Misfit strain–film thickness phase diagrams and related electromechanical properties of epitaxial ultra-thin lead zirconate titanate films

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Abstract

The phase stability of ultra-thin (0 0 1) oriented ferroelectric PbZr 1– x Ti x O 3 (PZT) epitaxial thin films as a function of the film composition, film thickness, and the misfit strain is analyzed using a non-linear Landau–Ginzburg–Devonshire thermodynamic model taking into account the electrical and mechanical boundary conditions. The theoretical formalism incorporates the role of the depolarization field as well as the possibility of the relaxation of in-plane strains via the formation of microstructural features such as misfit dislocations at the growth temperature and ferroelastic polydomain patterns below the paraelectric–ferroelectric phase transformation temperature. Film thickness–misfit strain phase diagrams are developed for PZT films with four different compositions ( x = 1, 0.9, 0.8 and 0.7) as a function of the film thickness. The results show that the so-called rotational r-phase appears in a very narrow range of misfit strain and thickness of the film. Furthermore, the in-plane and out-of-plane dielectric permittivities Ɛ 11 and Ɛ 33, as well as the out-of-plane piezoelectric coefficients d 33 for the PZT thin films, are computed as a function of misfit strain, taking into account substrate-induced clamping. The model reveals that previously predicted ultrahigh piezoelectric coefficients due to misfit-strain-induced phase transitions are practically achievable only in an extremely narrow range of film thickness, composition and misfit strain parameter space. We also show that the dielectric and piezoelectric properties of epitaxial ferroelectric films can be tailored through strain engineering and microstructural optimization.

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1. Introduction

Strain engineering of ferroelectric thin films has recently attracted much attention on account of the novel ferroelectric properties demonstrated in highly strained ferroelectric thin films. It is now well understood that the substrate-induced in-plane strain has a strong bearing on the ultimate phase stability of a ferroelectric thin film. Particularly in the case of epitaxial, single-crystalline systems, recent breakthroughs [1–3] demonstrate that one is able to create in these thin films ferroelectric phases that may not be generally found in the bulk parent compound under ambient conditions. Examples of the premise above include strain-induced ferroelectricity at room temperature in SrTiO 3 (STO) [1] and rotational phases in ultra-thin PbTiO 3 (PTO) [3]. Furthermore, these observations are supported by theoretical studies that predict unconventional phases under large mechanical strains, in particular for in-plane tensile strains [4,5]. Published reports show that compressive strains (in the plane of the film–substrate interface) may enhance the tetragonal out-of-plane polarization [6,7], while tensile strains induce in-plane rotational phases of the polarization [3]. It was also shown that the impact of
in-plane compressive stresses is significantly more pronounced when the variations in the Curie transition temperature are compared to the polarization [8].

A critical point of note is that a majority of the above experiments were demonstrated for fully commensurate single-domain thin films, i.e., the interfacial strain between the ferroelectric thin film and underlying substrate (or electrode buffer layer as the case may be), was fully conserved by distortion of the lattice and not relaxed by the generation of a periodic pattern of interfacial dislocations at the film–substrate interface or by ferroelastic twin (polydomain) formation below the ferroelectric phase transformation temperature. Defect-free microstructures can only be realized in ultra-thin films since the generation of these microstructural features (dislocations and/or polydomains) depends on the interplay between the reduction in the overall elastic energy of the system due their formation and their eigen-energies. Therefore, there exists a critical film thickness for both mechanisms. While the absence of such microstructural features in monodomain ferroelectric ultra-thin films results in a simpler system for theoretical analysis, we note that there are now complications due to the electrical boundary conditions generating depolarization fields arising from the incomplete compensation of the polarization charges (even under the presence of real electrodes) and the termination of the ferroelectric layer [9–12].

For thicker films either misfit dislocations or ferroelastic domains (or both) may form and hence relax the lattice mismatch strain and the eigenstrain of the ferroelectric phase transformation [13,14]. Indeed, phase-field simulations that incorporate such elastic energy relaxation mechanisms predict phase stability that is markedly distinct from previous thermodynamic predictions [15–17]. However, the electrical boundary conditions mentioned above may still have a significant bearing on the ferroelectric phase stability and domain morphology of thick ferroelectric films [18,19].

The influence of the misfit strain must be applied with caution or its effect may be heavily overestimated. For example, while phenomenological models as well as phase-field models predict the rotational phases in PTO to be stable for a wide window of experimentally achievable in-plane tensile strains, these rotational variants for PTO have been observed experimentally only in the very special case of an ultra-thin film (5 nm) on an orthorhombic substrate (DyScO$_3$) [3] and its formation might be related to the anisotropic in-plane strain state [20–22]. Furthermore, when the thickness of the ferroelectric film was increased to greater than 10 nm, these rotational phases disappeared and the conventional $c$lacl$e$la-type domain pattern was observed [23]. More recently, Noheda et al. [24] have shown how the ultimate phase in the PTO layer can be easily tuned by controlling the dislocation formation process.

