PHASE-FIELD SIMULATION OF PHASE TRANSITIONS, DOMAIN STABILITIES AND STRUCTURES IN FERROELECTRIC THIN FILMS

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by

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Abstract

In this study, we use the phase-field model to study the phase transitions, domain stabilities, domain structures and domain evolutions in a series of representative ferroelectric thin films, including PbTiO$_3$, BaTiO$_3$, SrTiO$_3$, and BiFeO$_3$. The effect of temperature, mechanical and electrostatic boundary conditions as well as the size effect on the above ferroelectric properties were systematically investigated.

We modify the previous phase-field model to study the domain stability and evolution in ferroelectric thin films under anisotropic strains. The effect of anisotropic strains on the phase transitions and domains structures of PbTiO$_3$ and BaTiO$_3$ thin films is studied using both thermodynamic calculations and phase-field simulations. The misfit strain - misfit strain domain stability diagrams, i.e. the graphical representations of stable ferroelectric phases and domain structures as a function of strains, are predicted at several representative temperatures. The similarity and significant differences between the diagrams from thermodynamic calculations assuming single domains and from phase-field simulations are analyzed. Typical domain structures as a result of anisotropic misfit strains are presented.

A modified thermodynamic potential for strontium titanate bulk crystal is developed from interpreting experimental data with phase-field simulations. This modified potential is then applied to study the transition temperatures and domain stabilities in SrTiO$_3$ thin films grown on different substrates with different strain states. The results will be compared with experimental measurements on polarizations in SrTiO$_3$ thin films grown on DyScO$_3$ and GdScO$_3$ substrates.
Phase-field model is also employed to study the domain stabilities and phase transitions in BiFeO$_3$ thin films. It will be shown that the morphotropic phase boundary, or rhombohedral to tetragonal phase boundary predicted by phase-field method has very good agreement with experimental observations in BiFeO$_3$ films deposited on LaAlO$_3$ and YAlO$_3$ substrates. Domain switching near the morphotropic boundary is studied. We also analyze the strain dependence on the coercive field and remnant polarization for BiFeO$_3$ thin films grown on PMN-PT with tensile strains.

A three dimensional phase-field model is applied to model the thickness effect on the domain stability in ferroelectric thin films, by introducing the strain relaxation mechanism and critical thickness for dislocation formation using both Matthews-Blakeslee (MB) and People-Bean (PB) models. PbTiO$_3$ thin films are chosen as the example to construct the strain – thickness domain stability diagram. The relative domain fractions as a function of film thickness are also simulated and compared with experiment results in PbTiO$_3$ thin films grown on SrTiO$_3$ and KTaO$_3$ substrates.
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Chapter 1 Introduction

1.1 Introduction

Ferroelectrics are a class of materials possessing a spontaneous polarization that can be reoriented between crystallographically defined states in a single crystal by an electric field [1-2]. Ferroelectrics have three main technological applications based on three related physical characteristics [3]: First, the spontaneous electric polarization could be used as binary data storage media in which opposite polarization represent the 1 or 0 data bits. Second, ferroelectrics can convert mechanical energy to electrical energy and vice versa, due to the coupling of electric polarization and structure of the material, this leads to the widespread use in transducer applications such as piezoelectric actuators and sonar detectors. Finally, they have large dielectric permittivity leading to applications in capacitors.

The most studied ferroelectric material is that known as the perovskite oxides, which is a very large family of composition ABO₃, where A and B each represent a cation element or mixture of two or more such elements or vacancies. The physical properties of this kind of materials depend on both composition and cationic ordering, so the material could be either metallic or insulating, and exhibit many different types of structural and magnetic orders. The ideal perovskite structure has been shown in Figure 1.1. The structure of the high-temperature paraelectric phases has space group *Pm̅₃m* for most ferroelectric perovskites oxides. The atomic positions of A and B atoms in the ABO₃ structure have two equivalent configurations: if the A atom occupies the corner of the cube, the B atom is at the center and there is an oxygen atom at the center of each face;
alternatively, if the B atom is at the corner, the A atom is at the center and oxygen atoms are located at the midpoint of each edge. At the paraelectric-ferroelectric transition temperature (so called Curie point), the perovskite oxide transforms from a cubic phase to a ferroelectric tetragonal phase ($P4mm$) with spontaneous polarization generated, and the basic element responsible for ferroelectricity is electric dipole $\mathbf{p}$ defined by $\mathbf{p} = q\mathbf{r}$, where $q$ is the magnitude of the charge and $\mathbf{r}$ is the displacement vector pointing from the negative charge to the positive charge. The paraelectric to ferroelectric transition and the creation of dipoles are illustrated in Figure 1. Above the Curie temperature ($T_c$), no dipoles created since the charge centers are arranged in way that cancels overall, as shown in Figure 1.1 (a). This is so called paraelectric state and the perovskite structure $\text{ABO}_3$ has a cubic structure. However, below the Curie temperature as shown in Figure 1.1 (b), the electric dipoles are created by the shift of the ions and lattice distortions. The dipole-dipole interaction is the primary driving force for the long-range ordering of the dipole moment [4], which yields the net ferroelectric spontaneous polarization. As shown in Figure 1.1, the paraelectric to ferroelectric transition also results in a change in lattice parameters and create the spontaneous strain $\varepsilon_{ij}^0$ which couples to the spontaneous polarization:

$$
\varepsilon_{ij}^0 = Q_{ijkl} P_k P_l
$$

(1.1)

where $Q_{ijkl}$ are the electrostrictive coefficients [5].
The spontaneous polarization is usually not uniformly aligned along the same direction in ferroelectric materials. The regions with uniformly oriented spontaneous polarization are called ferroelectric domains, and the boundaries separating different domains are called domain walls. There will also be electrostatic energy generated from the inhomogeneous distribution of the spontaneous polarizations. In addition, to keep the mechanical continuity between the ferroelectric domains with different spontaneous strains, elastic strain is generated during the phase transition. The existence of external constraints, like the applied strain or stress will also significantly changes the elastic energy, and results in the formation of domain structures [7-8]. The equilibrium ferroelectric domain structures are determined by the minimizing the total free energy of the system, including the bulk Landau energy, the elastic energy, the domain wall energy and the electrostatic energy.

The development ferroelectric thin films started from 50~60 years ago when progress in thin film processing techniques made the ferroelectric thin films an ideal
material for the fabrication of nonvolatile memories [9–11]. Almost at the same time, ferroelectric thin films became an important type of materials with the development of the laser and transistor technologies. In 1980s, the practical memory devices were successfully developed based on the ferroelectric materials processing and integration technique. New processing techniques involved the use of organometallic precursors for coprecipitation, sol-gel method, chemical vapor deposition (CVD), metalorganic decomposition (MOD), etc. With these technique, especially the advances in processing of complex ferroelectric oxides at the mid-1980s [11-12] the ferroelectric memories were developed with the discovery of the high temperature superconductive oxides. Then in 1987, ferroelectric memory integrated with silicon complementary metal-oxide semiconductor (CMOS) was developed [13].

For oxide ferroelectrics with perovskite structures [e.g., BaTiO$_3$, (Ba,Sr)TiO$_3$, PbTiO$_3$, Pb(Zr,Ti)O$_3$], chemically and structurally compatible perovskite substrate materials are needed. The general structure of a ferroelectric thin film growth on a substrate is shown in Figure 1.2(a) [14]. The top surface of the film is considered as stress-free and the bottom surface coherently constrained by the substrate. There is an eigenstrain distribution within the film, describing the crystallographic relationship between a parent phase and a product phase for a structural phase transition. Figure 1.2(b) [15] is the schematic of a fully coherent epitaxial ferroelectric film biaxially strained to match an underlying substrate. Both the ferroelectric film and substrate have ABO$_3$ perovskite structures as shown in Figure 1.2(b), with the larger A ion (red and green) nominally centered within a corner-shared framework of octahedra, the smaller B ion nominally centered within these octahedra, and oxygen at the vertices of the octahedra.
The properties of ferroelectric thin films could be significantly different from those of bulk materials due to the substrate constraint. Strain can be imparted into thin films through differences in lattice parameters and thermal expansion behavior between the film and the underlying substrate. It has been shown experimentally [16-20] as well as theoretically [21-24] that the ferroelectric transition temperature can be raised by hundreds of degrees by either tensile or compressive biaxial strains, due to the strong coupling between strain and polarization. Epitaxial strains may also lead to different equilibrium domain states in ferroelectric thin films, compared with its bulk states.

1.2 Research objectives

As we discussed in the last section, the domain stabilities and structures of ferroelectric thin films are determined by the minimization of the total free energy. Many
factors can affect the total free energy such as the mechanical and electric boundary conditions, size and shape of the thin film, applied electric fields as well as the presence of free charge carriers and local defects. Moreover, both elastic and electrostatic energies are non-local energy contributions, which depend on the long range elastic and electrostatic interactions due to the inhomogeneous distributions of the elastic and electric field.

Phase-field model has been proved to be a powerful tool for modeling the microstructure evolution in many different materials [25]. Different from other classical interface - track approaches, phase-field model describes a microstructure, both the compositional/structural domains and their interfaces, as a whole by using a set of field variables. Typical examples of field variables include the concentration or composition of an equilibrium phase, long-range order parameters describing structural heterogeneities, spontaneous polarization describing a ferroelectric domain or spontaneous magnetization for a ferromagnetic domain, etc., depending on different types of material or different problems we are going to model. The field variables change continuously from one phase/domain to another across the interfacial regions. The temporal and spatial distributions of the field variables and then the microstructure are governed by the Cahn-Hilliard nonlinear diffusion equation [26] and the Allen-Cahn (time-dependent Ginzburg-Landau) [27] equation.

\[
\frac{\partial c(r,t)}{\partial t} = M \nabla^2 \left( \frac{\partial F}{\partial c(r,t)} \right) \tag{1.2}
\]

\[
\frac{\partial \eta_s(r,t)}{\partial t} = -L_{n\eta} \left( \frac{\partial F}{\partial \eta_s(r,t)} \right) \tag{1.3}
\]
where $L_{pq}$ and $M$ are kinetic coefficients related to atom or interface mobility, $c$ is conserved field variable, $\eta_i$ is non-conserved field variables, and $F$ is the total free energy of the system. The numerical solutions of these two equations provide the microstructure morphology as well as the statistic information from the simulated microstructure. Since there is no need to track the interfaces, phase-field model can be used to study complicated three-dimensional microstructures without any a priori assumptions of the microstructure. In the past decade, the phase-field method has been extensively employed to simulate microstructure evolutions during phase transformations, including spinodal decomposition [28-31], precipitation of an ordered phase from a disordered matrix [32-34], cubic to tetragonal transformation [35], grain growth [36-38], and martensite transformations [39,40].

The goal of this thesis is to extend phase-field models to understand and predict the phase transitions, domain stabilities and domain structures in a series of classical ferroelectrics thin films, which involve the long-range elastic and electrostatic interactions. The specific objectives are as follows:

1. Apply phase-field models and thermodynamic analysis to study the effects of substrate constraint on the domain stabilities and structures in PbTiO$_3$ and BaTiO$_3$ thin films subjected to unequi-biaxial strains.

2. Improve the Landau-Devonshire thermodynamic potential of strontium titanate bulk crystal, by interpreting phase-field simulations and experimental measurements in three different SrTiO$_3$ thin films samples with different strain states.
(3) Apply the modified thermodynamic potential to investigate the phase transitions and domain stabilities in SrTiO$_3$ thin films. Construct the strain - temperature diagram for equi-biaxially strained SrTiO$_3$ thin film, and strain - strain domain stability diagram at several representative temperatures for SrTiO$_3$ thin films subjected to unequi-biaxially strains.

(4) Use both phase-field method and thermodynamic calculation to predict the domain stabilities and domain structures in multiferroic BiFeO$_3$ thin films, specifically the distorted rhombohedral phase to tetragonal phase transitions observed by experiment.

(5) Apply phase-field model to predict the thickness effect on domain stability in ferroelectric thin films, taking into account the ferroelectric domain structures, the electrostrictive effects, substrate constraint, as well as the strain relaxation from the thickness effect. PbTiO$_3$ thin films grown on SrTiO$_3$ and KTaO$_3$ substrates will be chosen as two representative examples to study the thickness dependent domain stabilities.

1.3 Thesis structure

This thesis is organized as 8 chapters.

Chapter 1 consists of the general background of ferroelectric materials, followed by the research objectives and thesis structure.

In Chapter 2, the effects of unequi-biaxial strain on the domain stability of epitaxial PbTiO$_3$ thin films are studied using phase-field simulation.
In Chapter 3, both thermodynamic calculations and phase-field method are applied to study the effect of unequal biaxial strain on the domain stability of epitaxial BaTiO$_3$ thin films.

In Chapter 4, a modified Landau-Devonshire thermodynamic potential is presented by interpreting phase-field simulations and experimental observations in three different SrTiO$_3$ thin film samples with different strain states.

In Chapter 5, the modified thermodynamic potential, developed in chapter 4, is applied to study the phase transitions and domain stabilities in (001) SrTiO$_3$ thin films.

In Chapter 6, phase-field model is extended to multiferroic BiFeO$_3$ thin films, to study the ferroelectric domain stabilities in this system, specifically on the strain-driven morphotropic phase boundary in this system.

In Chapter 7, a phase-field model taking into account the thickness effect is employed to study the domain stabilities as a function of film thickness in PbTiO$_3$ thin films. We will also compare the simulations results with experimental measurements on the domain fractions in PbTiO$_3$ thin films grown on SrTiO$_3$ and KTaO$_3$ substrates.

Chapter 8 includes final conclusions and discussions on some future directions.
References


Chapter 2 Phase-field simulations of domain stabilities and structures in PbTiO$_3$ thin films

2.1 Introduction

PbTiO$_3$ is a prototypic ferroelectric perovskite and a component for a number of important piezoelectric solid-solution systems including PbZrO$_3$-PbTiO$_3$ (PZT), Pb(Zn$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ (PZN-PT), and Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ (PMN-PT). The phase transition behavior in a bulk PbTiO$_3$ single crystal is relatively simple; it exhibits a single transition from paraelectric cubic phase to ferroelectric tetragonal phase. However, the phase transition may become more complicated in a thin film state. It has been shown theoretically [1-4] as well as experimentally [5-7] that epitaxial strains may lead to different equilibrium domain states from the corresponding bulk and the ferroelectric transition temperature can be raised by hundreds of degrees by either tensile or compressive biaxial strains.

The thermodynamics of strain effect on phase transitions in ferroelectric thin films was pioneered by Pertsev et al [1] who published the first misfit strain-temperature diagram for PbTiO$_3$ under a symmetrical biaxial strain and a single-domain assumption for all the possible ferroelectric states. However, significantly different domain stability diagrams [1, 3, 8-10] were obtained if one considers the possibility of domain structure formation under symmetrical biaxial strains. More recently, the isothermal “misfit strain – misfit strain” domain stability diagrams under anisotropic biaxial strains were constructed for PbTiO$_3$ films using thermodynamic calculations and a single-domain assumption. [11-14] Therefore, the main objective of this work is to construct a “misfit
strain – misfit strain” domain stability diagram for PbTiO₃ thin films by taking into account three-dimensional domain structures. For this purpose, we employ the phase-field approach for ferroelectric phase transitions and domain structures in thin films.

