

Structural characteristics of ferroelectric phase transformations in single-domain epitaxial films

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(Received 5 November 2003; accepted 26 March 2004)

Structural characteristics of phase transformations in epitaxial ferroelectric films are analyzed via a Landau–Devonshire thermodynamic formalism. It is shown that the phase transformation temperature, the lattice parameters, and the order of the phase transformation are a strong function of the misfit strain and are considerably different compared to unconstrained, unstressed single crystals of the same composition. Depending on the internal stress state, it is possible that the structural aspects of the paraelectric–ferroelectric phase transformation may be completely obscured in the presence of epitaxial strains. The thickness dependence of epitaxial stresses due to relaxation by misfit dislocations during film deposition is incorporated into the model using an “effective” substrate lattice parameter. There is a good quantitative agreement between the theoretical analysis and experimental observations reported in the literature on the variations in the lattice parameters and the phase transformation temperature with film thickness in epitaxial BaTiO₃ films. © 2004 American Institute of Physics. [DOI: 10.1063/1.1751630]

I. INTRODUCTION

Structural characteristics of phase transformations, the phase transformation temperature, and the overall nature of the phase transformation in thin film materials may differ significantly from their bulk or single-crystal form due to the presence of internal stresses. In compositionally homogeneous thin films internal stresses arise due to a variety of reasons, including the lattice mismatch between the film and substrate if the films are epitaxial, the difference in thermal expansion coefficients (TECs) of the film and the substrate, the self-strain of the phase transformation if the material is grown above the phase transformation temperature, and defects such as dislocations and vacancies. Experimental results in thin films of a wide variety of materials systems (including superconducting, ferroelectric, magnetic, and ferroelastic oxides) indicate that internal stresses strongly alter not only structural behavior of phase transformations but also the electrical, electromechanical, magnetic, and elastic properties.¹ The changes in phase transformation characteristics in thin films have been discussed qualitatively to provide an explanation to the observed experimental results for a particular material system. However, a unified approach that *quantitatively* describes the nature of phase transformations in thin films is lacking. It is quite obvious that internal stresses should result in a shift of the phase transformation temperature, but what is not so obvious is the sometimes not so subtle effect of the two-dimensional clamping of the substrate which is usually much thicker than the film. The clamping effect is essentially due to the coupling between

the order parameter of the phase transformation and the internal stresses² and may be unavoidable even for perfectly matched film–substrate systems.

During recent years, there have been several experimental studies to understand the effect of internal stresses on structural characteristics of the ferroelectric phase transformation in thin films. For example, it was shown that the lattice parameters of (001) BaTiO₃ (BT) films grown on (001) SrTiO₃ (ST) substrates do not exhibit an abrupt change due to the cubic to tetragonal phase transformation over a rather large temperature range, including the bulk phase transformation temperature.^{3–8} Raman scattering observations in epitaxial barium strontium titanate films on (001) MgO show that the ferroelectric phase transformation is shifted to higher temperatures and the paraelectric phase has tetragonal symmetry.^{9,10} The increase in ferroelectric phase transformation temperature was also observed for BT films epitaxially grown on (001) MgO substrates and has been attributed to the stresses induced by substrates.¹¹ Similar results were obtained for epitaxial incipient ferroelectric (001) ST films on (001) LaAlO₃ substrates.¹² Theoretical results indicate that it is even possible to stabilize a ferroelectric phase in ST epitaxial films.¹³ It is important to note that in addition to (or rather associated with) these variations in the structural characteristics, there is also a strong dependence of the electrical, electromechanical, and pyroelectric properties on the internal stresses as demonstrated both experimentally and theoretically.^{2,13–21}

Therefore, it is crucial to understand the nature of the phase transformations in epitaxial ferroelectric thin films. Furthermore, this effort may also lead to a better description of ferroelectric superlattices for which there is an interest in recent years due to potential technological applications. In this article, a rigorous, yet simple thermodynamic formalism is developed to describe the structural characteristics of epi-

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taxial ferroelectric thin films. As a specific example, the cubic-to-tetragonal phase transformation in BT is analyzed but the developed approach is quite general and equally applicable to any structural phase transformation with appropriate modifications.

