Effect of Mechanical Boundary Conditions on Phase Diagrams of Epitaxial Ferroelectric Thin Films

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(Received 1 May 1997; revised manuscript received 14 January 1998)

A phenomenological thermodynamic theory of ferroelectric thin films epitaxially grown on cubic substrates is developed using a new form of the thermodynamic potential, which corresponds to the actual mechanical boundary conditions of the problem. For single-domain $BaTiO_3$ and $PbTiO_3$ films, the "misfit-temperature" phase diagrams are constructed. It is found that the 2D clamping of the films, apart from a shift of the temperature of the ferroelectric transition, results in a change of its order. A change of the sequence of the phases and the appearance of phases forbidden in the bulk crystals are predicted. [S0031-9007(98)05421-0]

PACS numbers: 77.55.+f, 77.22.Ch, 77.80.Dj

During the past decade, ferroelectric thin films attracted considerable attention of physicists. On one hand, their ferroelectric, dielectric, and piezoelectric properties were found to be promising for microelectronic and micromechanical applications [1]. On the other hand, the physical properties of ferroelectric thin films were found to be substantially different from those of bulk ferroelectrics. Both experimental [2,3] and theoretical [4–8] studies identified several phenomena which occur in thin films due to size effects or the pseudo-2D nature of the object. However, up to now, no adequate thermodynamic theory was developed despite several attempts made in this direction [9–12]. The point is that all of these studies do not allow for the actual mechanical boundary conditions existing in a thin film epitaxially grown on a substrate.

In this Letter, a new form of the thermodynamic potential is derived and used to develop phase diagrams for epitaxial single-domain thin films of two classical perovskite ferroelectrics—$BaTiO_3$ (BT) and $PbTiO_3$ (PT). The dielectric properties of the films are analyzed and related to those of a system with two coupled instabilities—ferroelectric and structural [13].

We consider here only films with thicknesses h much larger than the ferroelectric correlation length, i.e., practically films with $h > 50$ nm. In this case, the "microscopic" size effects similar to those considered in Refs. [4,8] may be neglected. We also do not discuss some macroscopic effects additional to the mechanical clamping of the film. However, our theory provides the basis for the analysis of these effects. For example, it is straightforward to show that the depolarizing-field-induced shift of the transition temperature [7] can be easily incorporated into it.

First, let us find the thermodynamic potential which minima correspond to the equilibrium thermodynamic states of a thin film epitaxially grown on a substrate. Since there are no tractions acting on the free surface of the film, the stresses σ_3, σ_4, and σ_5 must be zero on this surface. (We use the Voigt matrix notation and the rectangular Cartesian frame of reference with the x_3 axis perpendicular to the film/substrate interface.) On the other hand, the lattice matching between the film and a thick substrate implies that the in-plane strains u_1, u_2, and u_6 of the film at the film/substrate interface are totally controlled by the substrate, which is assumed to be sufficiently thick. In the considered case of a single-crystalline single-domain film, internal elastic fields are homogeneous so that the above conditions hold throughout the film volume. For these "mixed" mechanical conditions, clearly, the minima of the standard elastic Gibbs function G [10] (with polarization and stress used as independent variables) do not correspond to the equilibrium thermodynamic states (they are associated with the equilibrium thermodynamic states at fixed stresses). It is easy to show that, for the discussed 2D-clamping case, the sought thermodynamic potential is given by the following Legendre transformation of G

$$\tilde{G} = G + u_1\sigma_1 + u_2\sigma_2 + u_6\sigma_6 . \qquad (1)$$

This is a general expression for the thermodynamic potential of a thin ferroelectric film on a thick substrate.

In this paper, we consider the case of a (001) ferroelectric thin film epitaxially grown in a cubic paraelectric phase on a cubic (001) substrate. In this case, evidently, $u_1 = u_2$ and $u_6 = 0$. If the film/substrate interface is commensurate [14], then $u_1 = u_2 \equiv u_m$, where the misfit strain $u_m = (b - a_0)/b$ can be calculated from the substrate lattice parameter b and the equivalent cubic cell constant a_0 of the free standing film. If some interface relaxation takes place, the real substrate lattice parameter b should be replaced in this equation by the effective substrate lattice parameter b^* [15]. One can find the final form of $\tilde{G}(\vec{P}, u_m, T)$ by using Eq. (1) and the well-known expression for the elastic Gibbs function of a "cubic"