### 2.2 Simulation details

We consider a (001)-oriented PbTiO₃ thin film on an orthorhombic substrate, i.e. under anisotropic misfit strains. A rectangular coordinate system, \( x=(x_1, x_2, x_3) \) is set up with the \( x_1, x_2 \) and \( x_3 \) axes along the [100], [010] and [001] crystallographic directions, respectively. The ferroelectric domain structure is described by the spatial distribution of the spontaneous polarization vector \( \mathbf{P}(x) = (P_1, P_2, P_3) \). The temporal evolution of \( \mathbf{P} \) and the domain structures are governed by the time-dependent Ginzburg-Landau (TDGL) equations,

\[
\frac{\partial P_i(x,t)}{\partial t} = -L \frac{\delta F}{\delta P_i(x,t)}, i = 1,2,3, \tag{2.1}
\]

where \( L \) is the kinetic coefficient related to the domain-wall mobility, and \( F \) is the total free energy of the system. \( \delta F / \delta P_i(x,t) \) is the thermodynamic driving force for the spatial and temporal evolution of \( P_i(x,t) \). The total free energy \( F \) includes the bulk free energy, elastic deformation energy, domain wall energy and electrostatic energy, i.e.

\[
F = \int_V [f_{\text{bulk}}(P) + f_{\text{elast}}(P, e_{ij}) + f_{\text{wall}}(P_{i,j}) + f_{\text{elec}}(P_i, E_i)]dV, \tag{2.2}
\]

where \( V \) is the volume of the film and \( dV = dx_1dx_2dx_3 \). In this work, it is assumed that the strain field \( e_{ij} \) and electric field \( E_i \) are always at equilibrium for a given polarization field distribution. The bulk free energy density of PbTiO₃ is described by a six-order
Landau-Devonshire polynomial [15] with free energy coefficients collected from literature:[1,16] $\alpha_1 = 3.8 \times (T - 479) \times 10^5$, $\alpha_{11} = -7.3 \times 10^7$, $\alpha_{12} = 7.5 \times 10^8$, $\alpha_{111} = 2.6 \times 10^8$, $\alpha_{112} = 6.1 \times 10^8$, $\alpha_{123} = -3.7 \times 10^9$, $c_{11} = 1.746 \times 10^{11}$, $c_{12} = 7.937 \times 10^{10}$, $c_{44} = 1.11 \times 10^{11}$, $Q_{11} = 0.089$, $Q_{12} = -0.026$, $Q_{44} = 0.0675$ (in SI units and $T$ in °C). The contribution of domain walls to the total free energy is introduced through the polarization gradient, $f_{\text{wall}}$.

The elastic energy density is given by

$$f_{\text{elas}} = \frac{1}{2} c_{ijkl} f_{ijkl} e_{ijkl} = \frac{1}{2} c_{ijkl} (e_{ij} - e_{ij}^0)(e_{ij} - e_{ij}^0), \quad (2.3)$$

where $e_{ij} = e_{ij} - e_{ij}^0$ is the elastic strain, $e_{ij}$ is the total strain of the film compared to the parent paraelectric phase, and $c_{ijkl}$ is the elastic stiffness tensor. Both $e_{ij}$ and $e_{ij}^0$ are defined using the cubic phase as the reference, and $e_{ij}^0 = Q_{ijkl} P_k P_l$ where $Q_{ijkl}$ is the electrostrictive coefficient tensor. The details of the calculation of the total strain $e_{ij}$ in a (001)-oriented film under a biaxial strain are described in our previous publications. [3,10]

In this work, the average film/substrate misfit strains $e_{x_1} = \bar{\varepsilon}_{11}$ and $e_{x_2} = \bar{\varepsilon}_{22}$ along $x_1$ and $x_2$ axes can be different because of a thermal mismatch and/or a lattice mismatch between a film and substrate. Here we assume $\bar{\varepsilon}_{12} = \bar{\varepsilon}_{21} = 0$. The over bar indicates an average over the film.

The electrostatic energy density of a given polarization distribution was obtained by solving the electrostatic equilibrium equation under specified electric boundary conditions.[17-18]
In the phase-field simulations, the temporal evolution of the polarization vector, and thus the domain structures were obtained by numerically solving the TDGL using the semi-implicit Fourier-spectral method. [19] We employed $128\Delta x \times 128\Delta x \times 36\Delta x$ grid size, with periodic boundary conditions along the in-plane $x_1$ and $x_2$ axes. $\Delta x$ is the spacing between two nearest grid points. The thickness of the film was taken as $h_f = 20\Delta x$, and the region of the substrate allows to deform is assumed be $h_s = 12\Delta x$. Due to the lack of experimental data, an isotropic gradient energy coefficient $G$ is chosen with a value of $G/G_0=0.6$ where $G_0$ is related to the magnitude of $\Delta x$ through $\Delta x = \sqrt{G_{11\alpha}/\alpha_0}$ and $\alpha_0 = |\alpha|_{T=25^\circ C}$. The corresponding width of domain wall is about $1.5\Delta x$. The short-circuit boundary condition was employed to compute the dipole-dipole interactions. [20]

We performed a series of simulations under anisotropic substrate/film misfit strains along $x_1$ and $x_2$ axes, ranging from -0.05 (compressive strain) to +0.05 (tensile strain). Each simulation proceeded for 20000 time steps until the polarization distribution achieved steadiness.

2.3 Results and discussions

Examples of typical domain structures from our simulations are shown in Figure 2.1 in which different domain variants are labeled. Figure 2.1(a) is a typical tetragonal domain structure under large compressive strains for both $x_1$ and $x_2$ directions ($e_{s1} = e_{s2} = -0.010$), in which there are two types of $c$-domains of $(0,0,\pm P_3)$ separated by $180^\circ$ domain walls. For the case with large tensile strains ($e_{s1} = e_{s2} = 0.015$) along both $x_1$ and $x_2$ directions (Fig 2.1(b)), only $a_1 (\pm P_1,0,0)$ and $a_2 (0,\pm P_2,0)$ twin domains exist. At
intermediate strains, all three kinds of domains, c, a₁, and a₂ are present (Figure 2.1(c)). All the domain structures and domain wall orientation results are consistent with our previous simulations carried out under symmetric strains. [3,10]

The domain structures under anisotropic misfit strains can be significantly different compared to the symmetric case. Figure 2.1(d) shows a domain structure containing only c and a₁ domains for $e_{x_1} = 0.010$ and $e_{x_2} = -0.010$, i.e., a tensile strain along $x_1$ direction and compressive strain along $x_2$. The a₁ domains are plates aligning about 45° from the film/substrate interface. As expected, $c+a_2$ domain structures are obtained when we reverse the strains along $x_1$ and $x_2$ axes ($e_{x_1} = -0.010$ and $e_{x_2} = 0.010$), as shown in Figure 2.1(e). The domain morphology is drastically different from the symmetric case of $e_{x_1} = e_{x_2} = 0.010$ (Figure 2.1(b)).

Figure 2.1(f) exhibits a domain structure under a very high strain anisotropy with a tensile strain along the $x_2$ direction $e_{x_2} = 0.035$ and the same compressive strain along the $x_1$ direction ($e_{x_1} = -0.010$) as in Figure 2.1(e). Compared with Figure 2.1(e) which has $c+a_2$ domain structure, Figure 2.1(f) contains only $a_2$ domains. The two types of $a_2$ domain $(0,\pm P_2,0)$ are separated by 180° domain walls. Similarly, only $a_1$ domains are present for $e_{x_1} = 0.035$ and $e_{x_2} = -0.010$. 
Figure 2.1 Domain morphologies in PbTiO₃ thin films under different anisotropic misfit strains: (a) $c$ domain at $e_{s1} = e_{s2} = -0.010$; (b) $a_1 + a_2$ domain at $e_{s1} = e_{s2} = 0.015$; (c) $c + a_1 + a_2$ domain at $e_{s1} = e_{s2} = 0.005$; (d) $c + a_1$ domain at $e_{s1} = 0.010$ and $e_{s2} = -0.010$; (e) $c + a_2$ domain at $e_{s1} = -0.010$ and $e_{s2} = 0.010$; (f) $a_2$ domain at $e_{s1} = -0.010$ and $e_{s2} = 0.035$
Figure 2.2 Misfit strain-misfit strain domain stability diagram for PbTiO$_3$ thin film at $T=25^\circ$C from phase-field simulation. Scattered symbols separating $c$, $a_1$, $a_2$, $c+a_1$, $c+a_2$, $a_1+a_2$, $c+a_1+a_2$ phase regions.
Figure 2.3 Misfit strain-misfit strain domain stability diagram for PbTiO$_3$ thin film at $T=25^\circ$C: scattered symbols are phase boundaries from phase-field simulation separating $c$, $a_1$, $a_2$, $c+a_1$, $c+a_2$, $a_1+a_2$, $c+a_1+a_2$ phase regions, and solid lines are from thermodynamic calculations including 1. $c$ phase ($P_1=P_2=0, P_3 \neq 0$), 2. $a_1$ phase ($P_1 \neq 0$ and $P_2=P_3=0$), 3. $a_2$ phase ($P_2 \neq 0$ and $P_1=P_3=0$), 4. $ca_1$ phase ($P_1 \neq 0$, $P_2=0$, $P_3 \neq 0$), 5. $ca_2$ phase ($P_1=0$, $P_2 \neq 0$, $P_3 \neq 0$), 6. $a_1a_2$ phase ($P_1 \neq 0$, $P_2 \neq 0$, $P_3=0$), 7. $r$ phase ($P_1 \neq 0$, $P_2 \neq 0$, $P_3 \neq 0$).
Based on the simulation results, a domain stability diagram, i.e., a representation of stable ferroelectric phases and domain structures as a function of misfit strains is constructed under $T = 25^\circ C$ (Figure 2.2). Under sufficiently large compressive strains, the stable state consists of pure $c$ domains with 180 degree domain walls. A twin structure of $a_1+a_2$ domains is the stable under relatively large tensile strains along both directions. The anisotropic strains (compressive strain at one direction and tensile strain at the other direction, vice versa) lead to either $c+a_1$ or $c+a_2$ domain structures. Purely $a_1$ or $a_2$ domain states are possible only under unrealistically large ($> \sim 3.0\%$) compressive or tensile strain long either one of the two in-plane directions. In the central part of the diagram, there is a stability region for the $c+a_1+a_2$ domain structure.

In Figure 2.3, we compare the domain stability diagram (the red lines) using thermodynamic calculations assuming single domains for each ferroelectric state [11-14] and that from the phase-field simulations (scattered symbols as in Figure 2.2). It is emphasized that the diagram from the phase-field approach is generated without any a priori assumption on the possible domain wall orientations. All the data points shown in Figure 2.2 and 2.3 were obtained by starting from an initial paraelectric state. As a result, the $a_1$, $a_2$, or $a_1+a_2$ or $c+a_1$ or $c+a_2$ or $c+a_1+a_2$ domain configurations under different substrate constraints were automatically predicted using this approach. On the other hand, in the thermodynamic analysis [11-14], the domain diagram (Figure 2.3) containing $c$-phase, $r$-phase ($P_1, P_2, P_3$), $a_1$-phase ($P_1, 0, 0$), $a_2$-phase ($0, P_2, 0$), $ca_1$-phase ($P_1, 0, P_3$), $ca_2$-phase ($0, P_2, P_3$), or $a_1a_2$ phase ($P_1, P_2, 0$) was obtained under the same anisotropic substrate constraints using single-domain assumptions. As one can see in Figure 2.3, the predicted diagram using phase-field simulations is not only quantitatively but also qualitatively
different from that from thermodynamic calculations. First of all, all the new phases predicted by thermodynamic calculations, $r, ca_1, ca_2,$ and $a_1a_2$ in Figure 2.3, are artifacts resulted from the single-domain assumption. Secondly, thermodynamic calculates indicate that a moderate anisotropic strain of 1.0% e.g., $e_{s1} = 1.0\%$ and $e_{s2} = 0.0$, would be sufficient to stabilize purely $a_1$ domains while phase-field simulations show that stabilizing purely $a_1$ or $a_2$ domains would require anisotropic strain levels ($> 3.0\%$ along one of the two in-plane directions coupled with $\sim -1.0\%$ along the other in-plane direction) that are unlikely to be achieved in real thin film growth processes. Finally, the stability field for purely $c$-domains predicted by phase-field simulations is significantly narrower than that from thermodynamic calculations.

The isotropic ($e_{s1}=e_{s2}$) misfit strain-temperature domain stability diagram was also reproduced in Fig. 4. We noticed that although it is essentially the same as that we obtained previously\(^3\), there is a shift of the $c/c+a_1+a_2$ boundary, e.g. from $e_{s1}=e_{s2}=-0.010$ at $0\,^\circ C$ in reference [3] to around $e_{s1}=e_{s2}=-0.005$ in the present calculations. The boundary between the regions with $c+a_1+a_2$ domains and $a_1+a_2$ is around $e_{s1} = e_{s2} = 0.010$ largely remains the same. The shift of the boundary between $c$ domain and $c+a_1+a_2$ is caused by the fact that the electrostatic interactions in an inhomogeneous domain structure were ignored in the original work [3]. In the present calculation, a short-circuit boundary condition was assumed. The film surface charge is then compensated, and thus no depolarization field is produced. It should be noted that the polarization charges at the internal domain walls are not entirely compensated and thus they can affect the volume fractions of different domain variants. The constant electrical potential on the surfaces
Figure 2.4 Misfit strain-temperature domain stability diagram for PbTiO$_3$ thin film under isotropic strains.
promotes the formation of $c$ domains [17], leading to the enlargement of $c$ domain region in Figure 2.4.

2.4 **Summary**

In summary, a misfit strain-misfit strain phase/domain stability diagram was constructed for PbTiO$_3$ thin films at room temperature using phase-field simulations. It takes into account both elastic and electrostatic interactions under a short-circuit boundary condition. The predicted domain stability for anisotropic strains at room temperature is qualitatively different from those obtained using thermodynamic calculations based on the single-domain assumption.
References


Chapter 3 Thermodynamic calculations and phase-field simulations of domain stabilities in BaTiO$_3$ thin films

3.1 Introduction

Barium titanate is a classic oxide ferroelectric with the perovskite structure. It was the basis for the first generation of ceramic transducers and has wide applications in ceramic capacitors. [1] In the past two decades, there has been increasing interest in epitaxial BaTiO$_3$ thin films due to their good electrical and optical properties. [2-5] It has been shown that the phase transition temperatures of BaTiO$_3$ thin films could be significantly increased by the misfit strains from the lattice and/or thermal expansion mismatches between the films and their substrates.[3,6-8] A number of strain domain stability diagrams, the graphical representation of ferroelectric phases as a function of strain have been generated from thermodynamic calculations under a single domain assumption or assuming a simplified two-dimensional domain structure.[2,4,9-10] By using the phase-field approach, domain structures of BaTiO$_3$ thin films under isotropic biaxial strains were studied, and a “temperature - strain” phase diagram was constructed.[11] It was recently demonstrated that strain could also lead significant variations in the coercive fields of BaTiO$_3$ thin films. [12]

Epitaxial BaTiO$_3$ thin films are often grown on orthorhombic substrates such like GdScO$_3$, [3] which lead to an anisotropic in-plane misfit strain state. The effect of anisotropic misfit strains on the ferroelectric domain stability of the films could be very different from the isotropic misfit strains. So it is desirable to investigate the effects of anisotropic misfit strains on the domain structures and properties of BaTiO$_3$ thin films.
However, all the published diagrams [13-15] under anisotropic strains were determined from thermodynamic analysis under a single domain assumption. Moreover, the 6\textsuperscript{th}-order Landau-Devonshire potential [16] was employed in these calculations and the misfit strain is limited to relatively small compressive strains ($\leq 0.4\%$). [2, 10, 17] Recently, an 8\textsuperscript{th} order potential [18] was developed, which made it possible to construct strain stability diagrams under full range of anisotropic strains.