Thus a rather fine detail that emerges is that the influence of both mechanical (strain) and electrical boundary conditions diminish with increasing thickness of the film, and that in order to fully appreciate strain engineering in epitaxial ferroelectric thin films, theoretical models must take into account the thickness of the films for fully accurate phase stability predictions. Motivated by this challenge, we recently presented such a full-scale non-linear thermodynamic model that yields the phase stability of (0 0 1) oriented PTO epitaxial thin films taking into consideration both thickness-induced electrical boundary (depolarization field) effects as well as the real (effective) misfit strain in the films that incorporates the thickness-dependent relaxation via the formation of misfit dislocation and ferroelastic polydomain patterns. Indeed, the computed film thickness-misfit strain phase diagrams for PTO demonstrate that the rotational phases such as the $a_0$, $a_0$-, or $r$-phases appear in a very narrow range of misfit strain and thickness of the film. It was shown that for experimentally used thickness or strains (or both) that are often within this window, the film is a single-phase tetragonal ($c$-phase) or in a $e$la$e$la polydomain state, thus highlighting the critical role of mechanisms such as dislocations and domains.

In this study, we apply the fundamental model previously reported for PTO to the treatment of epitaxial (0 0 1) PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) film compositions. In addition to the phase stability as a function of thickness, we also compute variations in the dielectric and electromechanical properties as a function of a multi-parameter space consisting of the temperature, film thickness, effective misfit strain, critical thicknesses for misfit dislocation and polydomain formation, interface-induced polarization gradients, and electrode screening length. The approach builds upon the previously published methodology of free energy functions for possible mono- and polydomain states where the most stable phase is determined as the one with the lowest free energy [25]. Since the film is clamped between two symmetrical electrodes, we assume the polarization inside the film is centrally symmetric along a $z$-axis along the film thickness resulting in zero gradient of polarization at the center. A significant advancement here is that the model computes the microstrain energies associated with polydomain structures and thus is able to take into account the non-linear dependence of the critical thickness for ferroelastic domain formation on the misfit strain and the polarization. It is shown that this self-consistent theoretical approach provides a complete description of dielectric and ferroelectric properties of epitaxial ferroelectric films as a function of the film thickness and can be used as a predictive tool to guide experimental studies.

2. Theoretical analysis

We start our analysis with a general Landau–Ginzburg–Devonshire (LGD) potential of a perovskite ferroelectric material:
$G_{\text{bulk}} = a_1(P_1^2 + P_2^2 + P_3^2) + a_{11}(P_1^4 + P_2^4 + P_3^4) + a_{12}(P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2) + a_{111}(P_1^4 + P_2^4 + P_3^4) + a_{112}(P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2 + P_3^2 P_1^2 + P_3^2 P_2^2)
+ a_{123}(P_1 P_2 P_3)^2 - \frac{1}{2}s_{11}(\sigma_1^2 + \sigma_2^2 + \sigma_3^2)
- s_{12}(\sigma_1 \sigma_2 + \sigma_1 \sigma_3 + \sigma_2 \sigma_3) - \frac{1}{2}s_{44}(\sigma_1^2 + \sigma_2^2 + \sigma_3^2)
- Q_{11}(\sigma_1 P_1^2 + \sigma_2 P_2^2 + \sigma_3 P_3^2) - Q_{12}(\sigma_1 (P_2^2 + P_3^2))
+ s_{12}(P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2)
- Q_{44}(\sigma_1 P_1 P_2 + \sigma_2 P_1 P_3 + \sigma_3 P_1 P_2)
(1)$

where $P_i$ are the components of the total polarization vector. In Eq. (1), $a_{ij}$, $a_{ijk}$ and $a_{ik}$ are the dielectric stiffness coefficients, $\sigma_i$ are the components of the external stress tensor in the contracted notation, and $Q_{ij}$ are the electrostrictive coefficients. The first-order dielectric stiffness is given by the Curie–Weiss law, $a_1 = (T - T_C^\infty)/2\theta_0 C$, where $T_C^\infty$ and $C$ are the bulk Curie temperature and constant, respectively.

The free energy of the same ferroelectric in thin film form grown epitaxially on a thick cubic substrate with orientational relationship (0 0 1)$_{\text{ferroelectric}}/(0 0 1)$_{\text{substrate}} can be determined from a Legendre transformation as follows [26]:

$$G = \frac{\mu_m^2}{s_{11} + s_{12}} + a_1'(P_1^2 + P_2^2 + P_3^2) + a_3'(P_1^4 + P_2^4 + P_3^4) + a_{111}(P_1^4 + P_2^4 + P_3^4) + a_{112}(P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2 + P_3^2 P_1^2 + P_3^2 P_2^2)
+ a_{123}(P_1 P_2 P_3)^2 + \frac{1}{2}s_{11} \left(\frac{dp_3}{dz}\right)^2 - \frac{1}{2}E_d P_3
(2)$$

We note that Eqs. (1) and (2) are LGD expansions of the total polarization although the electric displacement, the ferroelectric contribution to the polarization, an “order parameter” linearly coupled with the polarization (describing a pseudo-proper ferroelectric), and soft-mode displacements can serve as expansion parameters as well. These have been discussed in detail by Tagantsev [27]. In the present case, the total polarization is the most appropriate order parameter as the equations of state will yield the equilibrium polarization(s) as a function of the internal strain and electric fields.