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ferroelectric [16]:

$$G = a_1(P_1^2 + P_2^2 + P_3^2) + a_{11}(P_1^4 + P_2^4 + P_3^4) + a_{12}(P_1^2P_2^2 + P_1^2P_3^2 + P_2^2P_3^2) + a_{111}(P_1^6 + P_2^6 + P_3^6) + a_{112}[P_1^4(P_2^2 + P_3^2) + P_3^4(P_1^2 + P_2^2) + P_2^4(P_1^2 + P_3^2)] + a_{123}P_1^2P_2^2P_3^2 - \tfrac{1}{2}s_{11}(\sigma_1^2 + \sigma_2^2 + \sigma_3^2) - s_{12}(\sigma_1\sigma_2 + \sigma_1\sigma_3 + \sigma_3\sigma_2) - \tfrac{1}{2}s_{44}(\sigma_4^2 + \sigma_5^2 + \sigma_6^2) - Q_{11}(\sigma_1P_1^2 + \sigma_2P_2^2 + \sigma_3P_3^2) - Q_{12}[\sigma_1(P_2^2 + P_3^2) + \sigma_3(P_1^2 + P_2^2) + \sigma_2(P_1^2 + P_3^2)] - Q_{44}(P_2P_3\sigma_4 + P_1P_3\sigma_5 + P_2P_1\sigma_6), \quad (2)$$

where all of the stress components should be eliminated with the aid of the aforementioned mechanical conditions in the film: $\partial G/\partial\sigma_1 = \partial G/\partial\sigma_2 = -u_m$, $\partial G/\partial\sigma_6 = 0$, and $\sigma_3 = \sigma_4 = \sigma_5 = 0$.

The knowledge of the potential $\tilde{G}(\vec{P}, u_m, T)$ as a function of temperature T, polarization P_i, and misfit strain u_m enables the complete thermodynamic description of the films in question, including the (u_m, T)-phase diagram for the single-domain state. We have calculated this phase diagram for BT and PT films using the parameters [17] of the elastic Gibbs function, which were taken from Refs. [16,18–21].

The 2D clamping, evidently, lowers the symmetry of the paraelectric phase from cubic to tetragonal. As a result, five low-temperature phases become possible in the film instead of three in the bulk material. For these five phases, we introduce the following notation: (i) the c phase, where $P_3 \neq 0$ and $P_1 = P_2 = 0$; (ii) the a phase, where $P_1 \neq 0$ and $P_3 = P_2 = 0$; (iii) the ac phase, where $P_1 \neq 0$, $P_3 \neq 0$, and $P_2 = 0$; (iv) the aa phase, where $P_1 = P_2 \neq 0$ and $P_3 = 0$; and (v) the r phase, where $P_1 = P_2 \neq 0$ and $P_3 \neq 0$. To determine equilibrium thermodynamic states of the BT and PT films, we calculated all of the minima of $\tilde{G}(\vec{P}, u_m, T)$ with respect to the components of the polarization and then selected the phase which corresponds to minimum minimorum. We found that, in PT, the a and ac phases are always unstable, whereas, in BT, only the a phase is unstable at all investigated temperatures and values of the misfit strain. The phase diagrams showing the stability ranges of the remaining equilibrium states are presented in Fig. 1.

In order to explain these diagrams, we discuss the thermodynamic potential $\tilde{G}(\vec{P}, u_m, T)$, which can be written as

$$\tilde{G} = a_1^*(P_1^2 + P_2^2) + a_3^*P_3^2 + a_{11}^*(P_1^4 + P_2^4) + a_{33}^*P_3^4 + a_{13}^*(P_1^2P_3^2 + P_2^2P_3^2) + a_{12}^*P_1^2P_2^2 + a_{111}(P_1^6 + P_2^6 + P_3^6) + a_{112}[P_1^4(P_2^2 + P_3^2) + P_3^4(P_1^2 + P_2^2) + P_2^4(P_1^2 + P_3^2)] + a_{123}P_1^2P_2^2P_3^2 + \frac{u_m^2}{s_{11} + s_{12}};$$

$$a_1^* = a_1 - u_m\frac{Q_{11} + Q_{12}}{s_{11} + s_{12}}, \qquad a_3^* = a_1 - u_m\frac{2Q_{12}}{s_{11} + s_{12}}, \quad (3)$$

