Domain Structures of Epitaxial Perovskite Ferroelectric Films: Part I. Theory

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Abstract

Possible equilibrium domain structures due to elastic interactions between the film and the substrate as a result of a cubic-tetragonal transformation observed in epitaxial perovskite ferroelectric films are analyzed. Domain structures are compared in terms of their elastic energies. The formation of both two- and three-domain states is taken into account. Maps which shows domain stability regions are developed in coordinates of misfit strain and tetragonality of the lattice of the ferroelectric phase.

1. Introduction

In recent years, there has been a considerable interest in epitaxial ferroelectric (FE) films because of their attractive physical properties for potential applications such as elements of non-volatile random access memories (NVRAM) and static random access memories (SRAM), high dielectric constant capacitors, optical waveguides, and pyroelectric detectors. This renewed interest in FEs such as $PbTiO_3$, $BaTiO_3$, and $PbTiO_3$-$PbZrO_3$ solid solutions (PZT) is due to remarkable progress during the last decade in film deposition techniques including sol-gel processing, pulsed laser deposition (PLD), metalorganic chemical vapor deposition (MOCVD), and rf-sputtering. The same techniques may produce on many occasions highly aligned FE films grown on appropriately selected substrates. Epitaxy provides superior properties for many electronic and optoelectronic applications since it lacks grain boundaries as in the case of polycrystalline films and has a low density of dislocations, which both act as scattering centers and deteriorate properties of the film.

FEs undergo a structural phase transition at temperatures close to the Curie point. Since this transformation takes place in a mechanically restricted area in epitaxial films,

a large elastic energy arises which may be reduced by formation of domain structures consisting of variants of the ferroelectric phase. The concept of domain formation in epitaxial films was first developed in [1,2] and later applied to epitaxial ferroelectric films [3].

The domain structure of the film determines its properties and performance. That is why there has been an increase in the amount of research on the theoretical description of domain configurations [4-8]. However, excluding [1-3], none of the theoretical models has taken into account the possibility of the formation of three-domain heterostructures. Furthermore, all previous models use a combined parameter called either the tetragonality of the misfit strain [3] or the relative coherency strain [5,6] which contains in it information on both the misfit between the film and the substrate and the tetragonality of the film. In this paper, we develop simple and practical maps in the plane of misfit strain and tetragonality of the film showing expected domain structures and the relative domain populations as a function of temperature. The next paper (Part II) will deal with some practical examples illustrating the capability of these maps.

2. Theory

FEs with a perovskite structure such as $PbTiO_3$ undergo a cubic-tetragonal phase transformation at the Curie temperature (T_C). Three different orientational variants (or domains) may form as shown in the inner circle of Figure 1 and these variants are characterized by the self-strain tensors:

$$\hat{\varepsilon}_1^0 = \begin{pmatrix} \varepsilon_c & 0 & 0 \\ 0 & \varepsilon_a & 0 \\ 0 & 0 & \varepsilon_a \end{pmatrix} \hat{\varepsilon}_2^0 = \begin{pmatrix} \varepsilon_a & 0 & 0 \\ 0 & \varepsilon_c & 0 \\ 0 & 0 & \varepsilon_a \end{pmatrix} \hat{\varepsilon}_3^0 = \begin{pmatrix} \varepsilon_a & 0 & 0 \\ 0 & \varepsilon_a & 0 \\ 0 & 0 & \varepsilon_c \end{pmatrix} \quad (1)$$

where $\varepsilon_a = (a - a_0)/a_0, \varepsilon_c = (c - a_0)/a_0, a$ and c are the lattice parameters of the film in FE state, and a_0 is the lattice parameter of the film in paraelectric (PE) state.