The phase-field approach has been successfully employed to construct domain stability diagrams for PbTiO\textsubscript{3} thin films under anisotropic strains. [19] The obtained phase diagram shows significant difference from thermodynamic calculations. In this chapter, we will firstly report the room temperature misfit strain–misfit strain diagrams from thermodynamic calculations using the 8-th order thermodynamic potential, which exhibits significant difference from previous diagrams using the 6-order potential. In the second part, the misfit strain–misfit strain diagrams from phase-field simulations will be presented, at several representative temperatures for BaTiO\textsubscript{3} thin films. The typical domain morphologies from the phase-filed simulations under different anisotropic strains and temperatures will be also discussed.

3.2 Results and discussions

3.2.1 Thermodynamic calculations

A ferroelectric domain structure illustrates the spatial distribution of the spontaneous polarization vector $\mathbf{P}(\mathbf{x}) = (P_1, P_2, P_3)$. The properties of a BaTiO\textsubscript{3} single crystal bulk under stress-free condition is described by an 8\textsuperscript{th} order polynomial in polarization components, [18]
where the coefficients $\alpha_{ij}$, $\alpha_{ijk}$, and $\alpha_{ijkl}$ are constants, and $\alpha_i$ is linearly dependent on temperature and obeys the Curie-Weiss law.[18,20]

When ferroelectric domains formed in a strained BaTiO$_3$ film, an elastic energy is generated, and the corresponding elastic energy density is given by

$$f_{\text{elas}} = \frac{1}{2} c_{ijkl} e_{ij} e_{kl} - \frac{1}{2} c_{ijkl} e_{ij}^0 e_{kl}^0, \quad (3.2)$$

where $c_{ijkl}$ is the elastic stiffness tensor, $e_{ij}$ and $e_{ij}^0$ are the elastic strain and stress-free strain, respectively. $e_{ij} = e_{ij} + e_{ij}^0$ is the total strain. Here both $e_{ij}$ and $e_{ij}^0$ are defined using the cubic phase as the reference, and $e_{ij}^0 = Q_{ijkl} P_k P_l$ where $Q_{ijkl}$ represents the electrostrictive coefficient. Therefore, changing from a stress-free boundary condition to a clamped one modifies the second-order and the fourth-order terms of the Landau free energy polynomial in Eq.(3.1), and thus the nature of a ferroelectric transition and its transition temperature.[2,21]

In this work, a (001)-oriented BaTiO$_3$ thin film on an orthorhombic substrate is considered. A rectangular coordinate system, $x=(x_1, x_2, x_3)$ is set up with the $x_1$, $x_2$ and $x_3$ axes along the [100], [010] and [001] crystallographic directions, respectively. The average film/substrate misfit strains $e_{i1}=\varepsilon_{11}$ and $e_{i2}=\varepsilon_{22}$ along the in-plane $x_1$ and $x_2$ axes

$$f_{\text{bulk}} = \alpha_i (P_i^2 + P_i^2 + P_i^2) + \alpha_{i1} (P_i^2 + P_i^2 + P_i^2) + \alpha_{i2} (P_i^2 + P_i^2 + P_i^2)$$

$$+ \alpha_{i3} (P_i^2 + P_i^2 + P_i^2) + \alpha_{i4} (P_i^2 + P_i^2 + P_i^2) + \alpha_{i5} (P_i^2 + P_i^2 + P_i^2) + \alpha_{i6} (P_i^2 + P_i^2 + P_i^2)$$

$$+ \alpha_{i7} (P_i^2 + P_i^2 + P_i^2) + \alpha_{i8} (P_i^2 + P_i^2 + P_i^2) + \alpha_{i9} (P_i^2 + P_i^2 + P_i^2) + \alpha_{i10} (P_i^2 + P_i^2 + P_i^2)$$

$$+ \alpha_{i11} (P_i^2 + P_i^2 + P_i^2) + \alpha_{i12} (P_i^2 + P_i^2 + P_i^2) + \alpha_{i13} (P_i^2 + P_i^2 + P_i^2) + \alpha_{i14} (P_i^2 + P_i^2 + P_i^2)$$

$$+ \alpha_{i15} (P_i^2 + P_i^2 + P_i^2) + \alpha_{i16} (P_i^2 + P_i^2 + P_i^2)$$

(3.1)
are different. The details of the calculation of the total strain $\varepsilon_{0}$ in a (001)-oriented film under a biaxial strain are described in Refs. [21, 22].

The thermodynamically most stable single-domain state is obtained by minimizing the bulk free energy density and the elastic energy density under a given misfit strain and temperature. In this chapter all calculations correspond to room temperature ($T = 25^\circ C$). The Landau energy coefficients, the electrostrictive coefficients and the elastic stiffness are listed in Ref. [20]. The corresponding “misfit strain - misfit strain” diagrams assuming a single-domain state is shown in Figure 3.1, with misfit strains ranging from -2% to 2% along both axes. We obtained seven stable single domain states: three are tetragonal described by $a_1 (P_1 \neq 0, P_2=P_3=0)$, $a_2 (P_2 \neq 0, P_1=P_3=0)$ and $c (P_3 \neq 0, P_1=P_2=0)$; three are orthorhombic labeled as $O_{12} (P_1 \neq 0, P_2 \neq 0, P_3=0)$, $O_{13}(P_1 \neq 0, P_2=0, P_3 \neq 0)$ and $O_{23}(P_1=0, P_2 \neq 0, P_3 \neq 0)$, and the rhombohedral phase ($P_1 \neq 0, P_2 \neq 0, P_3 \neq 0$). Compared with the strain diagrams generated from the 6th-order potential, [14,15] the new diagram is significantly different. The domain stability near the center of the diagram is not clearly addressed on the old diagram, [14] but on this new diagram, rhombohedral phase is shown to be stable. The tetragonal and orthorhombic phase regions and boundaries separating these regions are also quantitatively different. This diagram is essentially the same as the recently reported diagram generated from the same thermodynamic potential [23].

### 3.2.2 Phase-field simulations

As mentioned above, the “misfit strain - misfit strain” diagram generated from the thermodynamic analysis assumes single domain states. To incorporate the possibility of
multidomain and/or multiphase states in the phase diagram, we employed the phase-field approach by considering that the polarization field as well as the local strain are inhomogeneous. The temporal evolution of $P$ from nonequilibrium to equilibrium and the domain structures are governed by the time-dependent Ginzburg-Landau (TDGL) equations,

$$\frac{\partial P_i(x,t)}{\partial t} = -L \frac{\delta F}{\delta P_i(x,t)}, \quad i = 1, 2, 3,$$

(3.3)

where $L$ is the kinetic coefficient which is related to the domain movement, $t$ is time and $F$ is the total free energy. To determine the stability of domain structure, the contribution of domain wall energy $F_{\text{wall}}$ and electrostatic energy $F_{\text{elec}}$ should be considered. Thus the total free energy $F$ as a function of polarization is expressed as

$$F = V \left[ f_{\text{bulk}}(P_i) + f_{\text{elas}}(P_i, \varepsilon_{ij}) + f_{\text{grad}}(P_i, j) + f_{\text{elec}}(P_i, E_i) \right],$$

(3.4)

where $V$ is the volume of the film, $f_{\text{grad}}(P_i, j)$ and $f_{\text{elec}}(P_i, E_i)$ are the gradient energy and electrostatic energy densities, $P_{ij}$ is the spatial derivative of $i^{th}$ component of polarization $P$ with respect to the space vector component $j$, $E_i$ is the electric field which depends on the polarization distribution and the electric boundary conditions on the film surfaces. The calculation details of these energy terms are addressed in Ref. [24].

The temporal evolution of the polarization field and thus the domain structures are obtained by numerically solving the TDGL equations using the semi-implicit Fourier spectral method. [25] In the computer simulations, we employed a model of $128\Delta x \times 128\Delta x \times 36\Delta x$ grid size, with periodic boundary conditions along the in-plane $x_1$ and $x_2$ axes. The thickness of the substrate and the film are taken as $h_s = 12\Delta x$ and
$h_f = 20\Delta x$, respectively. Isotropic domain wall energy was assumed and the gradient
energy coefficient $G_{11}/G_{110}=1.0$ where $G_{110}$ is related to the magnitude of $\Delta x$ through
$\Delta x = \sqrt{G_{110}/\alpha_0}$ and $\alpha_0 = |\alpha_n|_{T=25^\circ C}$. The initial polarization field is created by assigning a
zero value at each cell plus a small random noise. Using the material constants listed in
Refs.14 and 16, we performed numerous simulations under anisotropic misfit strains
along $x_1$ and $x_2$ axes ranging from -0.02 (compressive strain) to +0.02 (tensile strain).
The short-circuit boundary condition was employed to compute the dipole-dipole
interactions.[24] Each simulation proceeded for 60000 time steps (normalized time step
is 0.05) until the polarization distribution achieved steadiness, i.e., no significant changes
of the domain structure take place with prolong simulation. We also performed the
simulations from different initial random noises to check the results.

Based on the phase-field simulation results, the “misfit strain – misfit strain”
diagram is constructed, as shown in Figure 3.2. The thermodynamic diagram is also
presented as red lines for comparison. It is noted that the domain stability diagram from
the phase-field simulations is dramatically more complicated with many regions of multi-
domain states. It is emphasized that although we use same notations in the figure for
both results from the thermodynamic calculations and the phase-field simulations (such
as tetragonal $c$, $a_1$, $a_2$ or orthorhombic $O_{12}$, $O_{13}$, $O_{23}$), the terminology “single phase” is
used in the phase-field simulations to replace the “single domain” from the
thermodynamic calculations. The difference is that each single phase obtained from
phase-field approach always contains the coexisted equivalent polarization variants, for
example, $(0, 0, P_3)$ and $(0, 0, -P_3)$ in pure $c$ phase, $(+P_1, +P_2, 0), (+P_1, -P_2, 0), (-P_1, +P_2, 0)$
and $(-P_1, -P_2, 0)$ in $O_{12}$ phase. But in thermodynamic analysis, the single domain region
stands for one of the equivalent variants, like single $c$ domain stands for pure $c^+$ or $c^-$ domain.

The difference between these two diagrams is obvious. The diagram constructed form the phase-field approach has a stable binary phase region between every two neighbor single phase regions as a transitory area. Thus we have six regions of binary phases ($c+O_{13}$, $O_{13}+a_1$, $a_1+O_{12}$, $O_{12}+a_2$, $a_2+O_{23}$, $O_{23}+c$). We also have three regions of three phase mixtures ($c+O_{13}+a_1$, $c+O_{23}+a_2$, $O_{12}+a_1+a_2$) and two multiphase regions containing five and six phases near the center of the domain stability diagram, as shown in Figure 3.2. We should point out that the phase diagram from the phase-field approach is generated without any *a priori* assumption on the possible domain structures, and some of the domain structures are only close to the equilibrium state or may be even metastable. It is also noted that the diagonal of this diagram showing the domain configuration sequence as $c \rightarrow c+a_1+a_2+O_{13}+O_{23} \rightarrow c+a_1+a_2+O_{12}+O_{13}+O_{23} \rightarrow a_1+a_2+O_{12} \rightarrow O_{12}$, which is also consistent with the “strain-temperature” diagrams from our previous simulations.[11]

Examples of the room temperature domain structures at from the simulations are shown in Figure 3.3 and Figure 3.4. Different domain variants are identified by colors and labeled in the figures. Figure 3.3(a) exhibits a typical tetragonal domain structure under large compressive strains for both $x_1$ and $x_2$ directions ($e_{x1}=e_{x2}=-0.010$), in which there are two types of $c$-domains of $(0, 0, P_3)$ and $(0, 0,-P_3)$ separated by $180^\circ$ domain walls. Single $a_1$ domain (Figure 3.3(b)) is stable only when a large tensile strain is applied at the $x_1$ axis and a large compressive strain is at the $x_2$ axis. Figure 3.3(c) is the general orthorhombic $O_{12}$ domain structure with large tensile strains applied on both axes.
(here \( e_{s1}=e_{s2}=0.015 \)). Figure 3.3(d) is another interesting domain structure induced by anisotropic strains. When choosing an appropriate tensile strain along one axis and compressive strain along the other (vice versa), we can get the pure \( O_{13} \) or \( O_{23} \) phases. To simplify the exhibition of domain structure in orthorhombic domains, we only identify in Figure 3.3(d) the two types of \( O_{23} \)-domains ((0, \( \pm P_2, \pm P_3 \)) and (0, \( \pm P_2, \mp P_3 \))) instead of all four variants (\( e_{s1}=-0.015 \) and \( e_{s2} = 0.005 \)). The same treatment is applied to \( O_{12} \) and \( O_{13} \) domains. Figures 3.4(a) to 3.4(f) are the multi-domain structures containing at least two phases. Complex domain patterns are formed under these states with the domain wall orientation not well defined.

To compare with the stabilized domains at room temperature, we also construct the misfit strain – misfit strain phase diagrams for BaTiO\(_3\) thin films at a higher temperature (\( T=100^\circ\text{C} \)), as shown in Figure 3.5. Some representative domain structures at this temperature are listed in Figure 3.6. Compare with the diagram at \( T=25^\circ\text{C} \), it is evident that the stabilized regions for 3 orthorhombic phases (\( O_{12}, O_{13} \) and \( O_{23} \)) shrink at higher temperature, while the 3 tetragonal phase regions (\( a_1, a_2 \) and \( c \)) all expand. Thus it is possible for a BaTiO\(_3\) thin film strained at some certain values (like \( e_{s1}=e_{s2}=0.5\% \)) to have a tetragonal to orthorhombic transition when cooling from high temperature.

In addition to the phase diagrams at \( T=25^\circ\text{C} \) and \( T=100^\circ\text{C} \), we also investigate the domain stabilities of BaTiO\(_3\) thin films at extremely low temperature, for example, \( T=0\text{K} \) or -273\(^\circ\text{C} \). The corresponding domain stability diagram is presented in Figure 3.7. It could be seen that the tetragonal \( c \) domain will still be stable if compressive strain applied to both axes. However, relatively small magnitude of tensile strain at both axes will stabilize rhombohedra domain, instead of the orthorhombic or tetragonal domains at
higher temperatures at the same strain. Orthorhombic domains will be stable at relatively larger strains along both axes, for example, $O_{12}$ domain will be stable when 1% strains are applied along both x and y axes, and a compressive strain larger than 1% along x or y axis will stabilize $O_{13}$ or $O_{23}$ domains. There also exist the binary or ternary phase regions at the boundaries of this single phase areas.