II. THEORY

Consider a ferroelectric phase transformation where upon cooling the paraelectric cubic $Pm\bar{3}m$ (#221) phase transforms to a ferroelectric tetragonal $P4mm$ (#99) phase. This transformation is commonly observed in perovskite ferroelectrics such as $BaTiO_3$ and $PbTiO_3$. The phase transformation characteristics can be described via a Landau–Devonshire potential:

$$F(P, T) = F_0 + \alpha_1 P^2 + \alpha_{11} P^4 + \alpha_{111} P^6 - \frac{1}{2} S_{11} [\sigma_1^2 + \sigma_2^2 + \sigma_3^2] - S_{12} [\sigma_1 \sigma_2 + \sigma_1 \sigma_3 + \sigma_2 \sigma_3] - \frac{1}{2} S_{44} [\sigma_4^2 + \sigma_5^2 + \sigma_6^2] - Q_{11} \sigma_3 P^2 - Q_{12} P^2 (\sigma_1 + \sigma_2), \quad (1)$$

where F_0 is the energy in the paraelectric state, α_1 , α_{11} , and α_{111} are the dielectric stiffness coefficients, σ_{ij} the external stress, and S_{ij} the elastic compliances at constant polarization. The external stress is coupled with the polarization through the electrostrictive coefficients Q_{ij} . The tensor quantities in the above expression are given in the contracted notation. The temperature dependence of α_1 is given by the Curie–Weiss law, $\alpha_1 = (T - T_C)/2\epsilon_0 C$, where T_C and C are the Curie–Weiss temperature and constant, respectively, and ϵ_0 is the permittivity of free space. For a stress-free single crystal, Eq. (1) is reduced to

$$F(P, T) = F_0 + \alpha_1 P^2 + \alpha_{11} P^4 + \alpha_{111} P^6, \quad (2)$$

and the spontaneous polarization P_0 in the tetragonal phase can be obtained by the condition for thermodynamic equilibrium $\partial F / \partial P = 0$ such that

$$P_0^2(T) = \frac{-\alpha_1 + \sqrt{\alpha_1^2 - 3\alpha_{11}\alpha_{111}}}{3\alpha_{11}}. \quad (3)$$

Below T_C , the self-strains of the phase transformation that describe essentially the structural variations in the lattice, or the lattice distortion, are given by

$$x_1^0 = x_2^0 = \frac{a - a_0}{a_0} = Q_{12} P_0^2, \quad x_3^0 = \frac{c - a_0}{a_0} = Q_{11} P_0^2, \quad (4)$$

where a and c are the lattice parameters in the tetragonal ferroelectric state and a_0 is the lattice parameter of the cubic phase.

If $\alpha_{11} < 0$, the phase transformation from the parastate is of first-order (i.e., discontinuity in P_0 , a , and c at T_C and thermal hysteresis in the same parameters around T_C) and it is second-order if $\alpha_{11} > 0$ (i.e., gradual variation in P_0 , a , and c below T_C with no thermal hysteresis).

Suppose that the same ferroelectric is deposited epitaxially under short circuit electrical boundary conditions, i.e., with top and bottom electrodes, on a cubic substrate such

that $(001)_{\text{film}} // (001)_{\text{substrate}}$ at a deposition temperature $T_G > T_C$. The thickness of the substrate is taken to be much thicker than the film such that all the internal stresses are concentrated in the film and the substrate is stress-free. If the film thickness is comparable to substrate thickness, the internal stresses will be distributed between the film and substrate depending on their relative thickness and elastic moduli and will result in the bending of the bimorph layer.²² We further assume that the thickness of the film is smaller than the critical thickness for misfit dislocations, although we will relax this restriction when the thickness dependence of epitaxial stresses due to the formation of misfit dislocation during film growth is considered in the next section. The stress state in the film due to in-plane lattice matching results in equal biaxial in-plane components $\sigma_1 = \sigma_2$, with no shear stresses ($\sigma_4 = \sigma_5 = \sigma_6 = 0$), and no out-of-plane stress ($\sigma_3 = 0$). The free energy functional given in Eq. (1) has to be modified since it rather describes the effect of external stresses (work done on the system) and not the effect of internal stresses (potential to do work) with proper mechanical boundary conditions. This can be done via

$$\bar{F} = F + x_1 \sigma_1 + x_2 \sigma_2, \quad (5)$$

where $x_1 = x_2 = x_m = (a_s - a_0)/a_s$ is the in-plane misfit strain and a_0 is the equivalent cubic cell constant of the free standing film. Using $\partial F / \partial \sigma_1 = \partial F / \partial \sigma_2 = -x_m$ to express the stresses in terms of the misfit strain, the modified free energy is obtained after some rearrangement as

$$\bar{F}(P, T, x_m) = F_0 + \alpha_1^* P^2 + \alpha_{11}^* P^4 + \alpha_{111} P^6 + \frac{x_m^2}{S_{11} + S_{12}}, \quad (6)$$

where

$$\alpha_1^* = \alpha_1 - x_m \frac{2Q_{12}}{S_{11} + S_{12}}, \quad \alpha_{11}^* = \alpha_{11} + \frac{Q_{12}^2}{S_{11} + S_{12}}, \quad (7)$$

are the renormalized Landau coefficients.