In Eq. (2), $\mu_m$ is the polarization-free in-plane misfit strain for which the reference state is the pseudocubic lattice parameter of the ferroelectric. Here, $a'_1$, $a'_3$, and $a'_{11}$ are the re-normalized dielectric coefficients given by [26]:

$$a'_1 = a_1 - \mu_m \frac{Q_{11} + Q_{12}}{s_{11} + s_{12}}
(3)$$

$$a'_3 = a_1 - 2\mu_m \frac{Q_{11} + Q_{12}}{s_{11} + s_{12}}
(4)$$

$$a'_{11} = a_{11} + \frac{(Q_{11}^2 + Q_{12}^2) s_{11} - 2Q_{11} Q_{12} s_{12}}{2(s_{11}^2 - s_{12}^2)}
(5)$$

$\mu_m(L) = 1 - \frac{(1 - \mu_m)}{1 - \mu_m[1 - (L/L_c)]}
(9)$$

where $L$ is the film thickness and $L_c$ is typically the Matthews–Blakeslee (MB) [34] critical thickness for dislocation formation [30]. In our analysis of the misfit strain dependence on the thickness of the ferroelectric film, we have also compared the misfit strain dependence by the model suggested by People and Bean (PB) [32,33]. More recently, using comprehensive mechanical boundary conditions [35] the role of the spontaneous polarization on the critical thickness for dislocations has been theoretically modeled in the case of ferroelectric thin films on compliant substrates. For the thicknesses relevant to this study, it will be shown that $T_G$ is often greater than or very close to $T_c$ and hence the spontaneous polarization plays a very weak role.
The polarization gradient results in a depolarizing field given by:

$$E_d = -\frac{\partial (P - <P>)}{\partial \rho (L/2)}$$

where $P$ is the polarization along the [0001] direction at the electrode interface ignoring the depolarizing field, $<P>$ is the average polarization along the z-axis, $\rho$ is the screening length of the electrode, and $\rho$ is the dielectric constant of the electrode [25,36–39]. While it was recently proposed that the background dielectric constant may have some implications on the free energy and depolarization field [40–42], here we follow the approach of Kretschmer and Binder [28] where the “background” is free space with a dielectric response of $\epsilon_0$. This is also due to the fact that the total and not just the ferroelectric polarizations have been used as the expansion parameter in the LDG relations given in Eqs. (1) and (2), see e.g. the Appendix of Ref. [43].

The Euler–Lagrange equation follows from the condition of thermodynamic equilibrium such that:

$$\frac{\partial G}{\partial P_i} = \frac{\partial}{\partial (\rho / d\rho / dz)} \left[ \frac{\partial G}{\partial (\rho / d\rho / dz)} \right] = 0$$

resulting in:

$$g_{11} \frac{d^2 P_3}{dz^2} = 2a_1^2 P_3 + 4a_3^2 P_3^3 + 2a_1^3 (P_1^2 + P_2^2) P_3 + 6a_{111} P_3^5$$

$$+ 2a_{123} (P_1 P_2 P_3)^2 P_3 + a_{112} (2P_3 (P_1 + P_2^2)$$

$$+ 4P_1^3 (P_1^3 + P_2^3) - \frac{1}{2} E_d$$

We integrate Eq. (12) over $z$ in the limit between 0 and Z and the details of this approach were discussed in detail elsewhere [25,44]. The solution is given by:

$$\frac{1}{2} g_{11} \left( \frac{dP_3}{dz} \right)^2 = a_1^2 (P_3^2 - P_{00}^2) + a_3^2 (P_3^3 - P_{00}^3)$$

$$+ a_{13} (P_1^2 + P_2^2) (P_3^3 - P_{00}^3) + a_{111} (P_0^6 - P_{00}^6)$$

$$+ a_{112} (P_1 (P_2^2 - P_{00}^2) + P_2 (P_1^2 - P_{00}^2)$$

$$+ (P_1 + P_2) (P_3 (P_3 - P_{00}) + a_{123} [(P_1 P_2 P_3)^2 -$$

$$- (P_1 P_2 P_0) (P_3 - P_{00})}] \right) \frac{1}{2} E_d (P_3 - P_{00})$$

where $P_{00}$ is the out-of-plane polarization at the center of the film ($z = 0$). Substitution of Eq. (13) into Eq. (2) yields the free energy for the thin film:

$$G = \frac{\epsilon_0}{s_{11} + s_{12}} + a_1^2 (P_1^2 + P_2^2) + 2a_3 (P_3^3 - P_{00}^3) + a_{13} (P_1^2 + P_2^2)$$

$$+ 2a_{12} (P_1^2 - P_{00}^2) + 2a_{12} (P_2^2 - P_{00}^2) + 2a_{13} (P_1^2 + P_2^2)$$

$$- a_{11} (P_1^2 + P_2^2) P_{00}^2 + a_{11} (P_1^2 + P_2^2) + a_{11} (P_1^2 + P_2^2)$$

$$+ a_{12} (P_1^2 + P_2^2 - P_{00}^2) + a_{13} (P_1^2 + P_2^2 - P_{00}^2)$$

$$+ 2a_{12} (P_1^2 + P_2^2 - P_{00}^2) + 2a_{13} (P_1^2 + P_2^2)$$

$$- a_{12} (P_1 P_2 P_0) - E_d P_3 + \frac{1}{2} E_d P_0$$

The above relation can then be employed to determine all dielectric and piezoelectric properties. The relative dielectric permittivities follow from:

$$\frac{\epsilon_{ij}}{\epsilon_0} = \frac{1}{\epsilon_0} \left( \frac{\partial^2 G}{\partial P_i \partial P_j} \right)^{-1}$$

such that the in-plane and out-of-plane dielectric responses are:

$$\frac{\epsilon_{11}}{\epsilon_0} = \frac{1}{\epsilon_0} \left( 2a_1^2 + 12a_{11} P_1^2 + 2a_{12} P_2^2 + 4a_{13} (P_1^2 + P_2^2) - 2a_{13}^2 P_0^2$$

$$+ 30a_{111} P_1^4 + a_{112} (12P_1^2 + 2P_2^2 - P_{00}^2) + 2P_2^2$$

$$+ 4P_1^4 - 2P_0^4 + 4a_{123} (P_2 P_3)^2$$

$$- 2a_{123} (P_2 P_0)^2 \right)^{-1},$$

$$\frac{\epsilon_{33}}{\epsilon_0} = \frac{1}{\epsilon_0} \left( 4a_1^2 + 24a_{33} P_3^2 + 4a_{13} (P_1^2 + P_2^2) + 60a_{113} P_3^4$$

$$+ a_{112} (4P_1^4 + P_2^4) + 24P_3^2 (P_1^2 + P_3^2)$$

$$+ 4a_{123} (P_2 P_3)^2 \right)^{-1},$$

respectively.

The piezoelectric coefficients for polycrystalline ferroelectric thin films have been previously investigated using effective electromechanical moduli [45]. Here we are concerned with epitaxial thin films and hence the classical phenomenological definitions are used, i.e.

$$d_{ij} = \frac{\partial G}{\partial \sigma_i \partial e_j} \epsilon_{ik}$$

and by taking into account the clamping effect of the substrate, the effective piezoelectric coefficients of the thin film can be determined from [6,46–48]:

$$d_{33}^{eff} = d_{33} - \frac{2s_{12}}{s_{11} + s_{12}} d_{11} = d_{33} - \theta d_{11}$$

where $\theta = 2s_{12} / (s_{11} + s_{12})$ is an effective elastic compliance.

After obtaining the solutions of the polarization at the center of the film for the monodomain phases, the free energies and the dielectric and piezoelectric properties for all possible single-domain states can be calculated from Eqs. (14)–(19). We note that the effect of the strain relaxation by the formation of interfacial dislocations at the deposition temperature is built into the model for the monodomain states through the effective misfit strain (Eq. (9)). The monodomain phases as identified by Pertsev et al. [49] are: c-phase ($P_1 = P_2 = 0$, $P_3 \neq 0$), a-phase ($P_2 = P_3 = 0$, $P_1 \neq 0$), a-a-phase ($P_1 = P_2 = 0$, $P_3 = 0$), and r-phase ($P_1 = P_2 = P_3 = 0$).

For the polidomain states, we make use of the same formalism but combine it with the theory of dense domain structures [14,50,51] to address further strain relaxation to take into consideration the additional elastic energy due to the emergence of the self-strain as a result of the spontaneous polarization below the ferroelectric phase transformation temperature. For a phase mixture consist-
ing of in-plane orientational variants ($a_1$- and $a_2$-domains), a basic thermodynamic analysis shows that the fractions of the $a_1$- and $a_2$-domains are equal to each other and there is no critical thickness for the formation of this polydomain pattern [31]. The Landau potential for the $a_1/a_2/a_1/a_2$ structure is given by [44]:

$$G_{a1a2} = a'_1 P_S^2 + a'_1 P_S^4 + a_{111} P_S^6 + \frac{u_m^2}{s_{11} + s_{12}}$$

(20)

where

$$a'_1 = a_1 - \frac{(Q_{11} + Q_{12})}{s_{11} + s_{12}} u_m$$

(21)

$$a'_{11} = a_{11} + \frac{(Q_{11} + Q_{12})^2}{4(s_{11} + s_{12})}$$

(22)

$$P_S^2 = -a'_1 + \sqrt{a''_1 - 3a_{111}a'_1}$$

(23)

The in-plane relative dielectric permittivity follows from:

$$\frac{\varepsilon_{11}}{\varepsilon_0} = \frac{2}{\varepsilon_0} \left( \frac{\partial^2 G_{a1a2}}{\partial P_S^2} \right)^{-1} = \frac{1}{\varepsilon_0 (2a_{11}^c + 2a_{111}^c P_S^2 + 15a_{111}^c P_S^4)}$$

(24)

To calculate the out-of-plane dielectric response $\varepsilon_{33}$ we take the second derivative of the general free energy functional of Eq. (2) with respect to $P_3$ and then apply the conditions that $P_3 \rightarrow 0$ and $P_S^2 = P^3 + P_0^3$. For the $a_1/a_2$ domains the spontaneous polarization in the $a_1$- and $a_2$-domains are equal such that $P_1 = P_2$ and neglecting the small contribution from the sextic coefficient $a_{123}$ due to small $P_3$, we obtain:

$$\frac{\varepsilon_{33}}{\varepsilon_0} = \frac{2}{\varepsilon_0} \left( \frac{\partial^2 G_{a1a2}}{\partial P_S^2} \right)^{-1} = \frac{2}{\varepsilon_0 (2a_{11}^c + 2a_{111}^c P_S^2 + 15a_{111}^c P_S^4)}$$

(25)

Since there is no out-of-plane component of the total polarization vector which is parallel to the [1 1 0] direction of the film, $d_{33}^{eff} = 0$.