### 3.3 Summary

In summary, the misfit strain - misfit strain phase/domain stability diagram was constructed for BaTiO$_3$ thin films at room temperature using both thermodynamic calculations and phase-field simulations. It is expected that such diagrams will provide guidance for interpreting experimental measurements and observations as well as to the design of BaTiO$_3$ films with specified domain structures.
Figure 3.1 Misfit strain – misfit strain diagram of BaTiO$_3$ thin films at $T=25^\circ$C obtained by thermodynamic calculations.
Figure 3.2 Misfit strain-misfit strain domain stability diagram for BaTiO$_3$ thin films at $T=25^\circ$C: The black lines are the phase boundaries from the phase-field simulations and the red lines are the ones from the thermodynamic calculations and the same as shown in Figure 3.1.
Figure 3.3 Typical domain structures of single phase in BaTiO$_3$ thin films at $T=25^\circ$C: (a) Tetragonal $c$ domains at $e_{s1}=e_{s2}=-0.010$ (b) Tetragonal $a_1$ domains at $e_{s1}=0.015$ and $e_{s2}=-0.010$; (c) Orthorhombic $O_{12}$ domains at $e_{s1}=e_{s2}=0.015$; (d) Orthorhombic $O_{23}$ domains at $e_{s1}=-0.015$ and $e_{s2}=0.005$. 
Figure 3.4 Typical multidomain structures in BaTiO$_3$ thin films at $T=25^\circ$C: (a) Tetragonal $a_2 +$ Orthorhombic $O_{12}$ domains at $e_{s1}=0.00125$ and $e_{s2}=0.010$ (b) Tetragonal $a_1 +$ Orthorhombic $O_{13}$ domains at $e_{s1}=0.00875$ and $e_{s2}=-0.010$; (c) Tetragonal $c +$ Orthorhombic $O_{23}$ domains at $e_{s1}=-0.0125$ and $e_{s2}=-0.00125$; (d) Tetragonal $a_1+a_2 +$ Orthorhombic $O_{12}$ domains at $e_{s1}=e_{s2}=0.002$; (e) Tetragonal $c +$ Tetragonal $a_2 +$ Orthorhombic $O_{23}$ domains at $e_{s1}=-0.00375$ and $e_{s2}=0.00125$ (f) Multidomain structure containing all the above domains at $e_{s1}=e_{s2}=0.0005$. 
Figure 3.5 Misfit strain-misfit strain domain stability diagram for BaTiO$_3$ thin films at $T=100^\circ$C from phase-field simulations.
Figure 3.6 Typical multidomain structures in BaTiO$_3$ thin films at $T=100^\circ$C: (a) Tetragonal $a_1 +$ Tetragonal $c$ domains at $e_{s1}=0.0025$ and $e_{s2}=0.005$ (b) Tetragonal $a_2 +$ Tetragonal $c$ domains at $e_{s1}=0.005$ and $e_{s2}=0.0025$; (c) Tetragonal $a_2 +$ Orthorhombic $O_{23}$ domains at $e_{s1}=-0.015$ and $e_{s2}=-0.01$; (d) Tetragonal $a_1 +$ Orthorhombic $O_{12}$ domains at $e_{s1}=0.015$, $e_{s2}=0.005$. 
Figure 3.7 Misfit strain-misfit strain domain stability diagram for BaTiO$_3$ thin films at $T=0K$ from phase-field simulations.
References


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[20] \( a_1 = 4.124(T-115) \times 10^5 \), \( a_{11} = -2.097 \times 10^8 \), \( a_{12} = 7.974 \times 10^8 \), \( a_{111} = 1.294 \times 10^9 \), \( a_{112} = -1.950 \times 10^9 \), \( a_{123} = -2.500 \times 10^9 \), \( a_{1111} = 3.863 \times 10^{10} \), \( a_{1112} = 2.529 \times 10^{10} \), \( a_{1122} = 1.637 \times 10^{10} \), \( a_{1123} = 1.367 \times 10^{10} \), \( c_{11} = 1.78 \times 10^{11} \), \( c_{12} = 0.964 \times 10^{11} \), \( c_{44} = 1.22 \times 10^{11} \), \( Q_{11} = 0.10 \), \( Q_{12} = -0.034 \), \( Q_{44} = 0.029 \) in SI units and \( T \) in °C.


Chapter 4 A modified Landau-Devonshire thermodynamic potential for bulk Strontium Titanate

4.1 Introduction

SrTiO$_3$ has received considerable interest due to its low temperature properties, such as high dielectric constants and low microwave losses, as well as its room temperature electronic applications.[1] Bulk SrTiO$_3$ is an incipient ferroelectric in its pure, unstressed form and it is also well established that bulk SrTiO$_3$ crystals undergo a cubic to tetragonal antiferrodistortive (AFD) transition at 105 K in a stress free state, which is associated with staggered rotations of the TiO$_6$ octahedra around one of the cubic axes.[2-5] It has been predicted [6-10] and experimentally verified [10-15] that strain can induce room temperature ferroelectricity in SrTiO$_3$ thin films.

Both ferroelectric and AFD domain stabilities in strained SrTiO$_3$ thin films have been investigated extensively using Landau-Devonshire thermodynamic theory,[6,7,9,10] where the spontaneous polarization $\mathbf{p}=(p_1,p_2,p_3)$ and the structural order parameter $\mathbf{q}=(q_1,q_2,q_3)$ are chosen as the order parameters to describe the ferroelectric transition and the AFD transition, respectively. The structural order parameter $\mathbf{q}$ is related to the linear oxygen displacement that corresponds to simultaneous out-of-plane rotations of TiO$_6$ oxygen octahedra. The ferroelectric and AFD domain structures of SrTiO$_3$ thin films have also been predicted by the phase-field method.[9-10] In all existing thermodynamic analyses [6,7,9] and phase-field simulations,[9-10] a fourth-order polynomial in the
components of both order parameters is employed to describe the bulk stress-free free energy density \( f_{\text{bulk}}(p_i, q_i) \):

\[
f_{\text{bulk}}(p_i, q_i) = \alpha_i \left( p_i^2 + p_2^2 + p_3^2 \right) + \alpha_{12} \left( p_i^4 + p_2^4 + p_3^4 \right) + \alpha_{12} \left( p_i^2 p_2^2 + p_i^2 p_3^2 + p_2^2 p_3^2 \right) \\
+ \beta_i \left( q_i^2 + q_2^2 + q_3^2 \right) + \beta_{12} \left( q_i^4 + q_2^4 + q_3^4 \right) + \beta_{12} \left( q_i^2 q_2^2 + q_i^2 q_3^2 + q_2^2 q_3^2 \right) \\
- t_{11} \left( p_i^2 q_i^2 + p_2^2 q_2^2 + p_3^2 q_3^2 \right) - t_{12} \left[ p_i^2 (q_2^2 + q_3^2) + p_2^2 (q_1^2 + q_3^2) + p_3^2 (q_1^2 + q_2^2) \right] \\
- t_{44} (p_1 p_2 q_1 q_2 + p_2 p_3 q_2 q_3 + p_3 p_1 q_3 q_1),
\]

where \( \alpha_i \) and \( \beta_i \) are the Landau coefficients and \( t_{ij} \) is the coupling coefficient between \( p \) and \( q \). All these coefficients are assumed to be constant except \( \alpha_i \) and \( \beta_i \), which depend on temperature. The range in the reported bulk properties and in the Landau energy coefficients leads, however, to significantly different predictions of domain states, and thus different domain structures, under biaxial tensile strain. For example, the uncertainty of the fourth-order coefficient \( \alpha_{12} \) in Eq. (1) will result in two completely different polar states under tensile strains. An \( \alpha_{12} \) value of \( 5.5 \times 10^{-12} \text{ cm}^6 \text{ dyne/ esu}^4 \) (the average of the experimental value, \( \alpha_{12} = 9.28 \) at \( T=8 \text{ K} \)) and the value used in a previous calculation\([7] \) \( \alpha_{12} = 1.7 \) (both in cgs units \( 10^{-12} \text{ cm}^6 \text{ dyne/ esu}^4 \) ) favors the ferroelectric polarization along pseudocubic (the meaning of the subscript \( p \) ) \([010]_p/ [100]_p \).\([9] \) A smaller value, e.g., \( \alpha_{12} = 1.7 \)\([7,9] \) or \( 1.5 \)\([6] \) stabilizes a ferroelectric polarization along \([110]_p/ [1\bar{1}0]_p \).

To find the appropriate \( \alpha_{12} \) value, we compared the simulation results using two existing \( \alpha_{12} \) values with available experimental measurements of polarization directions.
Optical second harmonic generation (SHG) measurements demonstrated that a 500 Å thick (001) SrTiO₃ thin film grown on (110)-oriented DyScO₃ substrate with biaxial strain $e_{s1}=e_{s2}=0.94\%$[12] ($e_{s1}$ stands for the misfit strain between the substrate and thin film along the [100]$_p$ axis while $e_{s2}$ is along the [010]$_p$ axis) exhibited a $[1\overline{1}0]_p/[1\overline{1}0]_p$ polar state, which is consistent with both thermodynamic calculations[6,7] and phase-field simulations[9] using $\alpha_{12}=1.7$ or 1.5. The $[1\overline{1}0]_p/[1\overline{1}0]_p$ polar state, an orthorhombic $Amm2$ structure, also agrees with first-principle calculations[8] for SrTiO₃ under biaxial tensile strain. In contrast, samples with anisotropic in-plane strains, (001) SrTiO₃ grown on (110) DyScO₃[10] ($e_{s1}=1.03\%, e_{s2}=1.06\%$) and (001) SrTiO₃ grown on (110) GdScO₃ [15] ($e_{s1}=1.46\%, e_{s2}=1.59\%$) develop ferroelectric polarization along both in-plane [010]$_p$ and [100]$_p$ axes, leading to domain twinning at lower temperatures. To be consistent with these experimental findings $\alpha_{12}=5.5$ should be employed [10] instead of 1.7 or 1.5 in order to produce the $[010]_p/[100]_p$ polar states in these two asymmetrically strained films. Since none of the reported $\alpha_{12}$ values can reproduce experimental observations under the different strains, an accurate prediction of the polar states for tensile strained SrTiO₃ thin films requires a more precise value of $\alpha_{12}$ in the Landau-Devonshire potential (Eq.(1)).

From these simulations it is obvious that the coefficient $\alpha_{12}$ affects the relative thermodynamic stability of the $[110]_p$ and $[100]_p$ polar states under a biaxial tensile strain and polarization values. In the early electric-field induced Raman scattering measurement [16], the value of $\alpha_{12}$ is determined from $\omega_s^\perp$, the measured phonon frequency components perpendicular to an applied electric field along the (001)-direction. This phonon frequency $\omega_s^\perp$ is the only measured physical property to determine $\alpha_{12}$ and
at the same time, $\omega_n^\perp$ is not used to determine other Landau coefficients. Therefore, $\alpha_{12}$ does not affect other physical quantities of SrTiO$_3$ such as Curie temperature, elastic constants, and electrostrictive coefficients. Thus we are able to adjust $\alpha_{12}$ without changing the other parameters to improve the Landau-Devonshire thermodynamic potential for SrTiO$_3$.

In this chapter we obtain the appropriate $\alpha_{12}$ by taking into account the available experimental data and phase-field simulations. We perform a series of simulations repeating the experimental cooling process, from the high temperature paraelectric state to the low temperature ferroelectric state, in three films with different strain states. In all these simulations we vary $\alpha_{12}$ from 1.7 to 5.5, while fixing all other input parameters. After examining the transition temperatures and polarization states as a function of different $\alpha_{12}$, we identify the most appropriate $\alpha_{12}$ as that satisfying all the existing experimental observations.

### 4.2 Results and discussions

In the phase-field model of strained pseudocubic (001) SrTiO$_3$ thin films, the temporal and spatial evolutions of the two order parameters $p$ and $q$ are governed by the three dimensional time dependent Ginzburg-Landau equations:[9]

\[
\frac{\partial p_i(x,t)}{\partial t} = -L_{p_i} \frac{\delta F}{\delta p_i(x,t)}, i = 1,2,3, \tag{4.2}
\]

\[
\frac{\partial q_i(x,t)}{\partial t} = -L_{q_i} \frac{\delta F}{\delta q_i(x,t)}, i = 1,2,3, \tag{4.3}
\]
where $L_p$ and $L_q$ are the kinetic coefficients related to the ferroelectric and ferroelastic domain mobilities, respectively. $F$ is the total free energy, including the bulk free energy, elastic deformation energy, electrostatic energy, and domain wall energy, i.e.,

$$F = \int_V \left[ f_{\text{bulk}}(p_i,q_i) + f_{\text{elas}}(p_i,q_i,\varepsilon_i) + f_{\text{grad}}(p_{i,j},q_{i,j}) + f_{\text{elec}}(p_i,E_i) \right] dV \quad (4.4)$$

where $f_{\text{bulk}}(p_i,q_i)$ is in the same form as Eq.(4.1). The calculation details of $f_{\text{elas}}(p_i,q_i,\varepsilon_i)$, $f_{\text{grad}}(p_{i,j},q_{i,j})$, and $f_{\text{elec}}(p_i,E_i)$ are addressed in Refs. 9,17-18.

In this work, a (001)-oriented SrTiO$_3$ thin film on an orthorhombic substrate is considered. A rectangular coordinate system, $x=(x_1, x_2, x_3)$ is set up with the $x_1$, $x_2$ and $x_3$ axes along the [100], [010], and [001]$_p$ directions, respectively. The average film/substrate misfit strains $\varepsilon_{x_1} = \vec{\varepsilon}_{11}$ and $\varepsilon_{x_2} = \vec{\varepsilon}_{22}$ are along the in-plane $x_1$ and $x_2$ axes, respectively. Periodic boundary conditions were applied along the $x_1$ and $x_2$ axes. We took a $128\Delta x \times 128\Delta x \times 40\Delta x$ model size where $\Delta x$ is the grid spacing. The thickness of the film is $25\Delta x$. The kinetic coefficient in Eq. (4.2) is taken as $L_q/L_p=180$. The gradient energy coefficient is taken to be $G_q/G_p=0.012$ and $G_p/G_0=0.4$, where $G_0$ is related to the magnitude of $\Delta x$ through $\Delta x = \sqrt{G_0/\alpha_0}$ and $\alpha_0 = |\alpha_1|$. The corresponding ferroelectric domain wall thickness is about $1.5\Delta x$. Short-circuit boundary conditions were employed to calculate the dipole-dipole interactions. The initial polarization field is created by assigning a zero value at each cell modified by a small random noise. The material constants used in the simulation are from the literature [6,7,9,19] and listed in Ref. 20. These calculations use a background dielectric constant of 10. [21] Each simulation
proceeded for 60000 time steps (a normalized time step is 0.05) until the order parameter distributions achieved steadiness.

The transition temperatures and corresponding stable ferroelectric polarization states as a function of $\alpha_{12}$ determined from our simulations are summarized in Figures 4.1-4.3 for the three different strains. For symmetric strain $e_{s1}=e_{s2}=0.94\%$ (Figure 4.1), there are two transition temperatures on cooling from room temperature: $T_c$ stands for the paraelectric-to-ferroelectric transition temperature and $T_{AFD}$ for the structural transition temperature. The stable ferroelectric polarization directions corresponding to different $\alpha_{12}$ values and temperatures are labeled on the diagram. The stable AFD domains, which appear at temperatures lower than $T_{AFD}$, are not labeled since they have the same symmetry as earlier formed ferroelectric domains. It can be seen that both $T_c$ and $T_{AFD}$ are nearly independent of $\alpha_{12}$, but the stable direction of the ferroelectric polarization depends strongly on $\alpha_{12}$. Furthermore the $[110]_p/[1\overline{1}0]_p$ ferroelectric state, the experimentally observed state at symmetric strain, can be obtained by using $\alpha_{12}$ values from 1.7 to as large as 5.0. The $[100]_p/[010]_p$ polar states were predicted with $\alpha_{12}$ values between 5.2 and 6.0, while values between 5.0 and 5.2 resulted in a mixture of the two phases.