$$a_{11}^* = a_{11} + \frac{1}{2}\frac{1}{s_{11}^2 - s_{12}^2}[(Q_{11}^2 + Q_{12}^2)s_{11} - 2Q_{11}Q_{12}s_{12}], \qquad a_{33}^* = a_{11} + \frac{Q_{12}^2}{s_{11} + s_{12}},$$

$$a_{12}^* = a_{12} - \frac{1}{s_{11}^2 - s_{12}^2}[(Q_{11}^2 + Q_{12}^2)s_{12} - 2Q_{11}Q_{12}s_{11}] + \frac{Q_{44}^2}{2s_{44}}, \qquad a_{13}^* = a_{12} + \frac{Q_{12}(Q_{11} + Q_{12})}{s_{11} + s_{12}}.$$

It can be seen that the mechanical 2D clamping renormalizes the second-order and the fourth-order polarization terms. The values of the renormalized fourth-order coefficients for BT and PT are shown in Table I, where the nonrenormalized coefficients (a_{11} and a_{12}) are given in parentheses for comparison.

From the analysis of Eqs. (3), the following features of the phase transitions in BT and PT films can be singled out.

(i) The phase transition from the paraelectric state to single-domain ferroelectric states is of the second order in BT and PT films (instead of the first order in bulk crystals [21]). This is due to the positive sign of the coefficients a_{11}^*, a_{12}^*, and a_{33}^* (see Table I) [22].

(ii) This transition takes place at temperature $T_c = \max[T_1, T_3]$, T_3 and T_1 being the temperatures at which the paraelectric phase loses its stability with respect to the appearance of P_3 and $P_1 = P_2$. Setting $a_1^* = 0$ and $a_3^* = 0$, with the aid of Eqs. (3), we find

$$T_3 = T_0 + 2C\varepsilon_0\frac{2Q_{12}}{s_{11} + s_{12}}u_m,$$
$$T_1 = T_0 + 2C\varepsilon_0\frac{Q_{11} + Q_{12}}{s_{11} + s_{12}}u_m, \quad (4)$$

where C and ε_0 are the Curie-Weiss constant and the dielectric susceptibility of the vacuum $[(2C\varepsilon_0)^{-1} = \partial a_1/\partial T]$. Because in PT and BT $Q_{11} + Q_{12}$ is positive whereas Q_{12} is negative, T_c is always higher than the Curie-Weiss temperature T_0 of the bulk material. This explains a "seagull" shape of the transition line $T_c(u_m)$. The results (i) and (ii) differ qualitatively from that of Ref. [10] where, for the same system, a monotonical misfit dependence of the first-order ferroelectric phase transition temperature was predicted.

(iii) The phase diagrams of BT and PT are very different with respect to the transitions between various

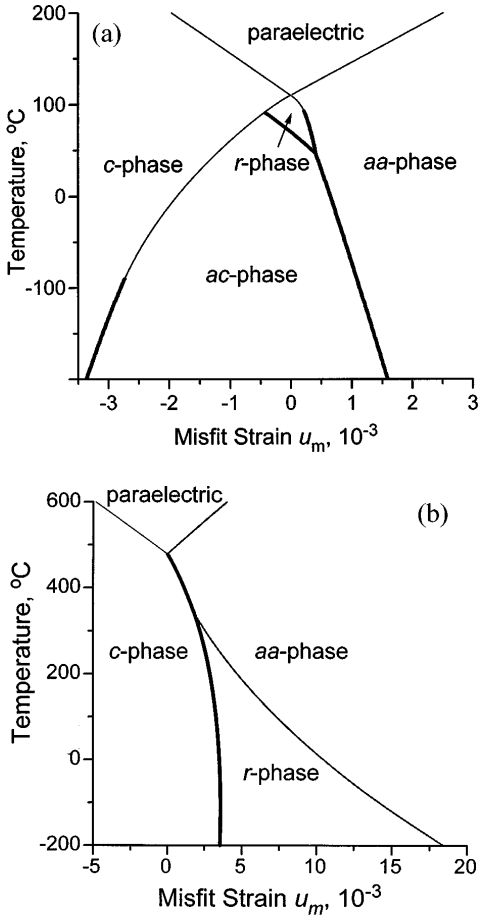

FIG. 1. Phase diagrams of (001) single-domain $BaTiO_3$ (a) and $PbTiO_3$ (b) thin films epitaxially grown on different cubic substrates providing various misfit strains u_m in the heterostructures. The second- and first-order phase transitions are shown by thin and thick lines, respectively. The quadruple and triple points at $u_m = 0$ correspond to the Curie-Weiss temperatures of these materials in the bulk form.