If the FE film described above is grown epitaxially on a cubic substrate such that $(001)_{\text{film}} \parallel (001)_{\text{substrate}}$, the misfit due to the difference in lattice parameters of the film and the substrate may be described by the following misfit strain tensors for each variant as:

$$\hat{\varepsilon}_1 = \begin{pmatrix} \varepsilon_M \varepsilon_T + \varepsilon_M + \varepsilon_T & 0 & 0 \\ 0 & \varepsilon_M & 0 \\ 0 & 0 & \varepsilon_M \end{pmatrix} \hat{\varepsilon}_2 = \begin{pmatrix} \varepsilon_M & 0 & 0 \\ 0 & \varepsilon_M \varepsilon_T + \varepsilon_M + \varepsilon_T & 0 \\ 0 & 0 & \varepsilon_M \end{pmatrix} \quad (2)$$

$$\hat{\varepsilon}_3 = \begin{pmatrix} \varepsilon_M & 0 & 0 \\ 0 & \varepsilon_M & 0 \\ 0 & 0 & \varepsilon_M \varepsilon_T + \varepsilon_M + \varepsilon_T \end{pmatrix} \quad (3)$$

where $\varepsilon_M = (a - a_s)/a_s$ is the misfit strain between the substrate and one side of the

base of the tetragonal film (hereafter referred to as the misfit strain), $\varepsilon_M = (c-a)/a$ is the tetragonality of the film, and a_s is the lattice parameter of the substrate.

Throughout this paper we assume that the thickness of the epilayer is much less than the substrate thickness, as well as other dimensions of the layer. The elastic stress field in such a configuration is concentrated inside the film and is uniform. For simplicity, we assume further that the film is elastically isotropic. The elastic energy of the stress field per unit volume is given by:

$$e = \frac{E}{2(1-\nu^2)} \left[\varepsilon_{xx}^2 + \varepsilon_{yy}^2 + 2\nu\varepsilon_{xx}\varepsilon_{yy} \right] \tag{4}$$

where ε_{xx} and ε_{yy} are the principal strains in the plane of the epitaxial layer determined by the misfit between the lattices of the layer and the substrate, E is the Youngs modulus, and ν is the Poissons ratio of the film. The exact expression for the elastic energy density taking into account anisotropy and relative thickness of the film with respect to the substrate as well is given in [1]. Using Eq. (2.3) and the misfit strain tensors in Eqs. (2.2), the elastic energies of three possible single domain states e_1, e_2 and e_3 are obtained and shown in Table 1. Since $e_1 = e_2$, they are elastically equivalent domain structures.

Table 1. Elastic energy densities and equilibrium domain fractions of possible domain structures

Domain Structure	Elastic Energy Density	Equilibrium Domain Fractions
(1)/(2)	$e_1 = e_2 = \frac{E\varepsilon_M^2}{1-\nu} \left[\frac{\varepsilon_T^2(\varepsilon_M+1)^2}{2\varepsilon_M^2(1+\nu)} + \frac{\varepsilon_T(\varepsilon_M+1)}{\varepsilon_M} + 1 \right]$	α_1 or $\alpha_2 = 1$
(3)	$e_3 = \frac{E\varepsilon_M^2}{(1-\nu)}$	$\alpha_3 = 1$
(1,2)	$e_{12}^0 = \frac{E}{4(1-\nu)} \left(2\varepsilon_M + \varepsilon_M\varepsilon_T + \varepsilon_T \right)^2$	$\alpha_2^0 = \frac{1}{2}$
(1,3)/(2,3)	$e_{13}^0 = e_{23}^0 = \frac{E\varepsilon_M^2}{2}$	$\alpha_3^0 = \frac{(1-\nu)\varepsilon_M + (\varepsilon_M+1)\varepsilon_T}{(\varepsilon_M+1)\varepsilon_T}$
(12,3)	$e_{12,3}^0 = 0$	$\alpha_3^0 = \frac{2\varepsilon_M + (\varepsilon_M+1)\varepsilon_T}{(\varepsilon_M+1)\varepsilon_T}$