For the other two anisotropically strained SrTiO$_3$ thin films ($e_{s1}=1.03\%, e_{s2}=1.06\%$ in Figure 4.2 and $e_{s1}=1.46\%, e_{s2}=1.59\%$ in Figure 4.3), there are three transition temperatures due to strain anisotropy. On cooling from room temperature, the first ferroelectric transition ($T_{c1}$) corresponds to the development of a polarization along the longer in-plane direction (i.e., the higher strain axis, here [010]) while the lowest
transition temperature ($T_{AFD}$) corresponds to the AFD transition. The intermediate transition temperature ($T_{c2}$) produces either twinning from a single variant [010]$_p$ to [010]$_p$/[100]$_p$ domain structure (with a large $\alpha_{12}$ such as 5.5) or rotation from [010]$_p$ to the [110]$_p$ direction (with smaller $\alpha_{12}$ values such as 1.7). Strictly speaking, the [010]$_p$ to [110]$_p$ transition should be divided into two stages, corresponding to the two intermediate transition temperatures: $T_{c2}$ for the beginning of the transition while the pure [110]$_p$ domain will not form until the temperature is below $T_{c2}'$, as labeled in Figures 4.2 and 4.3. As shown in Figures 4.2 and 4.3, an $\alpha_{12}$ value larger than 4.7 is sufficient to stabilize the [010]$_p$/[100]$_p$ twin structure, in agreement with experimental observations in these two films.
Figure 4.1 Predicted transition temperatures and directions of the spontaneous polarization as a function of $\alpha_{12}$ for SrTiO$_3$ thin films deposited onto (110) DyScO$_3$ substrates under a symmetric strain of $e_{s1} = e_{s2} = 0.94\%$. 
Figure 4.2 Predicted transition temperatures and directions of the spontaneous polarization as a function of $\alpha_{12}$ for SrTiO$_3$ thin film deposited onto (110) DyScO$_3$ substrates under asymmetric biaxial strains of $e_{s1} = 1.03\%$ and $e_{s2} = 1.06\%$.
Figure 4.3 Predicted transition temperatures and directions of the spontaneous polarization as a function of $\alpha_{12}$ for SrTiO$_3$ thin film deposited onto (110) GdScO$_3$ substrates under the asymmetric strains of $e_{s1}=1.46\%$ and $e_{s2}=1.59\%$. 
After examining the transition temperatures and polarization states as a function of $\alpha_{12}$ shown in Figures 4.1~4.3, we found that the polarization states predicted from $\alpha_{12}$ values between 4.7 and 5.0 are consistent with all of these recent experiments. An average of $4.85 \times 10^{-12}$ cm$^6$ dyn/esu$^4$ is then chosen for $\alpha_{12}$ and the transition temperatures determined from this updated $\alpha_{12}$ are summarized in Table 4.1 together with experimental measurements. The predicted ferroelectric and AFD domain stabilities are in reasonable agreement with experiments, although the transition temperatures from phase-field simulations are always lower than those measured. Such discrepancies likely arise from the uncertainties in the electrostriction and thermal expansion coefficients used in the modeling as well as the relaxor character of the films.[22]

4.3 Summary

In summary, we report an improved coefficient $\alpha_{12}$ in the Landau-Devonshire thermodynamic potential for SrTiO$_3$ utilizing recent experimental data and phase-field simulations. The transition temperatures and ferroelectric/AFD domain stabilities predicted from this modified potential agree well with experimental measurements. It is expected this modified potential will stimulate future experimental measurements of $\alpha_{12}$ and lead to a better understanding of the ferroelectric/AFD domain stabilities in SrTiO$_3$ thin films.
Table 4.1 Predicted transition temperatures of SrTiO$_3$ thin films under the same biaxial strain states utilized in experiments from phase-field simulations using $\alpha_{12} = 4.85 \times 10^{-12}$ cm$^6$ dyn/esu$^4$.

<table>
<thead>
<tr>
<th></th>
<th>$e_{s1} = e_{s2} = 0.94%$</th>
<th>$e_{s1} = 1.03%, e_{s2} = 1.06%$</th>
<th>$e_{s1} = 1.46%, e_{s2} = 1.59%$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experiment</strong></td>
<td>This work</td>
<td>Experiment$^c$</td>
<td>Experiment$^d$</td>
</tr>
<tr>
<td>$T_c$</td>
<td>~260 K</td>
<td>215 K</td>
<td>310 K</td>
</tr>
<tr>
<td></td>
<td>(0, $p_z$, 0)</td>
<td>(0, $p_z$, 0)</td>
<td>(0, $p_z$, 0)</td>
</tr>
<tr>
<td></td>
<td>213 K</td>
<td>210 K</td>
<td>210 K</td>
</tr>
<tr>
<td>($p_1$, $p_z$, 0)</td>
<td>~210 K</td>
<td>($p_1$, 0, 0) + ($0$, $p_z$, 0)</td>
<td>($p_1$, 0, 0) + ($0$, $p_z$, 0)</td>
</tr>
<tr>
<td>$T_{AFD}$</td>
<td>~213 K</td>
<td>~160 K</td>
<td>~150 - 175 K</td>
</tr>
<tr>
<td></td>
<td>($q_1$, $q_z$, 0)</td>
<td>($q_2$, 0, 0) + ($q_z$, 0)</td>
<td>($q_2$, 0, 0) + ($q_z$, 0)</td>
</tr>
</tbody>
</table>

$^a$From Ref. 12

$^b$From Ref. 14

$^c$From Ref. 10

$^d$From Ref. 15
References

[20] Materials constants for SrTiO$_3$ (except $\alpha_{12}$):

\[ \alpha_i = 4.5 \times 10^{-3} \left[ \coth(54 / T) - \coth(54 / 30) \right], \alpha_{11} = 2.1 \times 10^{-12}, \]

\[ \beta_i = 1.32 \times 10^{26} \left[ \coth(145 / T) - \coth(145 / 105) \right], \beta_{11} = 1.69 \times 10^{43}, \beta_{12} = 3.88 \times 10^{43}, \]

\[ Q_{11} = 5.09 \times 10^{-13}, Q_{12} = -1.50 \times 10^{-13}, Q_{44} = 1.065 \times 10^{-13}, \Lambda_{11} = 8.7 \times 10^{14}, \]

\[ \Lambda_{12} = -7.8 \times 10^{14}, \Lambda_{44} = -9.2 \times 10^{14}, c_{11} = 3.36 \times 10^{12}, c_{12} = 1.07 \times 10^{12}, \]

\[ c_{44} = 1.27 \times 10^{12}, t_{11} = -1.94 \times 10^{15}, t_{12} = -0.84 \times 10^{15}, t_{44} = 6.51 \times 10^{15} \text{ (in cgs units and } T \text{ in K).} \]


Chapter 5 Phase transitions and domain stabilities in epitaxial (001) SrTiO$_3$ thin films

5.1 Introduction

As introduced in the last chapter, SrTiO$_3$ is an incipient ferroelectric in its pure, unstressed form but has a ferroelectric instability manifested by its large dielectric constants at low temperature.[1] It is also well established that bulk SrTiO$_3$ crystals undergo a cubic to tetragonal antiferrodistortive (AFD) transition at 105 K in a stress free state, which is associated with staggered rotations of the TiO$_6$ octahedra around one of the cubic axes.[2-5] The properties of SrTiO$_3$ are extremely sensitive to dopants and external perturbations. Ferroelectricity can be induced as a result of small concentrations of dopants,[6] isotopic substitutions in the oxygen octahedra,[7] or mechanical pressure.[8-9] The development of thin film technologies has provided additional ways of inducing ferroelectricity in SrTiO$_3$ films. Significant enhancement of Curie temperatures ($T_c$) induced by in-plane misfit strain in SrTiO$_3$ thin films was experimentally achieved [10-15] and theoretically predicted by thermodynamic calculations [15-17] and first-principles calculations.[18] The “misfit strain - temperature” domain stability diagrams predicted by thermodynamics [15-17] exhibit various ferroelectric and antiferrodistortive phases, depending on both temperature and misfit strain. However, all the published diagrams from thermodynamic analysis [15-17] are determined by minimizing the Helmholtz free energy density in terms of temperature, polarization, and AFD structural order parameter under a single domain assumption. During a structural or ferroelectric phase transition, it is inevitable that multiple domains or heterophase structures form due
to the degeneracy of domain states and the release of strain energy. Moreover, the variations in the reported values of bulk properties and the Landau energy coefficients from different literature sources led not only to a wide range of possible transition temperatures at a given strain, but also to different ferroelectric states thus different stability diagrams.

In chapter 4, a modified Landau-Devonshire thermodynamic potential for SrTiO$_3$ is developed,[19] which made it possible to fully understand the existing experimental observations of ferroelectric/AFD states in epitaxial SrTiO$_3$ thin films.[12-15] In the past decade, phase-field model has been applied to predicting domain stability, structure, and evolution in a number of ferroelectric thin film systems under various mechanical and electrical boundary conditions.[20-24] For SrTiO$_3$ thin films, both the ferroelectric and AFD domain morphologies at a number of specific temperature and strain states were also predicted using phase-field method.[17] However, a complete domain stability diagram taking into consideration of multiphase and multi-domain is still lacking. Thus in the present work, we first construct a “misfit strain - temperature” domain stability diagram for the equi-biaxially strained (001) SrTiO$_3$ thin films using phase-field method and compare it with previous diagrams determined from thermodynamics[15-17] and first-principles.[18,25] Then we extend the model to study the domain stabilities under unequi-biaxial strains, corresponding to the cases of SrTiO$_3$ thin films grown on orthorhombic substrates like DyScO$_3$[12] and GdScO$_3$.[13] Isothermal misfit strain diagrams, i.e., the “misfit strain - misfit strain” stability diagrams at several representative temperatures are presented. Finally, we demonstrate the predicted phase transitions, domain stabilities, and domain morphologies of three SrTiO$_3$ thin films grown on
different substrates with either equi-biaxial or unequi-biaxial strain states that have been studied experimentally. It can be seen that the predicted phase transitions and domain states in all three available SrTiO$_3$ thin films agree very well with all the experimental observations.

5.2 Simulation details

In the phase-field model of strained pseudocubic (001) SrTiO$_3$ thin film, the spontaneous polarization $\mathbf{p} = (p_1, p_2, p_3)$ and the structural order parameter $\mathbf{q} = (q_1, q_2, q_3)$ are chosen as the order parameters to describe a proper ferroelectric transition and an AFD transition, respectively. The structural order parameter $\mathbf{q}$ is related to the linear oxygen displacement that corresponds to the simultaneous out-of-plane rotation of the TiO$_6$ octahedra around one of the fourfold symmetry axes. The temporal and spatial evolutions of the two order parameters $\mathbf{p}$ and $\mathbf{q}$ are governed by the time dependent Ginzburg-Landau equations:

$$\frac{\partial p_i(x,t)}{\partial t} = -L_p \frac{\delta F}{\delta p_i(x,t)}, i = 1,2,3, \quad (5.1)$$

$$\frac{\partial q_i(x,t)}{\partial t} = -L_q \frac{\delta F}{\delta q_i(x,t)}, i = 1,2,3, \quad (5.2)$$

where $L_p$ and $L_q$ are the kinetic coefficients related to the domain mobilities of $\mathbf{p}$ and $\mathbf{q}$, respectively. The total free energy $F$ includes the bulk free energy, elastic deformation energy, domain wall energy, and electrostatic energy, i.e.

$$F = \iiint \left[ f_{\text{bulk}}(p_i,q_i) + f_{\text{elas}}(p_i,q_i,\varepsilon_y) + f_{\text{wall}}(p_{i,j},q_{i,j}) + f_{\text{elec}}(p_i,E_i) \right] d^3x, \quad (5.3)$$
where $V$ is the volume of the film and $d^3x = dx_1 \, dx_2 \, dx_3$. A fourth-order polynomial in the components of both order parameters is employed to describe the bulk free energy density $f_{\text{bulk}}(p_i, q_i)$ \cite{16,17} under the stress-free condition:

\[
f_{\text{bulk}}(p_i, q_i) = \alpha_i \left( p_i^4 + p_i^2 q_i^2 + q_i^4 \right) + \beta_i \left( p_i^2 + q_i^2 \right) + \gamma_{i1} \left( p_i q_i \right) + \tilde{\gamma}_{i1} \left( q_i \right) + \gamma_{i2} \left( p_i^3 + q_i^3 \right) + \gamma_{i3} \left( p_i^2 q_i + q_i^2 p_i \right) + \gamma_{i4} \left( q_i^2 q_i + p_i q_i + q_i p_i \right)
\]

where $\alpha_i$, $\beta_i$, are the Landau coefficients and $t_{ij}$ is the coupling coefficient of $p$ and $q$.

In a biaxially strained SrTiO$_3$ film, the elastic energy density with the formation of the ferroelectric and/or AFD domain is given by

\[
f_{\text{elas}}(p_i, q_i, \varepsilon_{ij}) = \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} = \frac{1}{2} c_{ijkl} (\varepsilon_{ij} - \varepsilon_{ij}^0)(\varepsilon_{kl} - \varepsilon_{kl}^0),
\]

where $c_{ijkl}$ is the elastic stiffness tensor, $\varepsilon_{ij}$ is the elastic strain, $\varepsilon_{ij}^0$ is the stress free strain as a result of ferroelectric and AFD transitions:

\[
\varepsilon_{ij}^0 = Q_{ijkl} p_k p_l + \Lambda_{ijkl} q_k q_l + \varepsilon_{ij}^0 + \varepsilon_{ij},
\]

where $Q_{ijkl}$ is the electrostrictive coefficient representing the coupling between the strain and polarization, and $\Lambda_{ijkl}$ is the linear-quadratic coupling coefficient between strain and structural order parameter. $\varepsilon_{ij} = \varepsilon_{ij} + \varepsilon_{ij}^0$ is the total strain. Here both $\varepsilon_{ij}$ and $\varepsilon_{ij}^0$ are defined using the pseudocubic phase as the reference. The details of the calculation of the total strain $\varepsilon_{ij}$ in a (001)-oriented film under biaxial in-plane strains are described in Ref. 20.
The domain wall energy is calculated through

\[
f_{\text{grad}}(p_{i,j}, q_{i,j}) = \frac{1}{2}(G_p p_{i,j} p_{i,j} + G_q q_{i,j} q_{i,j}), \tag{5.7}
\]

where \( G_p \) and \( G_q \) are the domain wall energy coefficients and \( p_{i,j} = \partial p_i / \partial x_j \), \( q_{i,j} = \partial q_i / \partial x_j \).

The electrostatic energy \( f_{\text{elec}}(p_i, E_i) \), induced by spatially inhomogeneous spontaneous polarizations, is calculated by \[26\]

\[
f_{\text{elec}}(p_i, E_i) = -\frac{\varepsilon_0 \kappa_{ij}}{2} E_i E_j - E_i p_i, \tag{5.8}
\]

where \( E_i \) is the electric field component. In the absence of an external electric field,

\[
f_{\text{elec}}(p_i, E_i) = -\frac{1}{2} E_i p_i, \tag{5.9}
\]

which is essentially the depolarization energy within an inhomogeneous domain structures due to the presence of domain walls, assuming that the top and bottom surfaces are charge-compensated and thus the depolarization energy due to the average polarization within the crystal is assumed to be zero. The electric displacement \( D_i \) is related to the electric field as

\[
D_i = \varepsilon_0 \kappa_{ij} E_j + p_i, \tag{5.10}
\]

where \( \kappa_{ij} \) is the relative dielectric permittivity of the film and was suggested to take the value of its paraelectric background.\[27,28\] Here we assume isotropic dielectricity, i.e., \( \kappa = \kappa_{11} = \kappa_{22} = \kappa_{33} \) and \( \kappa_{ij} = 0(i \neq j) \).
For the short-circuit boundary condition, we have \( \phi_1 = \phi_2 = \phi_0 \), if the electric potential \( \phi \) is specified as \( \phi_1 \) on the film bottom surface and as \( \phi_2 \) on the top surface, and

\[
E_i = -\phi_i ,
\]

(5.11)

The electrostatic potential can be obtained by solving the following electrostatic equilibrium equation:

\[
D_{ij} = 0 \text{ , or } \quad \varepsilon_\text{eff} \kappa (\phi_{11} + \phi_{22} + \phi_{33}) = p_{1,1} + p_{2,2} + p_{3,3}. \]

(5.12a)

Equation (5.12) is numerically solved under the described boundary conditions. Consequently, the electrostatic energy (the depolarization energy) can be obtained.