The effect of the internal stresses and the mechanical boundary conditions manifests itself in two ways. First, there is a change in the phase transformation temperature that varies linearly with the misfit strain x_m . The shift in T_C can be obtained via $\alpha_1^* = 0$ such that

$$\Delta T(x_m) = T - T_C = 4\epsilon_0 C \frac{Q_{12}}{S_{11} + S_{12}} x_m. \quad (8)$$

Secondly, the phase transformation characteristics are modified due to the two-dimensional clamping of the film by the substrate as described by α_{11}^* . If the phase transformation in unconstrained single-crystal is of first order (i.e., $\alpha_{11} < 0$), the phase transformation in an epitaxial film may be of second order depending on the magnitude of $Q_{12}^2 / (S_{11} + S_{12})$. It should be noted that α_{11}^* is *not* a function of the misfit strain x_m . Therefore, the nature of the phase transformation will be altered regardless of the misfit between the film and the substrate depending on the magnitude of the ratio $Q_{12}^2 / (S_{11} + S_{12})$.

TABLE I. The thermodynamic, elastic, and electrostrictive properties of BT (Refs. 23, 24); T_C , Curie temperature; C , Curie constant; a_{ij} , stiffness coefficients; S_{ij} , elastic compliances; Q_{ij} , electrostrictive coefficients.

T_C (°C)	130
C (10^5 °C)	1.7
α_{11} (10^6 m ⁵ /C ² F)	$3.6(T-175)$
α_{12} (10^8 m ⁵ /C ² F)	4.9
S_{11} (10^{-12} m ² /N)	8.3
S_{12} (10^{-12} m ² /N)	-1.57
Q_{11} (m ⁴ /C ²)	0.11
Q_{12} (m ⁴ /C ²)	-0.043

The minimization of the modified free energy with respect to the polarization of the film ($\partial\bar{F}/\partial P=0$) yields the spontaneous polarization as a function of the misfit strain, which is essentially given by Eq. (3) with the renormalized coefficients of Eqs. (7),

$$P_0^2(T, x_m) = \frac{-\alpha_{11}^* + \sqrt{\alpha_{11}^{*2} - 3\alpha_1^* \alpha_{111}}}{3\alpha_{111}}. \quad (9)$$

Structural aspects of the phase transformation also change due to the presence of internal stresses. The variation of the lattice parameters as a function of temperature in the tetragonal ferroelectric state can no longer be described by Eqs. (4) due to the elastic strains to match the lattice parameters of the film to the substrate as well as the clamping effect of the substrate. The out-of-plane component of the strain x_3 in the parastate is related to the misfit strain by

$$x_3 = -\frac{2S_{12}}{S_{11}}x_m. \quad (10)$$

It is clear that the film in its paraelectric phase assumes a tetragonal lattice due to elastic in-plane strains but should not exhibit ferroelectricity as the biaxial in-plane stress state can never give rise to noncentrosymmetric displacements (of e.g., of the Ti⁴⁺ and O²⁻ ions in BT) within the paraelectric lattice. Below T_C , the self-strain of the phase transformation should be taken into account in the calculation the out-of-plane lattice parameter. In the limit of linear elasticity, the out-of-plane lattice parameter can be calculated via

$$\frac{c-a_0}{a_0} = Q_{11}P_0^2(x_m) + x_3, \quad (11)$$

and the in-plane lattice parameter of the film is equal to the lattice parameter of the substrate for pseudomorphic films.

III. RESULTS AND DISCUSSION

As a prototypical example, consider the phase transformation characteristics of BT for which there exists a great deal of information on the thermodynamic parameters and physical properties (see Table I, Refs. 23, 24). The transformation from the cubic paraelectric state to the tetragonal ferroelectric state is of first-order with $T_C=130$ °C. The theoretical spontaneous polarization and the lattice parameters of single-crystal BT are plotted as a function of temperature in Figs. 1 and 2 (bold lines). In Fig. 1, we also plot the variation in the spontaneous polarization as a function of