The polydomain $c/a/c/a$ structure is a phase mixture consisting of out-of-plane $c$-domains and in-plane $a$-domains. The Landau potential for polydomain pattern has the form [44]:

$$G_{caco}(\phi_c^0) = 2a_1 P_S^2 - a_1 P_{0S}^2 + 2a_{11} P_{0S}^4 - a_{111} P_{0S}^6 + 2a_{111} P_S^6$$

$$- a_{111} P_{0S}^6 + \frac{u_m^2}{2s_{11}} - \phi_c^0 \frac{1}{2} E_d(2P_S - P_{0S})$$

(26)

with the re-normalized stiffness coefficients

$$a_1 = a_1 - \frac{Q_{12}}{s_{11}} u_m$$

(27)

$$a_{111} = a_{111} + \frac{Q_{11}^2}{2s_{11}}$$

(28)

$$P_{0S} = \sqrt{-a_{111} + \sqrt{a_{111}^2 - 3a_{111}a_1}}$$

(29)

$\phi_c^0$ in the free energy density of the polydomain $c/a/c/a$ structure denotes the $c$-domain volume fraction given by [44,49,52]

$$\phi_c^0 = 1 - \frac{(s_{11} - s_{12})(u_m - Q_{12} P_S^2)}{s_{11}(1 - \sqrt{h_c/L} |Q_{11} - Q_{12}| P_S^2)}, \quad 0 < \phi_c^0 < 1$$

(30)

where $h_c$ is the critical thickness for the formation of this polydomain pattern. Analogous to the MB criteria for the critical thickness of misfit dislocation formation, it is clear that $h_c$ should be a function of the misfit strain and the temperature [13,31,53,54]. In our previous report [44], $h_c$ was assumed to be a constant value for simplicity. Here, we take into account the non-linear dependence of $h_c$ on the thickness of the film as well as the misfit strain. Similar to the short-range strain fields of an array of periodic misfit dislocations at the film–substrate interface, there are alternating localized short-range strain fields resulting from the periodic deviation of the actual misfit strain from the average misfit on the interface between the polydomain layer and the substrate in the $c/a/c/a$ structure. To determine the critical film thickness of the $caco$ polydomain, we start off with the out-of-plane polarization $P_3$ of a monodomain $c$-phase incorporating the polarization variation in the film due to the electrical boundary conditions resulting in a depolarization field [25,44]:

$$P_3 = P_0^3 + \frac{a_3}{s_{11}} P_0\frac{2a_3 P_0^3}{s_{11}} + \frac{3a_{11} P_0^6}{s_{11}} + \lambda_{film-LR}^3 (P_3 - <P_3>)$$

(31)

With the assumption that the polarization in the $c$- and $a$-domains that make up the $caco$ pattern is given by the above relation, the self-strain tensors for the $c$- and the $a$-domains are:

$$\mathbf{u}_c^0 = \begin{bmatrix} Q_{12} P_S^2 & 0 & 0 \\ 0 & Q_{12} P_S^2 & 0 \\ 0 & 0 & Q_{11} P_S^2 \end{bmatrix}$$

(32)

We note that since $P_3$ is used to compute the self-strain components, the thickness dependence of both the polarization and the misfit strain are now incorporated into the analysis. The energy penalty for the polydomain pattern (analogous to the total energy increase due to the eigenstrains of misfit dislocations as a two-dimensional periodic pattern of misfit dislocations at the film–substrate interface is established) can be characterized via a microstrain energy $e'$ that defines the indirect periodic interaction between the $c$- and $a$-domains through the substrate. This eigen-energy is given by [13]

$$e' = (\mathbf{u}_c - \mathbf{u}_a) \mathbf{G} (\mathbf{u}_c - \mathbf{u}_a)$$

(33)

where $\mathbf{G}$ is a 4th-rank tensor and is dependent on the bulk elastic moduli $C$, as well as the normal vector to the interface plane $\mathbf{n}$. It can be expressed as

$$\mathbf{G} = \bar{C} - \bar{C} \mathbf{n} \mathbf{n}^T$$

(34)
where \( \mathbf{n} \) is a vector parallel to the \([1 0 1]\) (or \([0 1 1]\)) directions for the interdomain interfaces in the \(c/a/c\) domain pattern that forms in the ferroelectric layer.

Following Roytburd’s analysis [54], the critical thickness for the domain formation \( h_C \) is given by

\[
h_C = \frac{16\zeta^2 l}{(1 - \beta - \eta)^2}
\]

where \( \beta \) is the ratio of the film thickness to substrate thickness, \( \eta \) is the ratio of energy of direct interactions \( e^{DI} \) to the indirect interaction energy \( e^I \), \( \zeta \) is a numerical coefficient on the order of 1, and \( l = \gamma / \zeta \epsilon' \) is the characteristic length that depends on the specific surface energy of the interdomain interface [54]. For such polydomains, Khachaturyan [55] and Roytburd [54] have previously shown that for the polydomain state to exist, \( e^{DI} \) must be very close to zero. Typically, the film thickness is much smaller than the substrate thickness (\( \beta = 0 \)) and since \( e^{DI} \ll \epsilon' \) such that \( \eta = 0 \) [54], we thus have

\[
h_C = 16\zeta^2 l \cdot (\epsilon')^2
\]

Therefore, the critical thickness for the formation of the \(c/a/c\) polydomain pattern can now be calculated as a function of the pseudomorphic misfit and polarization self-strains.