In this work, a (001)-oriented SrTiO_3 thin film on an orthorhombic substrate is considered. A rectangular coordinate system, \( \mathbf{x}=(x_1, x_2, x_3) \) is set up with the \( x_1, x_2 \) and \( x_3 \) axes along the [100], [010] and [001] crystallographic directions, respectively. The average film/substrate misfit strains \( \varepsilon_{11} = \varepsilon_{22} \) and \( \varepsilon_{22} = \varepsilon_{33} \) are along the in-plane \( x_1 \) and \( x_2 \) axes, respectively. Periodic boundary conditions were applied along the \( x_1 \) and \( x_2 \) axes. A model size of \( 256 \Delta x \times 256 \Delta x \times 36 \Delta x \) is used with \( \Delta x \) being the grid spacing. The thickness of the film is \( 20 \Delta x \). The kinetic coefficient in equation (1) is taken as \( L_q/L_p=180 \). The gradient energy coefficients \( G_q/G_p=0.012 \) and \( G_p/G_0=0.4 \) where \( G_0 \) is related to the magnitude of \( \Delta x \) through \( \Delta x = \sqrt{G_0/\alpha_0} \) and \( \alpha_0 = |\alpha| \). The short-circuit boundary condition is employed to calculate the dipole-dipole interactions. We performed a series of simulations under different biaxial strains to investigate the domain stabilities under either equi-biaxial or unequi-biaxial strain states. To study the effect of
depolarization field on the Curie temperature, we compare the simulation results using two very different relative dielectric constants: $\kappa=1000$ (simulating the case of nearly compensated domain walls by unspecified free charges) [17] and a background dielectric constant $\kappa=10$. [27] The initial polarization and structural order parameter distributions are created by assigning a zero value at each grid plus a small random noise. The material constants used in the simulation are collected from literature [16,17,19,29] and listed in Ref 30. Each simulation proceeded for 60000 time steps or longer (normalized time step is 0.05) until the polarization and/or structure order parameter distributions achieved steadiness.

5.3 Results and discussions

Based on the simulations conducted at equi-biaxial strain state $e_{11}=e_{22}$ ranging from -2% to 2%, we constructed the “misfit strain - temperature” domain stability diagram for (001) SrTiO$_3$ thin films, as shown in Figure 5.1. Only nonzero components of polarizations and AFD structural order parameters of the stable phases are labeled in the corresponding regions. For example, $q_1+q_2$ represents tetragonal $(q_1,0,0)+(0,q_2,0)$ AFD domain, $p_1p_2$ the orthorhombic $(p_1,p_2,0)$ ferroelectric domain, and $(p_1,q_2+p_2,q_1)$ the coexistence of both ferroelectric $(p_1,0,0)+(0,p_2,0)$ and AFD $(q_1,0,0)+(0,q_2,0)$ domains.

We examined the effect of the dielectric constant on the predicted Curie temperatures ($T_c$). It is found there is no significant change of the predicted $T_c$ under tensile strains using different dielectric constants as the polarizations are always developed in-plane thus no depolarization field is generated perpendicular to the film surfaces. While under compressive strains, the $T_c$ predicted from $\kappa=10$ (the dashed line) is about 30~50K lower than that from a higher dielectric constant $\kappa=1000$, due to the relatively large
Figure 5.1 Misfit strain - temperature domain stability diagram of (100)p-oriented SrTiO$_3$ thin films. The black dot indicates the experimental strain $e_{s1}=e_{s2}=0.94\%$. 


depolarization field, which will compensate the out of plane polarization to reduce the $T_c$.

Although the predicted strain dependent transition temperatures assuming $\kappa=1000$ are similar to the results from thermodynamic predictions which entirely ignored the depolarization field,[16-17] significant differences exist on the predicted domain stabilities. Firstly, the current diagram suggests SrTiO$_3$ is not ferroelectric under zero strain condition down to the ground state (0K), which is consistent with both established theories[1,31] and experiments.[1,31,32] Secondly, it is demonstrated that at relatively small tensile strain and low temperature, both polarizations and AFD structural order parameters develop along the pseudocubic [100]$_p$/[010]$_p$ (subscript $p$ means “pseudocubic”) in-plane axes, i.e., a ferroelastic ($q_1+q_2$) or ferroelectric ($p_1q_2+p_2q_1$) twin structure. As the strain magnitude increases, there is a rotation from [100]$_p$/[010]$_p$ to [110]$_p$/[1-10]$_p$ for both polarization and AFD structure order parameters, indicating a transition from $p_1q_2+p_2q_1$ domain state to $p_1p_2,q_1q_2$ state, as shown in the diagram. This symmetry dependency on strain is also predicted by both thermodynamics[16] and first-principles calculations.[25] In this work, the critical strain separated this two phase regions is around 0.3% at 0K, which is between the values from thermodynamics[16] (0.1%) and first-principles[25] (0.442%). Moreover, the diagram from thermodynamic analysis using an earlier Landau-Devonshire potential [16] demonstrated that a very small compressive strain between -0.022% and -0.05% stabilizes ($p_1p_2$, $q_3$) phase, i.e., the coupling of ferroelectric $p_1p_2$ phase and AFD $q_3$ phase, when temperature is lower than 30K. Our thermodynamic calculation using the updated potential obtained a similar phase stability in this narrow region, however, phase-field simulations showed that only AFD $q_3$ phase is stable. (Figure 5.1)
In an earlier experimental study, both optical second harmonic generation (SHG) and confocal scanning optical microscopy (CSOM) measurements demonstrated that a 500 Å thick (001) SrTiO$_3$ thin film on an (101)-oriented DyScO$_3$ substrate with biaxial strain $e_{s1}=e_{s2}=0.94\%$ [12,17] exhibits a [110]$_p/[1-10]_p$ polar state, which is consistent with our phase diagram. To further compare with experiments, the ferroelectric and AFD structural domain morphologies of SrTiO$_3$ thin film at $e_{s1}=e_{s2}=0.94\%$ and $T=100$K are shown in Figure 5.2. The four colors used to depict the films in Figure 5.2 (a) and (b) represent the four [110]$_p$ variants. The directions of the corresponding order parameter vector $\mathbf{p}$ or $\mathbf{q}$ on the variants are shown by the arrows. From the domain morphologies, it is evident that the polarization $\mathbf{p}$ and AFD order parameter $\mathbf{q}$ are always parallel to each other along [110]$_p$ in-plane directions. This [110]$_p/[1-10]_p$ domain state under a large symmetric tensile strain is also consistent with first-principles calculations.[18]

When SrTiO$_3$ thin films are grown on orthorhombic substrates such as DyScO$_3$[12] and GdScO$_3$[13], an unequi-biaxial strain state is generated, which may lead to totally different domain stabilities compared with equi-biaxially strained films. To investigate the domain stabilities under unequi-biaxial strains, we also constructed the “misfit strain - misfit strain” domain stability diagrams at 300K, 200K and 100K, as shown in Figures 5.3(a)~(d). These diagrams reveal a number of unique stable ferroelectric and/or AFD domain phases that could not be stabilized under equi-biaxial strains (Figure 5.1). For example, when there is a sufficiently large tensile strain applied along one axis and a smaller tensile strain along the other axis, the stable polarization and/or AFD structural order parameters are along [100]$_p$ and [010]$_p$ in-plane directions, producing a [100]$_p/[010]_p$ twin structure instead of the [110]$_p/[1-10]_p$ twins as for the equi-biaxial
Figure 5.2 Domain morphologies of SrTiO$_3$ thin films strained at $e_{s1}=e_{s2}=0.94\%$ at 100 K:

(a) ferroelectric domain (b) AFD structure domain.
strain case at the same temperature and magnitude of strain. This important difference in the relative stability of the [110]p/[1-10]p and [100]p/[010]p polar states explains why the prior SHG and CSOM measurements of SrTiO3 films at similar but equi-biaxial strains exhibit polar directions along the pseudocubic [110]p directions while the SHG measurements of asymmetrically strained films shows the [100]p/[010]p polar states.[12,13] Furthermore, if the anisotropy is large enough, the polarization or AFD structure order parameter directions will be along [100]p or [010]p direction only, which is again different from the [100]p/[010]p or [110]p/[1-10]p twin structures, as shown in all the three diagrams. Moreover, the stable regions of the [100]p/[010]p twin structure, i.e., the $p_1+p_2$ or $p_1q_2+p_2q_1$ phase area expands with decreasing temperature, indicating a domain twinning from a single variant [010]p or [100]p to [010]p/[100]p domain structure during a cooling process for the unequi-biaxially strained SrTiO3 thin films. This behavior was also confirmed by SHG measurements in both SrTiO3 thin films grown on DyScO3 [12] and GdScO3 [13], with $e_{s1}=1.03\%$, $e_{s2}=1.06\%$ and $e_{s1}=1.46\%$, $e_{s2}=1.59\%$, respectively. These two experimental strains, as well as the former isotropic case with $e_{s1}=e_{s2}=0.94\%$ are plotted in Figures 5.3(a)–(d) for comparison. On cooling from room temperature, there are three transitions simultaneously for the two unequi-biaxially strained SrTiO3 thin films. The representative domain structures following each of the three transitions are shown in Figure 5.4 ($e_{s1}=1.46\%$, $e_{s2}=1.59\%$) and Figure 5.5 ($e_{s1}=1.03\%$, $e_{s2}=1.06\%$) and the directions of the corresponding order parameter vectors are indicated by the arrows. The first ferroelectric transition corresponds to the development of a polarization along [010] axis (the higher strain axis) which stabilize the pure $p_2$ ferroelectric domain (Figures 4(a) and 5(a)). The intermediate transition
temperature produces the twinning from a single variant \([010]_p\) to \([010]_p/[100]_p\) domain structure (Figures 5.4(b) and 5.5(b)) while the lowest transition temperature corresponds to the AFD transition (Figures.5.4(c, d) and 5.5(c, d)). It is also noticed that the volume fraction of \(p_1\) domain in Figure 5.4(c) is less than that in Figure 5.5(c), indicating the larger magnitude of strain anisotropy for SrTiO\(_3\) thin film on GdScO\(_3\) than DyScO\(_3\). The predicted domain stabilities and structures in this work, as well as the phase transition temperatures reported earlier,[12,19] agree very well with all existing experimental measurements.[11,12,13,17]

5.4 Summary

Phase-field simulations were conducted to study the ferroelectric and antiferrodistortive domain stabilities and structures in strained SrTiO\(_3\) thin films. The obtained “misfit strain - temperature” domain/phase stability diagram exhibits significant difference from previous diagrams obtained by using thermodynamic analysis. The “misfit strain-misfit strain” stability diagrams under several representative temperatures were also constructed. These diagrams revealed the important difference between the stabilities of the \([110]_p/[1-10]_p\) and \([100]_p/[010]_p\) ferroelectric/AFD phases, and thus explained why the experimental measurements of SrTiO\(_3\) films at equi-biaxial strains exhibit \([110]_p\) phase while the equi-biaxially strained films shows the \([100]_p/[010]_p\) polar states. The predicted phase transition temperatures and domain structures of the three SrTiO\(_3\) thin films with either equi-biaxial or unequi-biaxial strains agree well with the available experimental results.
Figure 5.3 Misfit strain-misfit strain domain stability diagram of (001) SrTiO$_3$ films at (a) 300K, (b) enlargement of the square region in (a), (c) 200K, (d) 100K. The strain states for 3 SrTiO$_3$ thin films are plotted with different symbols: $\varepsilon_{s1}=\varepsilon_{s2}=0.94\%$ (●), $\varepsilon_{s1}=1.03\%$, $\varepsilon_{s2}=1.06\%$ (●), $\varepsilon_{s1}=1.46\%$, $\varepsilon_{s2}=1.59\%$ (●)
Figure 5.4 Domain morphologies of SrTiO$_3$ thin films strained at $e_{s1}=1.46\%$, $e_{s2}=1.59\%$: ferroelectric domains at (a) 300K, (b) 200K, (c) 100K and (d) AFD structure domain at 100K.
Figure 5.5 Domain morphologies of SrTiO$_3$ thin films strained at $e_{s1}=1.03\%$, $e_{s2}=1.06\%$: ferroelectric domains at (a) 212K, (b) 200K, (c) 100K and (d) AFD structure domain at 100K.
References


[30] Materials constants for SrTiO₃: \( \alpha_i = 4.5 \times 10^{-3} \left[ \coth \left( \frac{54}{T} \right) - \coth \left( \frac{54}{30} \right) \right] \),

\[
\begin{align*}
\alpha_{11} &= 2.1 \times 10^{-12}, \quad \alpha_{12} = 4.85 \times 10^{-12}, \quad \beta_{11} = 1.69 \times 10^{43}, \quad \beta_{12} = 3.88 \times 10^{43} \\
Q_{11} &= 5.09 \times 10^{-13}, \quad Q_{12} = -1.50 \times 10^{-13}, \quad Q_{44} = 1.065 \times 10^{-13}, \quad \Lambda_{11} = 8.7 \times 10^{14}, \quad \Lambda_{12} = -7.8 \times 10^{14} \\
\Lambda_{44} &= -9.2 \times 10^{14}, \quad c_{11} = 3.36 \times 10^{12}, \quad c_{12} = 1.07 \times 10^{12}, \quad c_{44} = 1.27 \times 10^{12}, \quad t_{11} = -1.94 \times 10^{15} \\
t_{12} &= -0.84 \times 10^{15}, \quad t_{44} = 6.51 \times 10^{15} \text{ (in cgs units and } T \text{ in K).}
\end{align*}
\]


Chapter 6 Phase-field simulation of domain stabilities and switchings in epitaxial (001) BiFeO$_3$ multiferroic thin films

6.1 Introduction

The material we are interested in this Chapter is BiFeO$_3$. There has been considerable interest in developing BiFeO$_3$ magnetoelectric materials recently, which are simultaneously antiferromagnetic and ferroelectric at room temperature [1-3]. Bulk BiFeO$_3$ single crystals have a Curie temperature of $T_C \approx 1103$ K, and a Néel temperature of $T_N \approx 643$ K. The ferroelectric phase of BiFeO$_3$ has a rhombohedrally distorted perovskite structure with space group $R3c$. The spontaneous polarization of BiFeO$_3$ is along the pseudocubic $<111>_c$ crystallographic directions, and hence there are eight possible polarization variants. Recently, large ferroelectric polarizations have been reported in heteroepitaxially constrained thin films of BiFeO$_3$ [1,4,5]. Strong dependence of polarization on film thickness has also been observed in experiments, and a likely explanation is the change of strains with film thickness [1]. However, the substrate strain effect on the spontaneous polarization of BiFeO$_3$ thin films is still unclear. For example, first-principles calculations showed [6,7] that the spontaneous polarization is rather insensitive to substrate strains compared to conventional ferroelectric systems, while a recent thermodynamic calculation showed a strong dependence of spontaneous polarization on substrate strains (film thickness) for (001)$_c$ oriented BiFeO$_3$ thin films [8]. In a recent thermodynamic analysis by Zhang [9,10], the Landau-type thermodynamic theory of ferroelectric thin films are extended to a number of different oriented ((001)$_c$, (101)$_c$, and (111)$_c$) epitaxial BiFeO$_3$ thin films with general substrate strains. The
calculations showed that the substrate effect on ferroelectric polarization of BiFeO$_3$ films depends on the film orientations and the types of substrate strains. For (001) oriented BiFeO$_3$ films, the normal substrate strains only rotate the polarization direction without changing its magnitude. While for (111) and (101) oriented BiFeO$_3$ films, normal substrate strains can alter the magnitude of the spontaneous polarization. The domain stabilities of BiFeO$_3$ thin films are also studied by phase-field method [11] and different domain structures are exhibited depending on both magnitude and sign of the misfit strains. However, all the existing thermodynamic calculations and phase-field simulations are limited in a relatively small magnitude of strains (-2% to 2%), and a complete strain – temperature domain stability diagram is still lacking.