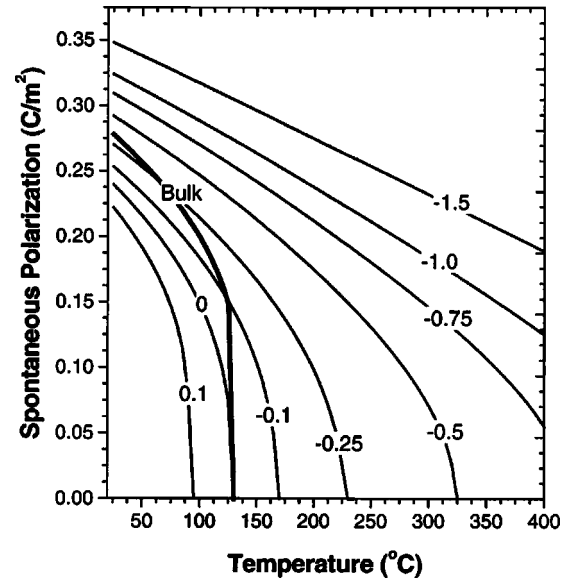


FIG. 1. The spontaneous polarization in BT calculated as a function of temperature for bulk and epitaxial films with different misfits. The misfit strain is given in percent.

misfit strain. In accordance with Eq. (8), it can be seen that T_C increases with increasing compressive misfit, stabilizing the ferroelectric phase at higher temperatures whereas tensile misfit decreases the transformation temperature. Figure 1 also shows that the spontaneous polarization is significantly enhanced in films under in-plane compression while in-plane tension tends to lower P_0 . It is important to point out that the phase transformation in epitaxial BT films is of second-order since $\alpha_{11}^* > 0$. This is very obvious for the case when $x_m=0$ for which there is no change in the transformation temperature as compared to bulk BT, but the phase transformation is of second-order and the spontaneous polarization is reduced by $\sim 10\%$ at room temperature.

In Figs. 2(a) and 2(b), the lattice parameters of BT are plotted both for bulk BT and for BT epitaxial films with compressive misfits [Fig. 2(a)] and with tensile misfits [Fig. 2(b)]. It should be kept in mind that the film cannot contract or expand freely in the film-substrate plane. Again, the clamping effect of the substrate is rather significant [see Fig. 2(a) for $x_m=0$], resulting in a second-order transformation and a decrease (increase) in the out-of-plane (in-plane) lattice parameter. Figure 2(a) also shows that the structural characteristics of the phase transformation may completely be obscured in the presence of compressive strains. The “jump” in the lattice parameters disappears for large enough compressive stresses which should not mean that the ferroelectric transformation has vanished, or conversely, that the ferroelectric phase is *induced* in the parastate due to internal stresses. This merely is an indication that the epitaxial stresses in this case are larger than the self-strain of the phase transformation and the onset of ferroelectricity can be determined using Eq. (8). Thus, although the film has tetragonal symmetry both above and below $T_C(x_m)$, it is paraelectric if $T > T_C(x_m)$ and ferroelectric if $T < T_C(x_m)$. An important conclusion that follows these results is that just the measurement of the lattice parameters at a given temperature in epi-

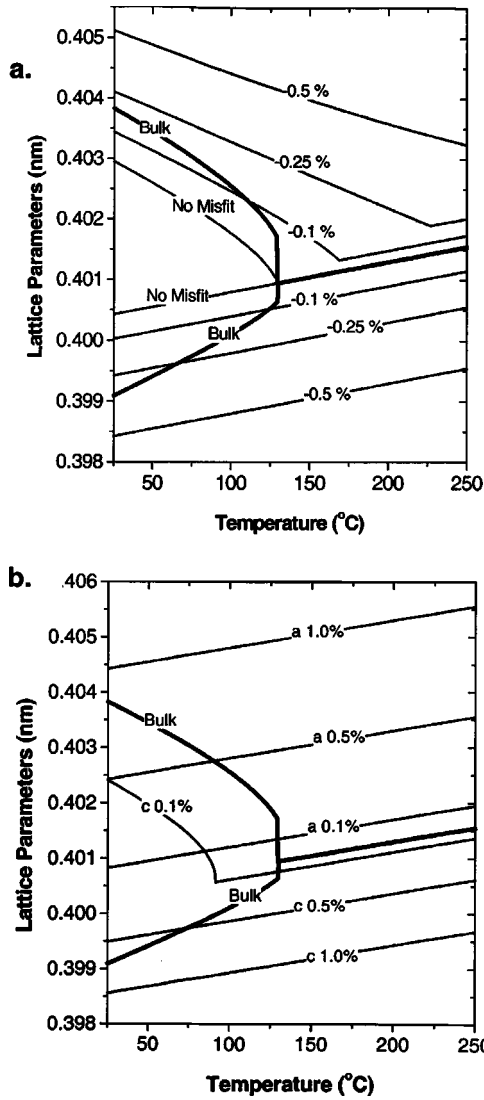


FIG. 2. The lattice parameters of BT calculated theoretically calculated as a function of temperature for bulk and epitaxial films with different (a) compressive and (b) tensile misfits. The misfit strain is given in percent.

taxial ferroelectric films alone cannot prove (or disprove) the existence of ferroelectricity. To determine the phase transformation temperature and/or to establish the presence of ferroelectricity, the hysteresis loop or the dielectric response should be measured as a function of temperature. For tensile strains, similar behavior is predicted with the in-plane lattice parameter being larger than the out-of-plane lattice parameter [see Fig. 2(b)].

