{\mathrm{fa}} > b_{\mathrm{fc}}$), respectively [14]. Misfit strain u_{m} of the a-phase ($u_{\mathrm{ma}} = (b_{\mathrm{s}} - b_{\mathrm{fa}})/b_{\mathrm{s}}$) differs generally from that of the c-phase ($u_{\mathrm{mc}} = (b_{\mathrm{s}} - b_{\mathrm{fc}})/b_{\mathrm{s}}$). The extension of the a-phase is half of L_{sa} ($= b_{\mathrm{fa}}/|u_{\mathrm{ma}}|$), and that of the c-phase is half of L_{sc} ($= b_{\mathrm{fc}}/|u_{\mathrm{mc}}|$). Fig. 3 shows the volume fraction of the a-phase $N_{\mathrm{a}}(= L_{\mathrm{sa}}/(L_{\mathrm{sa}} + L_{\mathrm{sc}}))$ (star line) and that of the c-phase $N_{\mathrm{c}}(= 1 - N_{\mathrm{a}})$ (triangle line) vs. b_{s} at room temperature. In the calculations we take $b_{\mathrm{fa}} = 0.408$ nm and $b_{\mathrm{fc}} = 0.392$ nm (the lattice constants of PTO film with 450 nm thickness grown on cubic KTaO$_3$ substrate at room temperature [8]). It can be concluded from Fig. 3 that if $b_{\mathrm{fa}} \rightarrow b_{\mathrm{s}}$ ($u_{\mathrm{ma}} \rightarrow 0$), the volume fraction of the a-phase N_{a} will approach 1 ($N_{\mathrm{c}} \rightarrow 0$) and the a-phase dominates in the film. The film possesses higher dielectric constant and is favored in capacitor device;

if $b_{fc} \rightarrow b_s$ ($u_{mc} \rightarrow 0$), the volume fraction of the a-phase N_a will approach zero ($N_c \rightarrow 1$) and the film will display an apparent absence of a-phase, which was observed in PTO film grown on $SrTiO_3$ ($b_s = 0.3905$ nm) substrate [8]. Such structure with highest remanent polarization is desired for memory application. And otherwise, the two phases, a-phase and c-phase, coexist in the film and form a unique periodic ($a/c/a/c$) phase structure since the film/substrate system is constructed by the repetition of the periodic arrays along the interface. Thus, a periodic step strain-distribution function lies at the interface. When $b_s = 0.3989$ nm, the volume fraction of the c-phase predicted by our theory is in good agreement with that of the experimental result (square in Fig. 3) observed in epitaxial PTO film grown on $KTaO_3$ substrate [8]. The system cools through the Curie temperature, and the phase formation in the film always attempts to minimize the misfit strain on the interface between the film and the substrate.

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