Recently, a strain-driven morphotropic phase boundary was observed in (001) BiFeO$_3$ thin film deposited on YAlO$_3$ (YAO) and LaAlO$_3$ (LAO) substrates. [12] Figure 6.1 is the SHG and AFM measurements of the phase fractions of the Tetragonal (T) phase and distorted rhombohedral (R) phase in these two films. Both measurements demonstrate that the tetragonal phase will be stabilized in BiFeO$_3$ thin films grown on LaAlO$_3$ and YAlO$_3$ with -4.29% and -6.8% compressive strains, respectively. This strain motivated distorted rhombohedral phase to tetragonal phase transition, or strain - driven morphotropic phase boundary is fundamentally distinguishable from the composition dependent morphotropic phase boundary [13-16] in Pb(Zr$_x$Ti$_{1-x}$)O$_3$ (PZT), Pb(Mg$_{0.33}$Nb$_{0.67}$)O$_3$-PbTiO$_3$ (PMN-PT), and Pb(Zn$_{0.33}$Nb$_{0.67}$)O$_3$-PbTiO$_3$ (PZN-PT) systems. Large piezoelectric effect [17] is observed near this morphotropic phase boundary, which makes this lead-free BiFeO$_3$ films are of great interest for probe-based data storage and actuator applications.
In this chapter, we will firstly construct the strain-temperature phase stability diagram for (001) BiFeO$_3$ thin film using both thermodynamic calculation and phase-field simulations. Then we will compare the remnant polarization and coercive field of different phases near the morphotropic phase boundary, from the simulated ferroelectric hysteresis loops. For comparison, we will also investigate the switching behavior for BiFeO$_3$ thin films subjected to substrates which will induce tensile strains, (001) oriented PMN-PT be employed as an example for a misfit strain range approximately from 0.36% to 0.52%.

### 6.2 Phase-field model

The phase-field model for ferroelectric BiFeO$_3$ thin films is very similar to the models we used in chapter 2 and chapter 3 for PbTiO$_3$ and BaTiO$_3$ thin films. The total free energy in terms of the spontaneous polarization includes the bulk free energy $F_{\text{bulk}}$, domain wall energy $F_{\text{wall}}$, elastic energy $F_{\text{elas}}$, and electrostatic energy $F_{\text{elec}}$, i.e.,

$$F = F_{\text{bulk}} + F_{\text{wall}} + F_{\text{elas}} + F_{\text{elec}},$$

(6.1)

The bulk free energy density is described by a conventional Landau-type of expansion

$$F_{\text{bulk}} = \int \left[ \alpha_1 (P_1^2 + P_2^2 + P_3^2) + \alpha_2 (P_1^4 + P_2^4 + P_3^4) + \alpha_{12} (P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2) \right] dV ,$$

(6.2)
Figure 6.1 [Figure 1D in ref 12] AFM and SHG measurement of phase fractions with thickness, including the area fraction (left axis) and the volume fraction (right axis) of the R phase.
where $\alpha_i$ and $\alpha_j$ are the phenomenological coefficients which determine the transition temperature, the spontaneous polarization, and the dielectric susceptibility in the bulk crystal. Assuming that polarization varies continuously across domain boundaries, the domain wall energy can be introduced through the gradients of the polarization field. For the sake of simplicity, we assume the domain wall energy to be isotropic, therefore it can be written as

$$F_{\text{wall}} = \frac{1}{2} \sum_{i,j} G_{11} \left[ (P_{1,i})^2 + (P_{1,j})^2 + (P_{2,i})^2 + (P_{2,j})^2 + (P_{3,i})^2 + (P_{3,j})^2 + (P_{3,i})^2 + (P_{3,j})^2 \right] dV,$$  \hspace{1cm} (6.3)

where $P_{i,j} = \partial P_i / \partial x_j$ and $G_{11}$ is gradient energy coefficient.

To consider the dipole-dipole interaction during ferroelectric domain evolution, the electrostatic energy of a domain structure is introduced through:

$$F_{\text{elec}} = -\int \mathbf{E} \cdot \mathbf{P} dV = -\frac{\varepsilon_0 K_{ij}}{2} E_i E_j - \varepsilon_i P_i,$$  \hspace{1cm} (6.4)

where the electric field $\mathbf{E}$ depends on the polarization distribution and the electric boundary conditions on the film surfaces. Calculation of electric fields for ferroelectric thin films is presented in Ref. 18.

If we assume that the interfaces developed during the ferroelectric phase transition as well as the interface between the film and the substrate are coherent, elastic strains will be generated in order to accommodate the structural changes, which are given by

$$e_{ij} = e_{ij} - e_{ij}^0$$  \hspace{1cm} (6.5)
where \( \varepsilon_{ij} , \varepsilon^0_{ij} \) are the elastic strains, total strains, and stress-free strains. The corresponding elastic energy can be expressed as

\[
F_{\text{elas}} = \frac{1}{2} \int c_{ijkl} e_{ij} e_{kl} dV = \frac{1}{2} \int c_{ijkl} [\varepsilon^0_{ij} - \varepsilon^0_{ij}] [\varepsilon_{ij} - \varepsilon^0_{ij}] dV
\]

where \( c_{ijkl} \) are the elastic stiffness tensor. The calculation of elastic energy for a film-substrate system [18] is obtained using a combination of the Khachaturyan’s mesoscopic elasticity theory [19] and the Stroh formalism of anisotropic elasticity [20].

The temporal evolution of the polarization field \( \mathbf{P} \) and thus the domain structures are governed by the time-dependent Ginzburg-Landau (TDGL) equations

\[
\frac{\partial P_i(t)}{\partial t} = -L \frac{\delta F}{\delta P_i(t)}
\]

where \( L \) is a kinetic coefficient related to the domain evolution. The TDGL equations can be numerically solved by using the semi-implicit Fourier spectral method [21].

### 6.3 Results and discussions

In the simulation, we employed a model of \( 256 \Delta x \times 256 \Delta x \times 36 \Delta x \) with \( \Delta x \) being the grid size, and periodic boundary conditions are applied along \( x_1 \) and \( x_2 \) axes in the film plane. The thickness of the film is taken as \( h_f = 20 \Delta x \). The material constants for the Landau free energy and the nonzero electrostrictive coefficients are from the literature [22] \( a_1 = 8.78(T-830) \times 10^5 \text{ C}^{-2} \text{m}^6 \text{N} \), \( a_{11} = 4.71 \times 10^8 \text{ C}^{-4} \text{m}^6 \text{N} \), \( a_{12} = 5.74 \times 10^8 \text{ C}^{-4} \text{m}^6 \text{N} \), \( Q_{1111} = 0.032 \text{ (C}^{-2}\text{m}^4) \), \( Q_{1122} = 0.016 \text{ (C}^{-2}\text{m}^4) \), and \( Q_{1212} = 0.01 \text{ (C}^{-2}\text{m}^4) \), where \( T \) is temperature.
in °C. For the calculation of elastic energy, we take the elastic constants to be isotopic and homogeneous, with shear modulus $\mu = 0.69 \times 10^{11}$ (N m$^{-2}$) and Poisson’s ratio $\nu = 0.35$, in order to avoid solving inhomogeneous elastic equations. The cell size in real space is chosen to be $\Delta x = l_0$, where $l_0 = \sqrt{G_{110}/\alpha_0}$ and $\alpha_0 = |\alpha_1|_{T=300K}$. We choose the gradient energy coefficients as $G_{11}/G_{110} = 0.6$. If $l_0 = 0.5$ nm, $G_{110} = 0.98 \times 10^{-10}$ (C$^{-2}$m$^4$N), and the domain wall energy density is about 0.085 (Jm$^{-2}$) for 71° domain walls. Short-circuit boundary condition is used in the following domain structure simulations. The initial polarization is created by assigning a zero value at each grid point plus a small random noise with uniform distribution.

6.3.1 Domain stability diagram of BiFeO$_3$ thin films

The obtained the strain-temperature phase stability diagram for (001) BiFeO$_3$ thin film as shown in Figure 6.2 with different phases labeled: cubic paraelectric (0, 0, 0), distorted rombohedral ($P_1, P_1, P_3$), tetragonal (0, 0, $P_3$) and orthorhombic ($P_1, P_1, 0$). We also predict the phase stabilities and their boundaries from thermodynamic analysis (solid lines) to compare with phase-field model (scattered symbols). Figure 6.3 reveals that the tetragonal to distorted rhombohedral phase boundary is around 4.3% compressive strain at room temperature from thermodynamic analysis, which is consistent with the density function calculations [12,23]. Assuming fully coherent, the misfit strain for BFO films grown on LAO and YAO are -4.29% and -6.8%. According to the strain diagram, BFO on LAO is near the morphotropic phase boundary and BFO on YAO is well within the T-phase region. Considering the uncertainty in the materials constants in the phase-field simulation and thermodynamic calculations, the predicted strain diagram and experimental observations are in very good agreement. We also compared the predicted

Interestingly, our phase-field simulations taking into account domain structures predicted a three-phase mixture region of T and distorted R phases as well as a monoclinic phase (P$_1$, 0, P$_3$) near the morphotropic boundary while our thermodynamic calculations reveals only the morphotropic phase boundary separating the T and distorted R phases. To further examine the relative phase fraction evolution across the T/R boundary, we also plot the volume fraction changes as a function of strain from phase-field simulation, as shown in Figure 6.3, the corresponding simulated domain structures at different strains are presented in Figure 6.4. In the phase evolution process from large to small compressive strain across the phase boundary, which is comparable to the strain relaxation process with increasing film thickness, the monoclinic (P$_1$, 0, P$_3$) (M phase) will appear as well as the increasing distorted rhombohedral phase accompanied by the decreasing tetragonal phase observed by the experiment. This monoclinic phase is thermodynamically metastable and it is observed from Figure 6.4 that it always existed between different domain variants of R and T phase as the “bridge” phase. Figure 6.3 also shows that the coexistence of T and R phases are mostly in the T-rich regions indicates small relaxation of the strain, while the further relaxation will stabilize R and M mixture phases.
Figure 6.2 Phase stability diagram of (001) BiFeO₃ thin film as a function of temperature and misfit in-plane strain. Scattered symbols are phase boundaries from phase-field simulation and solid lines are from thermodynamic calculations.
Figure 6.3 Phase fractions as a function of misfit strain across the morphotropic phase boundary in (001) BiFeO$_3$ thin films
Figure 6.4 Simulated domain structures at different strains: hase fractions as a function of misfit strain across the morphotropic phase boundary in (001) BiFeO$_3$ thin films: (a) Tetragonal phase at misfit strain -4.5%, blue and white show two tetragonal domain variants $(0, 0, P_3)$ and $(0, 0, -P_3)$. (b) Distorted rhombohedral phase at misfit strain -3.4% with eight equivalent domain variants. (c) Orthorhombic phase at misfit strain 3.0% with four in-plane $(P_1, P_2, 0)$ variants. (d) Mixture domain structure at misfit strain -4.05% with distorted rhombohedral phase, tetragonal phase and monoclinic phase $(P_1, 0, P_3)$ and $(0, P_2, P_3)$ as labeled.
6.3.2 Domain switching near the morphotropic phase boundary

To further investigate the ferroelectric properties near the morphotropic phase boundary, we study the switching behavior of BiFeO$_3$ thin films subjected to the strain states near the boundary, by applied an outside electric field and generate the hysteresis loops to compare the coercive field and remnant polarization. Based on the domain stability diagram (Figure 6.1), we choose two strains with different stabilized phases: a distorted rhombohedral film with -3.4\% strain and the other film strained at -4.15\% with a mixture of 20\% distorted rhombohedral phase, 60\% tetragonal phase as well as about 20\% monoclinic “bridge” phase (relative phase fractions at different strains could be found in Figure 6.2). For simplicity, we label the first film as R phase, and the second one as “R+T” phase.

In the simulation, we employed a model of $256\Delta x \times 256\Delta x \times 36\Delta x$ with $\Delta x$ being the grid size, the same simulation cell size as the previous domain structure simulations. The film thickness is taken as $20\Delta x$ and the cell size in real space is chosen to be $\Delta x = l_0 = 1$nm. For both films, a domain structure was first generated by performing the simulations without any applied electric field, starting from an initial paraelectric state with small random perturbations. In order to construct the P-E loop an electric field was then applied to the generated domain structure in the (001) direction. The domain structure from a previous simulation was used as the input at each increment of the electric field. The simulated results are presented in Figure 6.5, where the hysteresis loops of both films are plotted together compare the ferroelectric properties. It is observed that the mixture phase film (-4.15\% strain) demonstrates both higher coercive field and remnant polarization, compared with the distorted rhombohedral film strained at -3.4\%, indicating a better
ferroelectric property. This feature is also confirmed by experimental observations in BiFeO$_3$ films grown on LaAlO$_3$ substrates [25]. Interestingly, the magnitude of the polarization and coercive field for both films from phase-field simulations are also agree reasonably with experiments [25].

Figure 6.5 Hysteresis loops of BiFeO$_3$ thin films strained at -3.4% (distorted rhombohedral phase) and -4.15% (mixture of tetragonal and distorted rhombohedral phases) from phase-field simulations.

6.3.3 Strain effect on coercive field in tensile strained BiFeO$_3$ thin films

To further investigate the strain dependent switching behavior of BiFeO$_3$ thin films, we also study the strain effect on coercive field and remnant polarization in the BiFeO$_3$ thin films subjected to tensile strains. Figure 6.5 (Courtesy of Michael D. Biegalski at
Oak Ridge National Lab) is the experimental measurements summarize remnant polarization ($P_r$) and coercive field ($E_c$) as functions of the total film strain, in BiFeO$_3$ thin films grown on PMN-PT substrates at 80K, with the misfit strain spans from 0.36% to 0.51%. It is observed here $E_c$ strongly rises with strain, while the strain dependence of $P_r$ exhibits opposite behavior. Both of these two strain dependent properties will be compared with our phase-field simulations later.

We performed both thermodynamic calculations and phase-field simulations to construct the hysteresis loops BiFeO$_3$ thin films at the same experimental strains. At each strain, the coercive field and remnant polarization could be obtained directly from the hysteresis loops. For thermodynamic calculations, the equilibrium polarization is obtained by minimizing the bulk free energy (Eq. 6.2) and elastic energy (Eq.6.5) under an applied electric field perpendicular to the film surface, while a single domain assumption allowed us to ignore the polarization inhomogeneous. For phase-field simulations, the method to generate the hysteresis loops is essentially the same as the one we used at the compressive strains above.

Thermodynamic calculations of the strain dependent coercive field and remnant polarization are plotted in Figure 6.7, with the strain ranging from 0.36% to 0.52% as same in Figure 6.6. Both coercive field and polarization decrease with increasing strain, which is significantly different from the experimental observations as shown in Figure 6.6, where the coercive field exhibit opposite strain dependency. Previous simulations, including phase-field simulations [26], thermodynamic calculations [27-28] and molecular dynamics [29-30] for perovskite ferroelectrics (BaTiO$_3$, PbZr,TiO$_3$, BiFeO$_3$) all find a drop of $E_c$ with increasing strain for the tensile regime, which is consistent with
the current thermodynamic calculations. The magnitude of the remnant polarization is close to that measured experimentally, but the coercive field is much higher. This is because the nature of thermodynamic calculation, where a relatively large electric field is required to switching the polarization between two single domain states.