In epitaxial films, the magnitude of the internal stress is a function of the film thickness h . This is due to the thickness dependent relaxation of lattice mismatch-induced stresses by the formation of misfit dislocations during film growth.²⁵ The generation of misfit dislocations can be incorporated into the model using the thermodynamic analysis of Matthews and Blakeslee²⁵ and an “effective” substrate lattice parameter.²⁶ Matthews and Blakeslee predict a critical film thickness h_ρ corresponding to the onset of misfit dislocations. At the deposition temperature T_G , the equilibrium linear misfit dislocation density ρ is given as

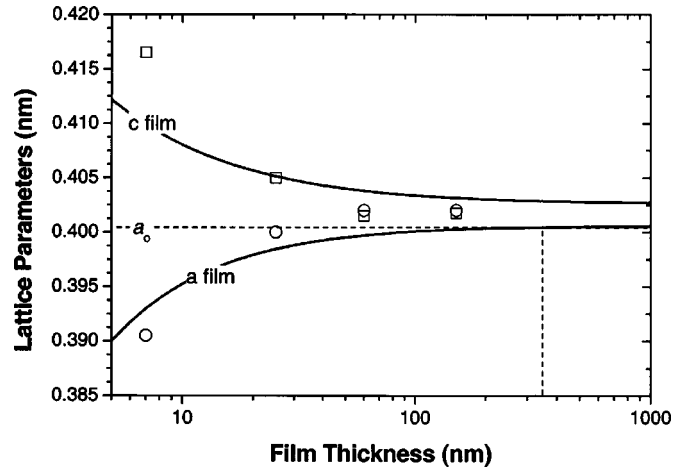


FIG. 3. The comparison between theoretically calculated lattice parameters of epitaxial (001) BT on (001) ST substrate as a function of film thickness (solid lines) with the reported experimental data (open squares and circles represent the out-of-plane and in-plane lattice constants, respectively, as reported by Terauchi *et al.*, See (Ref. 8).

$$\rho = \frac{x_m(T_G)}{a_0(T_G)} \left(1 - \frac{h_\rho}{h} \right). \quad (12)$$

If no additional dislocations form during cooling, then an “effective” substrate lattice parameter, \bar{a}_S can be defined as^{26,27}

$$\bar{a}_S = \frac{a_S(T)}{\rho a_S(T) + 1} \quad (13)$$

which can then be used to calculate the misfit strain instead of the actual lattice parameter. The basic limitation to the thermodynamic modeling of the effect of misfit dislocations is that the real critical thickness for dislocation formation and the linear equilibrium dislocation density may differ from the actual observed values because of kinetic factors.²⁸ However, for films grown close to equilibrium conditions, the Matthews–Blakeslee model generally provides a good estimate of the magnitude of the relaxation and the misfit dislocation density/spacing (see, e.g., Refs. 18 and 26).

Terauchi *et al.*⁸ have measured the variations in the lattice parameters of (001) BT films as a function of film thickness on (001) ST substrates grown at $T_G = 600^\circ\text{C}$ deposited by activated reactive evaporation. Taking into account the thickness dependent relaxation of the epitaxial strains at the film growth stage due to the formation of misfit dislocations, in Fig. 3 we plot the theoretical lattice parameters of BT as a function of film thickness together with the experimental results of Terauchi *et al.*⁸ The critical film thickness for misfit dislocation generation is calculated to be ~ 5 nm at T_G . As can be seen, theoretical results are in good agreement with the experimental measurements considering that there are no adjustable parameters in the theoretical analysis that uses the Matthews–Blakeslee critical thickness for dislocation formation.