The elastic energy can be reduced by the formation of two-domain states, which consist of mixtures of either two of the three possible variants (middle circle in Figure 1) with stress-free interfaces on $\{110\}_{\text{film}}$ [1-3]. If there is a periodic domain alternation with

a domain period much less than the layer thickness, two-domain states may be described by average misfit strain tensors as:

$$
\begin{aligned}
\hat{\varepsilon}_{12} &= (1-\alpha_2)\hat{\varepsilon}_1 + \alpha_2\hat{\varepsilon}_2 \quad \text{for (1,2) structure} \\
\hat{\varepsilon}_{13} &= (1-\alpha_3)\hat{\varepsilon}_1 + \alpha_3\hat{\varepsilon}_3 \quad \text{for (1,3) structure} \\
\hat{\varepsilon}_{23} &= (1-\alpha_3)\hat{\varepsilon}_2 + \alpha_3\hat{\varepsilon}_3 \quad \text{for (2,3) structure}
\end{aligned}
\tag{5}
$$

where $\alpha_i, i = 1,2,3$ are volume fractions of domain i in a domain mixture (j,i). The elastic energy densities are calculated as before and minimized with respect to the volume fraction of domains (i.e., $\partial e_{ij}/\partial \alpha_i = 0$). Equilibrium domain fractions (α_i^0) and elastic energies of two-domain states are given in Table I. Since elastic energies of (1,3) and (2,3) are equal, they are elastically equivalent structures.

In addition, three-domain structures (outer-most circle of Figure 1) may form by mixing two of the three two-domain structures. It has been shown that there is a stress-free compatible interface only if volume fractions of the common domain in each two-domain state are equal [1,2]. The average misfit strain for a second-order polydomain structure consisting of all three variants is as below:

$$
\hat{\varepsilon}_{12,3} = (1-\alpha_3)\hat{\varepsilon}_{12} + \alpha_3\hat{\varepsilon}_3 \quad \text{for (12,3) Domains}
\tag{6}
$$

The elastic energy of this kind of structure can be calculated using Eq. (2.3) and minimizing it with respect to α_3 shows that the strain energy is zero for a three-domain heterostructure (Table 1).

3. Domain Stability Maps

We consider equilibrium between domain states by comparing their elastic energies only. This is a simplified version of the actual situation which neglects microstresses that develop at the film-substrate interface and the contribution of interdomain interface energy to the total free energy of the system. Nonetheless, this simplification is good for relatively thicker films (thickness of the film $> 200-250$ nm) for which the elastic energy dominates the total energy of the system.

As shown in [3], the formation of three-domain states is thermodynamically unfavorable in films with a thickness less than a critical one. Thus, for relatively thinner films we consider equilibrium between single and two-domain states only. For this case, it can be shown that for any given pair of ε_M and ε_T, energies of single domain states (1) or (2) are higher than those of either single domain (3), two-domain (1,2), or (1,3)/(2,3). Therefore, single domain structures with their tetragonal axes in the plane of the film-substrate interface are not stable.
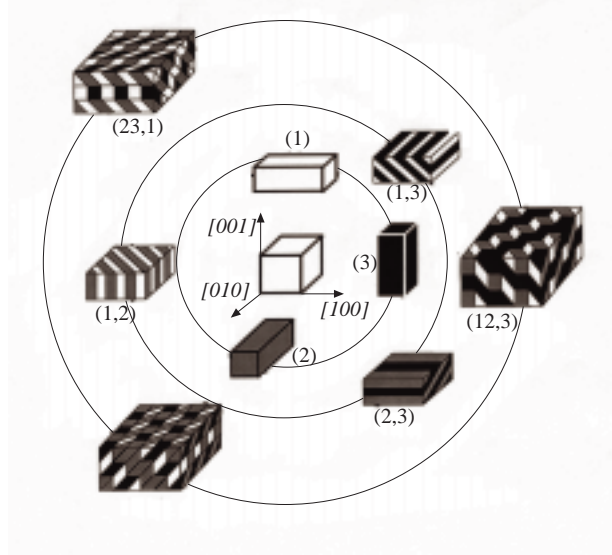
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Figure 1. Possible domain structures of the epitaxial film after cubic-tetragonal transformation [2]. The paraelectric state is at the center and the inner-most circle shows 3 different orientational variants. In ferroelectric literature, single domain states (1), (2) and (3) are called a_1, a_2 and c-type domains, respectively. (1,2) structure is called $\ldots a_1/a_2/a_1/a_2 \ldots$ pattern and (1,3)/(2,3) structures are simply $c/a/c$ patterns