low-temperature ferroelectric phases (see Fig. 1). In the case of BT, at the point $(T = T_0, u_m = 0)$ four phases meet (quadruple point), and in the vicinity of this point the diagram looks like a simple superposition of the two independent transition lines corresponding to the appearance of $P_1 = P_2$ and P_3. In contrast, for PT, the point $(T = T_0, u_m = 0)$ is a triple point. This difference can be explained by analyzing the interaction between the polarizations $P_1 = P_2$ and P_3, which play, in our problem, the role of two order parameters linked by the nonlinear coupling term $a_{13}^*(P_1^2 + P_2^2)P_3^2$. Following Ref. [13], we evaluate the strength of this interaction by the dimensionless parameter $\varphi = a_{13}^*/\sqrt{(2a_{11}^* + a_{12}^*)a_{33}^*}$. From the numerical values given in the table, it follows that, in BT, φ is very small in the vicinity of the quadruple point. This indicates a minor role of the discussed interaction so that the P_1- and P_3-related phase transitions appear to be virtually independent at least near this point. In PT, φ is positive and larger than unity. Accordingly, there is a substantial interaction between two competing order parameters, i.e., in the presence of one of them, the spontaneous appearance of the other is energetically less favorable or even impossible. This strong interaction leads to the elimination of the mixed r phase in PT in the vicinity of the $(T = T_0, u_m = 0)$ point, which becomes a triple one here instead of a quadruple point in BT.

(iv) In PT films at low temperatures, the 2D clamping stabilizes the aa phase and the r phase with two and three nonzero components of the polarization, which do not exist in a free bulk crystal [16]. The aa phase is orthorhombic, whereas the r phase is a monoclinic.

(v) An interesting feature of the phase diagram obtained for BT is that, at zero misfit strain, the predicted temperature-driven phase transformation in the film is qualitatively different from that occurring in the bulk crystal. This fact can be explained as follows. From inspection of Eqs. (3), it can be seen that the effect of 2D clamping is twofold. The mismatch between the substrate lattice parameter b and the lattice constant a_0 of the paraelectric phase is responsible for the splitting of the instability temperature and its shift [see the dependence of a_1^* and a_3^* on u_m in Eqs. (3)]. On the other hand, the 2D clamping suppresses the in-plane film strains, which results in a renormalization of the P^4 terms. This renormalization changes the order of the paraelectric to ferroelectric phase transition in BT films and influences the type of the low-temperature phase. Since, according to Eqs. (3), the renormalization is independent of the misfit strain u_m, the phase transformation in a thin film may be altered even at $u_m = 0$.

Consider now the dielectric properties of epitaxial films. In a conventional setup, the electric field is orthogonal to the film surfaces so that it does not interact directly with the in-plane components $P_1 = P_2$ of polarization. Thus, in this situation, P_1 should be considered as a "purely structural" order parameter. At the same time, the instability temperatures, which correspond to the appearance of the in-plane $P_1 = P_2$ and out-of-plane P_3 polarizations on cooling, are different [c.f. Eqs. (4)]. All in all, we may conclude that, with respect to the observed dielectric response ε_{33}, the behavior of thin films is equivalent to that of a system with two coupled instabilities (ferroelectric and structural). The analysis of this system [13]

TABLE I. Parameters of P^4 terms of the renormalized thermodynamic potential of $BaTiO_3$ and $PbTiO_3$ thin films epitaxially grown on a cubic substrate.