Furthermore, the stress relaxation due to the formation of the misfit dislocations can significantly alter the ferroelectric \leftrightarrow paraelectric phase transformation temperature [see Eq. (8) with $x_m(\rho)$ due to Eqs. (12) and (13)]. Figure 4

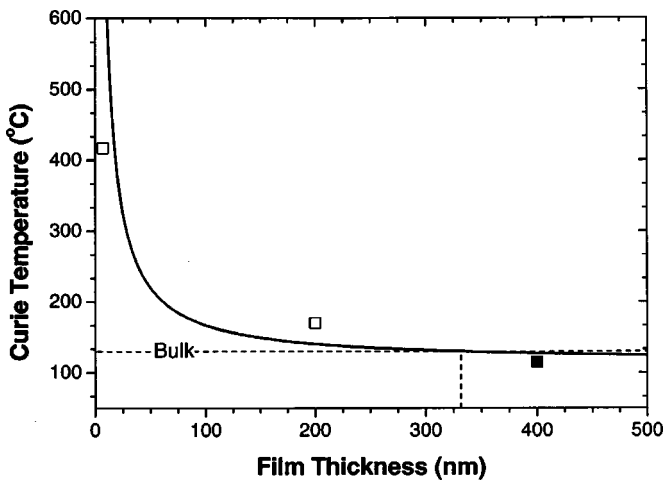


FIG. 4. The comparison between theoretically calculated Curie temperature of epitaxial (001) BT on (001) ST substrate as a function of film thickness (solid lines) with experimental data from Onodera *et al.* (Ref. 29) (open squares) and Iijima *et al.* (Ref. 30) (solid square).

shows the theoretically calculated Curie temperature vs film thickness for epitaxial (001) BT films on the (001) ST substrate (solid line). An increase in the film thickness leads to reduction of the compressive stresses in BT films on ST substrates by the formation of misfit dislocations and thus decreases the Curie temperature towards the bulk value. Theoretical analysis shows that the BT film is fully relaxed at the film thickness of ~ 330 nm, which is consistent with the variation of the lattice parameters with the film thickness as shown in Fig. 3. The small decrease in T_C for films thicker than 330 nm is due to the interplay between the misfit relaxation by interfacial dislocations at T_G and the thermal stresses that arise due to the (small) difference in the TECs of the film ($\sim 12 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) and the substrate ($11 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$) as the film is cooled from T_G to room temperature.

A comparison of the theoretical prediction with available experimental data from the literature is also provided in Fig. 4. Onodera *et al.*²⁹ have determined the Curie temperature of epitaxial BT films by specific heat measurements as a function of temperature. BT films with film thickness 6 nm and 200 nm were deposited on ST substrates using a reactive evaporation method. The Curie temperatures of these two samples were 417 °C and 170 °C, respectively, which agree with the theoretical results (open squares in Fig. 4). A good correlation was also found with another experimental study,³⁰ where a maximum in the dielectric response as a function of temperature was measured at 115 °C for 400 nm thick (001) BT films epitaxially grown on Pt-coated (001) ST substrates by activated reactive evaporation (solid square in Fig. 4).

Using the theoretical model developed in this study, we would like to discuss two more observations. The “absence” of a phase transformation⁶ has been observed in many experimental studies based on x-ray diffraction (XRD) results.^{5,6} First, Kim *et al.*⁶ investigated *in situ* the structural characteristics of 290 nm (001) BT films deposited on (001) MgO by rf-sputtering as a function of temperature. It was

found that the BT films had a tetragonal structure up to 600 °C. It was speculated that thermal strains were responsible for the disappearance of the phase transformation. As shown in this report, the reason for this is the fact that structural component of the phase transformation due to the non-centrosymmetric displacements of the ions in the BT lattice is overwhelmed by the epitaxial stresses. The absence/presence of ferroelectricity can only be confirmed by electrical measurements. In another experimental study, 600 nm thick (001) BT was grown on (001) ST using pulsed laser deposition⁷ at 700 °C. After annealing treatment at 450 °C, the sample was cooled to room temperature. XRD experiments were carried out up to 800 °C and results point out to the presence of a *c/a/c/a* polydomain structure²⁷ with decreasing volume fraction as the temperature is increased. Upon cooling, BT peak splitting is not observed prompting the authors to dub the cubic-to-tetragonal phase transformation in BT to be “irreversible.” However, the absence of two distinct BT peaks upon cooling is not a conclusive evidence for the presence of ferroelectricity. What really may be irreversible is the polydomain formation in BT under the specific conditions the experiments were carried out.

The formation of polydomain (twin) structures is another stress relaxation mechanism in epitaxial ferroelectric films.^{26,27,31–33} This mechanism is activated due to the self-strain of the ferroelectric phase transformation and the presence of an invariant plane between the orientational variants of the lower-symmetry ferroelectric phase. Polydomain formation is only possible if the internal stresses are tensile^{27,34} and the structural characteristics of the polydomain film should be similar (identical if there is complete relaxation³⁵ to the bulk material). It has been shown that if the internal stresses are compressive or the film thickness is below a critical thickness single-domain structures are favorable.^{26,27,31–33} The effect of polydomain structures and the formation of unusual phases associated with the rotation of the polarization vector due to internal stresses² on the phase transformation characteristics will be discussed in a future publication.