Using the above described methodology, the free energy of the \(c/a/c\) structure given in Eq. (26) can now be evaluated as a function of the misfit strain. The in-plane relative dielectric permittivity follows from

\[
\frac{\epsilon_{11}}{\epsilon_0} = \frac{1}{\epsilon_0(1 - \phi_c^0)} \frac{\partial^2 G_0}{\partial P^2} = \frac{1}{\epsilon_0(1 - \phi_c^0)(4\alpha_1 + 24\alpha_{111}P_S^2 + 60\alpha_{1111}P_S^4)}
\]

and the out-of-plane relative dielectric permittivity is

\[
\frac{\epsilon_{33}}{\epsilon_0} = \frac{1}{\epsilon_0\alpha_c^0 \frac{\partial^2 G_0}{\partial P^2}} = \frac{1}{\epsilon_0\alpha_c^0(4\alpha_1 + 24\alpha_{111}P_S^2 + 60\alpha_{1111}P_S^4)}
\]

Furthermore, the effective piezoelectric coefficient is given by

\[
d_{eff}^{33} = 2P_S \phi_c^0 \epsilon_{33} (Q_{11} - \theta Q_{12})
\]

3. Results and discussion

Fig. 1 plots the critical thicknesses for dislocation formation \( L_C \) and the critical thickness for the \(c/a/c\) polydomain formation \( h_C \) for four key PbZr\(_{1-x}\)Ti\(_x\)O\(_3\) film compositions: (a) PTO (\( x = 1 \)), (b) PZT10/90 (\( x = 0.9 \)), (c) PZT20/80 (\( x = 0.8 \)), and (d) PZT30/70 (\( x = 0.7 \)). We have included here the results predicted by MB as well as the PB models. One finds that the PB approach predicts a larger range of misfit strains over which the films can be pseudo-

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Fig. 1. Theoretical critical thickness for the misfit dislocation formation \( L_C \) (MB vs. PB) and the \(c/a/c\) polydomain formation \( h_C \) for different PZT compositions as a function of \( u_0^0 \): (a) PTO (\( x = 1 \)), (b) PZT10/90 (\( x = 0.9 \)), (c) PZT20/80 (\( x = 0.8 \)) and (d) PZT30/70 (\( x = 0.7 \)).
morphismically constrained. In other words, the critical thickness, \(L_{C}\), using the PB model can be several times higher than the MB predictions. Interestingly, the PB model has been recently demonstrated to be more appropriate for ferroelectric thin films [32,33]. Since we use the constrained pseudocubic lattice parameter at a deposition temperature \(T_G = 873\, \text{K}\) to compute this plot, \(L_C\) values are quite similar for all compositions as the lattice parameter of PZT films are not very different at \(T_G\) (see \(a_F\) values in Table 1). Of note here is that the trend predicted by Fig. 1 is very close to the results that included spontaneous polarization in the misfit strain; this underlies that when using \(T_G\)-based thermodynamic equilibrium approaches to the misfit dislocation formation, the effect of the spontaneous polarization is strong only when \(T_C\) is lower than the Curie temperature.

On the other hand, the critical thickness for the polydomain formation \(h_C\) has a stronger variation with the misfit strain, film thickness, and temperature. As it is closely tied to the polarization self-strain, in accordance with previous observations [56,57], we find that \(h_C\) is inversely varying with decreasing Ti concentration (i.e., as we move from PTO to softer PZT compositions). Thus, while \(h_C\) is very small for PTO (~10 nm), it increases to 50–70 nm for the PZT30/70 system. Secondly, for compositions closer to PTO we find that \(h_C\) is relatively insensitive to the misfit strain. However, \(h_C\) shows a strong non-linear dependence on the misfit as we move to the PZT30/70 system. For all cases, the regions most sensitive to misfit strain are those around the dashed vertical lines (i.e., pseudomorphic strain case), the regions most sensitive to misfit strain are those around the dashed vertical lines (i.e., pseudomorphic strain case), the regions most sensitive to misfit strain are those around the dashed vertical lines (i.e., pseudomorphic strain case). Finally, we find that under tensile strains, the value of \(h_C\) is larger than the corresponding compressive value.

Once the misfit strain as a function of the film thickness is determined, it becomes possible to compute the resulting changes in the out-of-plane (\(T_3\)) and in-plane (\(T_1\)) ferroelectric transition temperatures given by [44]:

\[
T_{3,\text{film}}^{\text{fim}} = T_C^{\infty} - \sqrt[3]{\frac{27a_0^2\alpha L_{e}C^0(P_z - \langle P_z \rangle)^2}{a^2L_e^2}} + \frac{4\mu_{in}(L)\varepsilon_0CQ_{12}}{s_{11} + s_{12}}
\]

and

\[
T_1 = T_C^{\infty} + \frac{2\mu_{in}(L)\varepsilon_0C(Q_{11} + Q_{12})}{s_{11} + s_{12}}
\]

This is a very important aspect of the calculation procedure. In this way, we ensure in a self-consistent manner such that only those regions of the misfit strain–thickness–composition space that return real values of \(T_3\) and/or \(T_1\) are processed in the free energy analysis.