When equilibrium between (1,2) and (1,3)/(2,3) is considered, following relation defining the equilibrium between those domain structures is obtained:

$$\varepsilon_T = \frac{\varepsilon_M}{\varepsilon_M + 1}\left[-2 \pm \sqrt{2(1-\nu)}\right] \tag{7}$$

If the positive root of this relation is used to calculate α_3^0 for the (1,3)/(2,3) structure (Table 1), it turns out to be negative (with $\nu = 0.33$ from hereafter), which is physically not possible. The negative root is thus the boundary between (1,2) and (1,3)/(2,3) on an $\varepsilon_M - \varepsilon_T$ plane along which $\alpha_0^3 \cong 0.58$ as shown in Figure 2 (solid line).

The boundary between (3) and (1,3)/(2,3) is given by the relation $\alpha_3^0 = 1$, i.e., $\varepsilon_M = 0$. The line $\alpha_3^0 = 0$, i.e., $\varepsilon_T = [-(1+\nu)\varepsilon_M]/[\varepsilon_M + 1]$, is the boundary between stable (1,2) and metastable (1,3)/(2,3) states (dashed line in Figure 2). It is also obvious that whenever the film is in compression, i.e., $\varepsilon_M > 0$, single domain state (3) is stable. It should be noted that ranges of ε_M and ε_T are held within practically possible values.

Similarly, if the formation of three-domain structures is possible, single domain states (1) and (2) are not stable for a given pair of ε_M and ε_T. In addition, it can be seen that structures (1,3)/(2,3) are also unstable because for any pair of ε_M and ε_T, their energy is always larger than either (3), (1,2) or (12,3). The lower and upper limits

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of α_3^0 ($\alpha_3^0 = 0$, i.e., $\varepsilon_T = [-2\varepsilon_M]/[\varepsilon_M + 1]$ and $\alpha_3^0 = 1$, i.e., $\varepsilon_M = 0$) for the three-domain structure define the boundaries between (1,2)-(12,3) and (12,3)-(3), respectively, as illustrated in Figure 3. Again, if the film is in compression, single domain state (3) is stable.
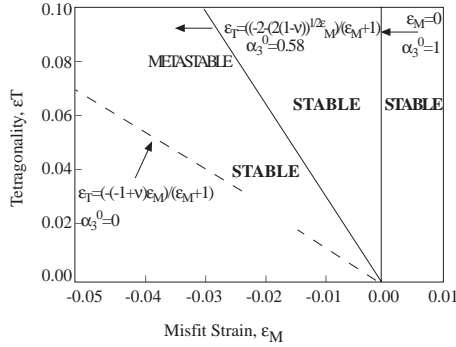

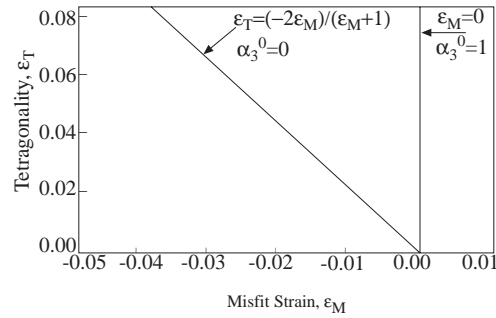**Figure 2.** Domain stability regions on an $\varepsilon_M - \varepsilon_T$ plane for single and two-domain structures

Figure 3. Domain stability regions on an $\varepsilon_M - \varepsilon_T$ plane for all possible domain structures

4. Conclusions

In this paper we have developed domain stability maps for epitaxial perovskite ferroelectric films by considering their elastic energies only. The possibility of formation of three-domain heterostructures is also considered for relatively thicker films. In Part II of this study (the following paper) we will illustrate the effectiveness of these maps with some examples and compare our predictions with results of experimental research from the literature.

Acknowledgments

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