The thermodynamic formalism presented in this article is equally applicable to any structural or ferroic phase transformation. This follows from a generalized Landau free energy function. Consider the expansion of the free energy of a structural or ferroic phase transformation of a homogeneous single-domain system with three order parameters η_i such that it is a harmonic function of the order parameters (and thus does not contain odd powers) is given by³⁶

$$F(\eta_i) = \alpha_{ij}\eta_i\eta_j + \beta_{ijkl}\eta_i\eta_j\eta_k\eta_l + \dots + \delta_{ijk}x_{ij}\eta_k + \frac{1}{2}q_{ijkl}x_{ij}\eta_k\eta_l + \frac{1}{2}C_{ijkl}x_{ij}x_{kl}, \quad (14)$$

where α_{ij} and β_{ijkl} , are the free energy expansion coefficients, δ_{ijk} and q_{ijkl} are the bilinear and linear-quadratic coupling coefficients between the order parameter and the strain x_{ij} , and C_{ijkl} are the elastic coefficients. The equilibrium order parameters can be determined by the equations of state, $\partial F/\partial \eta_i = 0$. Proper ferroelectric, ferromagnetic, and ferroelastic phase transformations can be described via the above relation with the polarization P_i , magnetization M_i ,

or the self-strain x_{ij}^0 as the order parameter, respectively. The modifications in the structural as well as physical characteristics of films undergoing a phase transformation can be determined in a manner similar to the one described in this article using the Landau potential given in Eq. (14).

IV. CONCLUSION

The structural characteristics of the ferroelectric phase transformation in epitaxial films were studied theoretically using a thermodynamic model. The phase transformation temperature varies linearly with the misfit strain between the film and the substrate. It was also shown that the effect of elastic clamping of the substrate might result in a change in the order of the phase transformation as well as significant variations in the spontaneous polarization. Depending on the internal stress state, the structural aspects of the phase transformation (i.e., “jump” in the lattice parameters near the transformation temperature) may not be observed, which should not mean that the ferroelectric transformation has disappeared, or that the ferroelectric phase can be induced. Taking into account the relaxation by the generation of misfit dislocation during film growth, the thickness dependence of the lattice parameters and the phase transformation temperature was studied as well. Theoretical results were found to be in good agreement with experimental observations reported in the literature. The methodology developed in this report can be translated to other thin film systems that exhibit a structural variation due to a phase transformation.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (NSF) under Grant No. DMR-0132918. The authors also would like to thank B. O. Wells, F. He (UConn), and J. V. Mantese (Delphi Research Laboratories) for many useful discussions.

¹See, for example, F. M. Granozio, F. Ricci, U. S. di Uccio, and J. C. Villegier, *Phys. Rev. B* **57**, 6173 (1998); T. M. Shaw, Z. Suo, M. Huang, E. Liniger, R. B. Laibowitz, and J. D. Baniecki, *Appl. Phys. Lett.* **75**, 2129 (1999); T. Zhao, F. Chen, H. Lu, G. Yang, and Z. Chen, *J. Appl. Phys.* **87**, 7442 (2000); Z. Q. Yang, R. Hendrikx, J. Aarts, Y. Qin, and H. W. Zandbergen, *Phys. Rev. B* **67**, 024408 (2003).

²N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, *Phys. Rev. Lett.* **80**, 1988 (1998).

³S. S. Kim and J. H. Je, *J. Mater. Res.* **14**, 3734 (1999).

⁴Y. Yoneda, H. Kasatani, H. Terauchi, Y. Yoshihiko, T. Terashima, and Y. Bando, *J. Cryst. Growth* **150**, 1090 (1995).

⁵J. P. Nair, N. Stavitski, V. Lyahovitskaya, I. Zon, and I. Lubomirsky, *Mater. Sci. Semicond. Process.* **5**, 195 (2002).

⁶Y. Yoneda, T. Okabe, K. Sakaue, and H. Terauchi, *Surf. Sci.* **410**, 62 (1998).

⁷C. Li, Z. Chen, D. Cui, Y. Zhou, H. Lu, C. Dong, F. Wu, and C. Hong, *J. Appl. Phys.* **86**, 4555 (1999).

⁸H. Terauchi, Y. Watanabe, H. Kasatani, K. Kamigaki, Y. Yano, T. Terashima, and Y. Bando, *J. Phys. Soc. Jpn.* **61**, 2194 (1992).

⁹Y. I. Yuzyuk, R. S. Katiyar, V. A. Alyoshin, I. N. Zakharchenko, D. A. Markov, and E. V. Sviridov, *Phys. Rev. B* **68**, 104104 (2003).