Fig. 2 shows the resultant \(T_3\) plots for the same four PZT compositions as in Fig. 1. To make a fair comparison we have used relative thickness (\(R_L\)) instead of real thickness where \(R_L = L/L_{*}\), \(L\) being the real film thickness and \(L_{*}\) is the critical correlation length [58,59]. The limits of the thickness range are from relative film thickness \(R_L\) of 4–20. The lower limit is derived from the fact that below this thickness the potentials are better described by atomistic models rather than continuum mean-field approaches. For the upper limit, the epitaxial films of PZT greater than this thickness self-assemble into a cellular ferroelastic polydomain structure to minimize the internal elastic energy due to self-strain (i.e., the tetragonality) [31,60,61], diminishing the primary role of substrate-induced effects. The final temperature for each point in the thickness–misfit strain space is a function of the interplay between the mechanical and electrical boundary conditions. Firstly,
decreasing the thickness induces a reduction in the out-of-plane polarization due to the depolarization field. On the other hand, for a fixed thickness, depending on the sign of the strain, $T_3$ may either increase (compressive) or decrease (tensile). Thus, on the compressive side we have two competing interactions that negate each other and hence $T_3$ appears to be relatively insensitive. Conversely, $T_3$ is very sensitive on the tensile side with both interactions now working in union. This effect seems to be in qualitative agreement with the general experimental results[3,62] where it has been shown that in-plane tensile strain rather than compressive is more effective in inducing interesting phase transitions. Overall, it can be summarized that an in-plane compressive strain increases $T_3$ while tensile strains have the opposite effect. Interestingly, the contours traced by the isothermal lines bear strong semblance to our previously published strain maps[44].

Fig. 2. Computed out-of-plane transition temperature $T_3$ for (a) PTO, (b) PZT10/90, (c) PZT20/80 and (d) PZT30/70 as a function of $u_m^0$. Fig. 4 is the computed film thickness–misfit strain phase diagram for the case of epitaxial (0 0 1) films at room temperature (RT) for (a) PTO, (b) PZT10/90, (c) PZT20/80 and (d) PZT30/70, respectively. The dotted and solid lines represent first- and second-order transformations, respectively, obtained by inspection of the sign of the fourth-order coefficients of the corresponding Landau potential. The (numerical) strain limits have been chosen with respect to the cubic oxide substrates that are commercially available. On the compressive strain side (negative strain), all four figures agree with the previous reports that the imposed compressive strains may simply enhance the tetragonal out-of-plane polarization [6,63] and thus the most stable phase is the $c$-phase. For thicknesses above the critical thickness for polydomain formation, all four systems are predicted to form a $c/a/c/a$ polydomain pattern with the range of stability of the polydomain structure diminishing with increasing Zr content. For example in the case of the PZT 30/70 composition, the critical thickness for the $c/a/c/a$ polydomain formation is well beyond the thickness range shown. Therefore, under equilibrium conditions, on the compressive side no rotational phase (i.e., $r$-phase) is found to be stable. Under tensile misfits, our computations find that the $r$-phase (associated with giant electromechanical properties predictions) exists only in an extremely narrow range of tensile misfit strain and thickness. These results are in contradiction from previous results obtained using thermodynamic calculations based on a single-domain assumption.
In fact (and particularly in tens of nanometer film regime) our results are in close agreement with more recent phase-field approaches [2,19], which find the rotational phases (or single-domain variants) such as the r-, a1-, or a2-phases to be distinctly absent. For example, in PTO (Fig. 4a) for R_L below h_C, the sequence of phase transfor-
mations follows $r \rightarrow aa \rightarrow a_1/a_2/a_1/a_2$ as a function of the misfit strain $u_m$, indicative of increasing inclination of the polarization vector towards the substrate–film interface with increasing tensile strain. Fig. 4b–d indicates that the phase diagrams for the other PZT compositions investigated here are quite similar to the one for PTO (Fig. 4a). Interestingly, our model does not find the monoclinic ac-phase, associated with several intriguing properties, to be present under any conditions. The overarching conclusion that can be drawn is that for polarization rotation to occur (such as $c \rightarrow r \rightarrow aa$), the thickness and the misfit strain on the films must be accurately controlled such that the excess elastic energy is not relaxed via misfit dislocations or polydomain formation. Indeed, recently Noheda et al. [24] have shown that by accurately controlling the film deposition conditions to create a perfect defect (dislocation)-free film leads to the formation of c-phase even for thicknesses in the 300 nm range.