Units for a's 10^8 m^5/FC^2	a_{11}^*	a_{33}^*	a_{12}^*	a_{13}^*	$\varphi = a_{13}^*/\sqrt{(2a_{11}^* + a_{12}^*)a_{33}^*}$
$BaTiO_3$ ($T = 110$ °C)	4.9 (−2.4)	0.9 (−2.4)	0.15 (4.9)	−0.24 (4.9)	−0.08
$PbTiO_3$	4.2 (−0.73)	0.5 (−0.73)	7.3 (7.5)	4.5 (7.5)	1.6

showed that, depending on the parameters of the thermodynamic potential, it can display a rich spectrum of dielectric properties ranging from normal ferroelectric to antiferroelectric behavior [13,23] or trigger phase transitions [24]. Thus, epitaxial thin films may demonstrate the aforementioned variety of dielectric properties. For BT and PT, the following anomalies of ε_{33} are expected at the transition lines shown in Fig. 1: (i) At the paraelectric/c-phase, the aa-phase/ac-phase, and the aa-phase/r-phase transition lines, ε_{33} should exhibit a Curie-Weiss-type anomaly in both the temperature and misfit strain dependences [see the expression for a_3^* in Eqs. (3)]. Depending on the external conditions, the anomaly can have the features corresponding to the second or first order ferroelectric phase transitions. Figure 2 shows this anomaly for BT in the case of the first order phase transition. (ii) The paraelectric/aa-phase transition as a "structural" one results in a change of slope of the $\varepsilon_{33}(T)$ and $\varepsilon_{33}(u_m)$ dependences. (iii) the c-phase/ac-phase, c-phase/r-phase, and ac-phase/r-phase transitions should be considered as structural transitions between two polar phases. Even when being of the second order such transition should give a jump of ε_{33} on crossing the transition line [13]. (For BT, in the case illustrated by Fig. 2, this jump equals 8.)

In summary, a new form of the thermodynamic potential consistent with the mechanical conditions in epitaxial thin films was developed. Using this potential, the "temperature-misfit strain" phase diagrams for epitaxial single-domain $BaTiO_3$ and $PbTiO_3$ ferroelectric thin films were calculated and the dielectric response of these films was analyzed. A drastic difference between the thermodynamic properties of thin films and bulk crystals is predicted.

When this paper was finished, we became aware of the article [25] where the phase transitions in a $BaTiO_3$ epitaxial thin film were theoretically studied. In some points, the results of that paper are consistent with ours, but there is a difference in others.

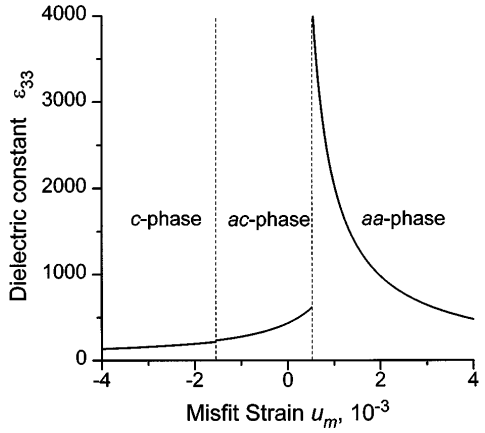

FIG. 2. Calculated dependence of the electric permittivity ε_{33} of epitaxial (001) single-domain $BaTiO_3$ films on the misfit strain u_m at room temperature.

A. K. T. acknowledges Swiss National Science Foundation for financial support.

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[17] The list of the parameters of G (in SI units, the temperature T in °C) used in the calculations. For $BaTiO_3$: $a_1 = 3.3(T - 110) \times 10^5$; $a_{11} = 3.6(T - 175) \times 10^6$; $a_{12} = 4.9 \times 10^8$; $a_{111} = 6.6 \times 10^9$; $a_{112} = 2.9 \times 10^9$; $a_{123} = 7.6(T - 120) \times 10^7 + 4.4 \times 10^{10}$; $Q_{11} = 0.11$, $Q_{12} = -0.043$; $Q_{44} = 0.059$; $s_{11} = 8.3 \times 10^{-12}$; $s_{12} = -2.7 \times 10^{-12}$, $s_{44} = 9.24 \times 10^{-12}$. For $PbTiO_3$: $a_1 = 3.8(T - 479) \times 10^5$; $a_{11} = -7.3 \times 10^7$; $a_{12} = 7.5 \times 10^8$; $a_{111} = 2.6 \times 10^8$; $a_{112} = 6.1 \times 10^8$; $a_{123} = -3.7 \times 10^9$; $Q_{11} = 0.089$, $Q_{12} = -0.026$; $Q_{44} = 0.0675$; $s_{11} = 8.0 \times 10^{-12}$; $s_{12} = -2.5 \times 10^{-12}$, $s_{44} = 9.0 \times 10^{-12}$.
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