¹⁰Y. I. Yuzyuk, J. L. Sauvajol, P. Simon, V. L. Lorman, V. A. Alyoshin, I. N. Zakharchenko, and E. V. Sviridov, *J. Appl. Phys.* **93**, 9930 (2003).

¹¹M. E. Marssi, F. L. Marrec, I. A. Lukyanchuk, and M. G. Karkut, *J. Appl. Phys.* **94**, 3307 (2003).

¹²F. He, B. O. Wells, S. M. Shapiro, M. v. Zimmerman, A. Clark, and X. X. Xi, *Appl. Phys. Lett.* **83**, 123 (2003).

¹³N. A. Pertsev, A. K. Tagantsev, and N. Setter, *Phys. Rev. B* **61**, R825 (2000).

¹⁴N. A. Pertsev, A. G. Zembilgotov, S. Hoffmann, R. Waser, and A. K. Tagantsev, *J. Appl. Phys.* **85**, 1698 (1999).

¹⁵Z. G. Ban and S. P. Alpay, *J. Appl. Phys.* **91**, 9288 (2002).

¹⁶A. L. Roytburd, S. P. Alpay, V. Nagarajan, C. S. Ganpule, S. Aggarwal, E. D. Williams, and R. Ramesh, *Phys. Rev. Lett.* **85**, 190 (2000).

¹⁷V. Nagarajan, S. P. Alpay, C. S. Ganpule, B. Nagaraj, S. Aggarwal, E. D. Williams, A. L. Roytburd, and R. Ramesh, *Appl. Phys. Lett.* **77**, 438 (2000).

¹⁸C. L. Canedy, H. Li, S. P. Alpay, L. Salamanca-Riba, A. L. Roytburd, and R. Ramesh, *Appl. Phys. Lett.* **77**, 1695 (2000).

¹⁹A. L. Roytburd, H. Li, S. P. Alpay, T. D. Tran, L. Salamanca-Riba, and R. Ramesh, *Appl. Phys. Lett.* **78**, 2354 (2001).

²⁰W. Chang, J. S. Horwitz, A. C. Carter, J. M. Pond, S. W. Kirchoefer, C. M. Gilmore, and D. B. Chrisey, *Appl. Phys. Lett.* **74**, 1033 (1999).

²¹B. H. Park, E. J. Peterson, Q. X. Jia, J. Lee, X. Zeng, W. Si, and X. X. Xi, *Appl. Phys. Lett.* **78**, 533 (2001).

²²A. L. Roytburd and J. Slutsker, *Acta Mater.* **50**, 1809 (2002).

²³*Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology*, edited by O. Madelung (Springler-Verlag, Berlin, 1982), Vol. 17.

²⁴Z. Li, S.-K. Chan, M. H. Grimsditch, and E. S. Zouboulis, *J. Appl. Phys.* **70**, 7327 (1991).

²⁵J. W. Matthews and A. E. Blakeslee, *J. Cryst. Growth* **27**, 118 (1974).

²⁶J. S. Speck and W. Pompe, *J. Appl. Phys.* **76**, 466 (1994).

²⁷S. P. Alpay and A. L. Roytburd, *J. Appl. Phys.* **83**, 4714 (1998).

²⁸W. D. Nix, *Metall. Trans. A* **20A**, 2217 (1989).

²⁹A. Onodera, Y. Kawamura, T. Okabe, and H. Terauchi, *J. Eur. Ceram. Soc.* **19**, 1477 (1999).

³⁰K. Iijima, T. Terashima, K. Yamamoto, K. Hirata, and Y. Bando, *Appl. Phys. Lett.* **56**, 527 (1990).

³¹B. S. Kwak, A. Erbil, J. D. Budai, M. F. Chrisholm, L. A. Boatner, and B. J. Wilkens, *Phys. Rev. B* **49**, 14865 (1994).

³²V. G. Koukhar, N. A. Pertsev, and R. Waser, *Phys. Rev. B* **64**, 214103 (2001).

³³N. Sridhar, J. M. Rickman, and D. J. Srolovitz, *Acta Mater.* **44**, 4085 (1996); **44**, 4097 (1996).

³⁴K. Lee, K. S. Lee, and S. Baik, *J. Appl. Phys.* **90**, 6327 (2001).

³⁵A. L. Roytburd, S. P. Alpay, L. A. Bendersky, V. Nagarajan, and R. Ramesh, *J. Appl. Phys.* **89**, 553 (2001).

³⁶E. K. H. Salje, *Phase Transitions in Ferroelastic and Co-Elastic Crystals: An Introduction for Mineralogists, Material Scientists, and Physicists* (Cambridge University Press, Cambridge, 1990).