We next discuss the relevance of the model predictions to reported experimental data for the PZT family of (0 0 1) epitaxial thin films. On the compressive side, the model is in complete agreement with a whole range of experimental studies by different groups who report that either the c-phase or the polydomain c/a/c/a structure are
the only two possibilities [10, 57, 64, 65]. Furthermore we find that the range of the $c/a$ phase is significantly reduced as one goes to higher Zr compositions, again in excellent agreement with previous experiments [57] as well as the linear elastic theory approach of Roytburd [13, 31, 54]. On the tensile side, experimental data is available for the systems with relatively larger self-strains (and tetragonality) such as PTO and PZT 20/80. Our calculations can also explain experimental observations for thicker PTO films. For example, Lee et al. [66] report polydomain mixture for (0 0 1) PTO deposited on (0 0 1) KTaO$_3$ and MgO substrates. Furthermore they show that KTaO$_3$ imposes a larger tensile strain than MgO, which leads to a mixture of $a_1/a_2/a_1/a_2$ and $c/a/c/a$-type structure. On the other hand, 5 nm PTO films deposited on orthorhombic DyScO$_3$ were recently investigated by Catalan et al. [3]. Their findings indicate the presence of the $r$-phase under anisotropic tensile strains, again in agreement with our predictions (Fig. 4a). Of note is that the orthorhombic $aa$-phase has not been reported experimentally yet and this may be due to the fact that it is difficult to probe phases with no out-of-plane polarization.

In order to complement the above discussion and to provide a more complete picture, we plot in Fig. 5 temperature–misfit strain phase diagrams of (0 0 1) PT and (0 0 1) PZT 30/70 for three different values of $R_t$ (5), (10), (16). These compositions represent the “hardest” and the “softest” ferroelectric films employed in our analysis. Once again, the dotted and solid lines represent first- and second-order transformations, respectively. Figs. 4 and 5 thus contain information on the variations in the equilibrium microstructure of an epitaxial PTO or PZT film as a function of the temperature at a given film thickness.

Fig. 6 plots the small-signal out-of-plane relative dielectric permittivity $\varepsilon_{33}/\varepsilon_0$ for (a) PTO, (b) PZT10/90, (c) PZT20/80 and (d) PZT30/70, respectively for a particular thickness ($R_t = 8$). As expected, at points in the misfit space where a phase transition occurs (i.e., from $c \to c/a, c/a \to r \to aa$) it finds that $\varepsilon_{33}/\varepsilon_0$ values diverge; these represent possible values of numerical misfit strains where enhanced dielectric constants may be practically achievable. The highest enhancement is found to be at the $r \to aa$ transition, which signifies the complete in-plane tilting of the polarization vector. The maximum values obtainable increase with increasing Zr content and this is a reflection of the intrinsic lattice softening as more Zr is added to the PZT system. It should be noted that for phases with in-plane polarization vectors ($aa$-phase and $a_1/a_2/a_1/a_2$ polydomain) the out-of-plane dielectric response is due to the field-induced polarization. For these phases, the in-plane dielectric coefficients are shown as insets, which are found to be typically much lower than the out-of-plane values.

Fig. 7 is a plot of the effective piezoelectric coefficient as a function of thickness and misfit strain. The piezoelectric coefficient follows the trends demonstrated by the out-of-plane dielectric constant with peaks around the phase transition points and softer PZT (i.e., higher Zr content compo-
sitions) show very high values. Although the $d_{33}^{eff}$ coefficient of the rotational $r$-phase is much higher than the other phases, our predicted numbers are significantly lower in comparison to previous predictions [67] due to the specific treatment to account for the constraint imposed by the substrate.

We note that the present analysis determines the equilibrium structure as dictated by the thermodynamics of the process and hence establishes the driving force. Therefore, the kinetics of the phase transformations and the temporal evolution of the microstructure cannot be provided by such formalism. To understand the role of non-equilibrium treatments such as superheating and supercooling on the first-order transformations in Figs. 4 and 5 and the formation of intermediate metastable structures, one has to employ dynamic methods such as phase-field modeling. The thermodynamic potentials for the mono- and polydomain phases as specified herein could certainly be the starting point for such simulations.

4. Conclusions

Misfit strain–film thickness phase diagrams for epitaxial PZT ferroelectric thin films are developed based on the non-linear LGD thermodynamic theory. In addition to the phase stability as a function of thickness, we also show variations in the dielectric and electromechanical properties as a function of a multi-parameter space consisting of the temperature, film thickness, effective misfit strain, critical thickness for misfit dislocation and polydomain formation, interface-induced polarization gradients, and electrode screening length. Our model finds that:

- The rotational $r$-phase can only exist in ultra-thin films where the film thickness is either below the MB critical thickness ($L_C$) or the critical thickness for ferroelastic polydomain formation ($h_C$).
- Within such limits the films with rotational $r$-phase may have very high dielectric response and electromechanical properties.
- Although Zr addition increases the stability window for other monodomain phases, it does not significantly affect the range of stability for the $r$-phase.
- The total absence of monoclinic $ac$-phase is in accordance with recent phase-field models [29] and contradicts previous single-domain thermodynamic theories [5].
- For relatively thicker films with a film thickness $L$ larger than both $L_C$ and $h_C$, depending on the magnitude and sign of the in-plane strains a complex microstructure may emerge that consists of both misfit dislocations and polydomain patterns such as the $clacl/a$ or the $a_1/a_2/a_3/a_4$ structures. The evolution of this complicated microstructure is in direct response to the internal stresses that develop during film growth and subsequent cooling from the deposition temperature.

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