The results from phase-field simulations are summarized in Figure 6.8–6.10. Figure 6.8 is the hysteresis loop of BiFeO$_3$ thin films strained at 0.36% at 80K and some representative domain structures where the domain variants are identified by different colours. The Polarization-Electric field loop was obtained by plotting the average polarization $P$ versus the normalized electric field $E/E_0$ along the (001) direction, where $E_0 = \alpha_0 P_0 = 3666 \text{kv/cm}$ and $P_0 = 0.52 \text{C/m}$ for BiFeO$_3$ single crystals. The switching process could be clearly reflected by the evolution of domain structure as shown in Figure 6.8. The initial domain structure (Figure 6.8(a)) contains all 8 kinds of variants ($r_1^+ = [111]_c$, $r_2^+ = [\overline{1}11]_c$, $r_3^+ = [\overline{1}\overline{1}]_c$, $r_4^+ = [1\overline{1}1]_c$, $r_1^- = [\overline{1}\overline{1}\overline{1}]_c$, $r_2^- = [\overline{1}\overline{1}]_c$, $r_3^- = [1\overline{1}1]_c$, $r_4^- = [1\overline{1}1]_c$). A sufficiently large electric field along (001) direction will switch the last four “down” variants and there will be only 4 “up” variants left, as shown in Figure 6.8(b). Similarly, there will be only 4 “down” variants under a large electric field applied to (00 -1) direction, as shown in Figure 6.8(d).

The hysteresis loops for BiFeO$_3$ thin films at different strains are plotted in Figure 6.9 and Figure 6.10 collects the remnant polarization and coercive field from the simulated loops. It is obvious both polarization and coercive field are dropping with increasing strain, consistent with thermodynamic calculations. The magnitude of the polarization is similar to that obtained by thermodynamics but the coercive field is much
smaller, which is much close to experiments. The discrepancy of the simulation and experiments are likely attributed to the kinetic factor during domain switching. Another possible reason is the ferroelectric nature of the substrate PMN-PT in this study, which may significantly affect the switching behavior of the BiFeO$_3$ thin films grown on it.

6.4 Summary

In this chapter we constructed the strain-temperature phase stability diagram for (001) BiFeO$_3$ thin film using both thermodynamic calculation and phase-field simulations. The predicted tetragonal to distorted rhombohedral phase boundary is around 4.3% compressive strain at room temperature from thermodynamic analysis, which is consistent with the density function calculations. The phase diagram from phase-field simulations and experimental observations are in very good agreement with BiFeO$_3$ films grown on LaAlO$_3$ and YAIO$_3$ with -4.29% and -6.8% strains respectively. Interestingly, our simulations taking into account domain structures predicted a three-phase mixture region of T and distorted R phases as well as a monoclinic phase near the morphotropic boundary. The volume fraction changes of these different phases as a function of temperature and external electric field near the morphotropic phase boundary was also presented. We also study the switching behavior of BiFeO$_3$ thin films with both compressive and tensile strains, by generating the hysteresis loops using phase-field method. It is demonstrated that the coercive field and remnant polarization obtained from simulations have a good agreement with experiments with BiFeO$_3$ films on LaAlO$_3$ substrates, but for BiFeO$_3$ thin films on PMN-PT substrates with 0.36%~0.52% tensile strain states, we observed decreasing coercive field as a function of misfit strain, which is strikingly opposite to experiments which needs to be further investigated.
Figure 6.6 (Courtesy of Michael D. Biegalski@Oak Ridge National Lab) Experimental ferroelectric properties of the BiFeO$_3$ film as a function of the absolute biaxial in-plane strain. Inset: P-E hysteresis loop recorded at 0.52% strain at 80 K.
Figure 6.7 Coercive field and remnant polarization as a function of misfit strain in BiFeO$_3$ thin films at $T=80$K, using thermodynamic calculations.
Figure 6.8 Phase-field simulations of hysteresis loop (top) and domain structures (down) in BiFeO$_3$ film with 0.36% strain at 80K. (a) Initial domain structure without applying electric field, (b) $E/E_0=0.2$, (c) $E/E_0=-0.15$, (d) $E/E_0=-0.2$, (e) $E/E_0=0.15$
Figure 6.9 Phase-field simulations of hysteresis loops of BiFeO$_3$ film with 0.1%, 0.36% and 0.52% strains at 80K.
Figure 6.10 Phase-field simulations of coercive field and remnant polarization as a function from misfit strain in BiFeO$_3$ thin films at $T=80$K.
References


Chapter 7 Phase-field simulations of thickness effect on domain stabilities in ferroelectric thin films

7.1 Introduction

It is well established that the domain/phase stabilities in epitaxial ferroelectric thin films are controlled by both mechanical and electrical boundary conditions [1-2]. It is also shown that the impact of misfit strain will significantly pronounce the variations in the Curie transition temperature more than the polarization [3-4]. With continued demand for portability in consumer electronics, it is becoming increasingly important to understand the size effect on properties of the active components in electronic devices. For example, for ferroelectric thin films, it has long been believed that there is a critical size on the order of hundreds of angstroms below which a spontaneous polarization cannot be sustained [5-6]. Fong et al. [7] reported the ferroelectric transition temperature $T_c$ versus film thickness, providing the experimental evidence of ferroelectricity in ultra-thin PbTiO$_3$ thin films down to vanishing small sizes. The thickness dependent evolution of ferroelectric phases and related domain structures at different mechanical and electric boundary conditions are reported in a series of thin films systems [4-11].

In earlier theoretical models on the misfit strain - temperature diagram, including thermodynamic calculations [12-13], ab initio method [14-15] as well as phase-field simulations [16-17], the boundary and geometric or size conditions are treated as almost independent parameters. The thickness dependence effects like strain relaxation were not included. In all these models, ferroelectric film is assumed to be fully constrained by the underlying substrate and there are internal stresses due to epitaxy and the eigenstrain of
the ferroelectric phase transformation. The thickness induced strain relaxation on the ferroelectric transitions and domain stabilities are then totally ignored. When the internal stresses due to lattice misfit are too large, this assumption is inappropriate because the stresses would be immediately relaxed by the generation of a periodic pattern of interfacial dislocations at the film-substrate interface at the growth temperature. Thus, the influence of the effective misfit strain must be applied with caution or its effect may be heavily overestimated.

Modeling thickness dependent domain stability in ferroelectric thin films was pioneered by Qiu et.al using a non-linear Landau-Ginzburg-Devonshire thermodynamic model, and the corresponding thickness - strain domain stability diagrams were constructed for (001) oriented PbTiO$_3$ [18] and PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) [19] epitaxial thin films. Similar approach was applied to Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ and SrTiO$_3$ thin films [20], and the corresponding thickness dependent properties were calculated. However, all of these thermodynamic analyses employed a single domain or simplified two dimensional domain structures as a prior assumptions, and a thickness - strain diagram taking into real three dimensional domain structures is still lacking.

In this chapter, we extend the previous phase-field model [16-17] to study the thickness dependent domain stabilities by introducing the strain relaxation mechanisms to calculate the real effective strain as a function of film thickness. We use PbTiO$_3$ thin film as a representative example to construct the thickness - strain domain stability diagram. We will also report the relative domain populations as a function of film thickness in PbTiO$_3$ thin films grown on SrTiO$_3$ and KTaO$_3$ substrates, and compare the simulation results with experimental measurements.
7.2 Theory

We model the thickness-dependent properties of strained ferroelectric films using the segregation model [20], where all misfit dislocations are assumed to reside within a thin buffer layer with thickness $h_B << h$, where $h$ is the film thickness. This treatment is different to other approaches where these defects are assumed to be roughly uniformly distributed within the film [21]. Elastic relaxation then occurs so that there is homogeneous strain in the film except for the buffer layer. The pseudomorphic misfit strain, or “idea misfit strain,” is calculated as $\varepsilon_0 = (a_s - a_f) / a_f$ where $a_s$ and $a_f$ are the substrate and film lattice parameters at the room temperature, respectively. The actual misfit strain or effective misfit strain $\varepsilon(h)$ at given temperature as a function of thickness is estimated by [18]:

$$\varepsilon(h) = 1 - \frac{(1 - \varepsilon_0)}{1 - \varepsilon_0 (1 - h_c / h)},$$

(7.1)

where $h_c$ is the critical thickness for dislocation formation, which is significant to determine the relaxation of strain as a function of thickness.

For ferroelectric films with the seminal work by Speck and Pompe, [22] the Matthews-Blakeslee (MB) model [23] has become the most popular approach for calculating the critical thickness. However, it has been shown that the MB model works well for metals but strongly underestimates the critical thickness in semiconductor films, particularly at relatively low strains [24-28]. For ferroelectric thin films the MB model also possibly underestimates the critical thickness as semiconductor films. For example, this model predicts for PbTiO$_3$ on (001) SrTiO$_3$ a relatively small critical thickness of
only 6.2 nm [29]. In particular, in the case of high quality films and substrates where initial dislocations are absent, the actual nucleation of friction force on the dislocations prevent the MB model to be directly applicable.[24-28] Therefore it is possible to grow coherently strained films on high quality substrates that are more than ten times thicker than that predicted by the MB model.[24-26] Alternative models were developed by People and Bean (PB)[24-25], which explains the observed critical thickness for semiconductor films much better than the MB model [24-26]. Thus in this chapter, we will employ both MB and PB model to determine the critical thickness for dislocation formation and compare the simulation results from both models.

The critical thickness for dislocation formation is given by Speck and Pompe[22] for the MB model and by Marée et al.[26] for the PB model:

\[
h_c^{MB} = \frac{\bar{b}(1 - \nu \cos^2 \beta)}{8\pi \cos \lambda(1 + \nu)} \frac{1}{\varepsilon_0} \ln \left( \frac{\alpha h_c^{MB}}{\bar{b}} \right),
\]

\[
h_c^{PB} = \frac{\bar{b}(1 - \nu)}{40\pi(1 + \nu)} \frac{1}{\varepsilon_0^2} \ln \left( \frac{h_c^{PB}}{\bar{b}} \right),
\]

where \( \bar{b} \) is the magnitude of the Burgers vector, \( \nu \) is the Poisson’s ratio, \( \varepsilon \) is the ideal misfit strain, \( \alpha \) is the cut-off parameter used to describe the continuum energy of the dislocation core, \( \beta \) is the angle between the dislocation line and the Burgers vector, and \( \lambda \) is the angle between the Burgers vector and line that lies within the interface and in a plane normal to the dislocation line. We assume misfit dislocations in PbTiO\(_3\) with Burgers vector of type \(<110>\), \( \alpha = 4 \), \( \beta = 90^\circ \), and \( \lambda = 45^\circ \) [22] and a Poisson’s ratio of 0.33 [18,29].
The critical thickness for dislocation formation predicted by MB and PB models are plotted in Figure 7.1 as a function of the idea misfit strain. The x axis of Figure 7.1 only includes the tensile strain part since the critical thickness is independent of the sign of the strain, i.e., the same magnitude of tensile and compressive strain will result in the same critical thickness. It is shown that under same ideal misfit strain, PB model will give a much larger critical thickness than MB model when the ideal misfit strain is smaller than 2.0%. For example, for cubic PbTiO₃ on SrTiO₃ at room temperature, the critical thickness according to the MB and PB models is 6.2 nm [29] and 48 nm, respectively, corresponding to the ideal misfit strain $\varepsilon_0$ about 1.28% compressive strain. The calculated MB critical thickness in Fig.1 is essentially the same as presented in Reference [18].

Based on the critical thickness determined from either MB or PB model, the actual or real misfit strain can be calculated as a function of thickness using equation (1), and two examples are given in Figure 7.2 and Figure 7.3 for PbTiO₃ thin films grown on SrTiO₃ and KTaO₃ substrates, respectively. As mentioned above, the ideal misfit strain $\varepsilon_0$ for cubic PbTiO₃ from cubic SrTiO₃ at room temperature is estimated as -1.28%, from the lattice parameter mismatch of cubic unstrained PbTiO₃ (3.956Å [29]) and SrTiO₃ (3.905Å [30]). Similarly, the misfit strain for PbTiO₃ thin film from KTaO₃ substrate is about 0.83% tensile strain, from the lattice parameter of cubic PbTiO₃ and KTaO₃ (3.989 Å [30-31]), also at room temperature. Here the estimated strain values using the room temperature lattice constants are different from those calculated at the growth temperature lattice constants for PbTiO₃, SrTiO₃ and KTaO₃ [18], but should be still a reasonable estimation of the room temperature strain states in these two systems.
In the phase-field model of ferroelectric thin films, the spontaneous polarization vector \( \mathbf{P}(\mathbf{x}) = (P_1, P_2, P_3) \) is chosen as the order parameter and its spatial and temporal evolutions are governed by the time-dependent Ginzburg-Landau (TDGL) equations:

\[
\frac{\partial P_i(\mathbf{x}, t)}{\partial t} = -L \frac{\delta F}{\delta P_i(\mathbf{x}, t)}, \quad i = 1, 2, 3, \tag{7.4}
\]

where \( L \) is the kinetic coefficient related to the domain-wall mobility, and \( F \) is the total free energy of the system. \( \delta F / \delta P_i(\mathbf{x}, t) \) is the thermodynamic driving force for the spatial and temporal evolution of \( P_i(\mathbf{x}, t) \). The total free energy \( F \) includes the bulk free energy, elastic deformation energy, domain wall energy and electrostatic energy, i.e.

\[
F = \int_V \left[ f_{\text{bulk}}(P_i) + f_{\text{elas}}(P_i, \epsilon_{ij}) + f_{\text{wall}}(P_{i,j}) + f_{\text{elec}}(P_i, E_i) \right] dV, \tag{7.5}
\]

where \( V \) is the volume of the film and \( dV = dx_1 dx_2 dx_3 \). The bulk free energy density of \( \text{PbTiO}_3 \) is described by a six-order Landau-Devonshire polynomial [32] with free energy coefficients collected from literature:[12,33] \( \alpha_1 = 3.8 \times (T - 479) \times 10^5 \), \( \alpha_{11} = -7.3 \times 10^7 \), \( \alpha_{12} = 7.5 \times 10^8 \), \( \alpha_{111} = 2.6 \times 10^8 \), \( \alpha_{112} = 6.1 \times 10^8 \), \( \alpha_{123} = -3.7 \times 10^9 \), \( c_1 = 1.746 \times 10^{11} \), \( c_{12} = 7.937 \times 10^{10} \), \( c_{44} = 1.11 \times 10^{11} \), \( Q_{11} = 0.089 \), \( Q_{12} = -0.026 \), \( Q_{44} = 0.0675 \) (in SI units and \( T \) in °C). The description of domain wall energy and electrostatic energy can be found in our previous publications [16, 17, 34].

The elastic energy density is given by

\[
f_{\text{elas}} = \frac{1}{2} c_{ijkl} \epsilon_{ij} \epsilon_{kl} = \frac{1}{2} c_{ijkl} (\epsilon_{ij} - \epsilon_{ij}^0)(\epsilon_{kl} - \epsilon_{kl}^0), \tag{7.6}
\]
where \( e_{ij} - e_{ij}^0 \) is the elastic strain, \( e_{ij} \) is the total strain of the film compared to the parent paraelectric phase, and \( c_{ijkl} \) is the elastic stiffness tensor. Both \( e_{ij} \) and \( e_{ij}^0 \) are defined using the cubic phase as the reference, and \( e_{ij}^0 = Q_{ijkl} P_k P_l \) where \( Q_{ijkl} \) is the electrostrictive coefficient tensor. The details of the calculation of the total strain \( e_{ij} \) in a (001)-oriented film under a biaxial strain are described in our previous publications [16-17]. In this work, the average film/substrate misfit strains \( e_{i1} = e_{22} = e(h) \) along \( x \) and \( y \) axes, and \( e(h) \) is dependent on the film thickness and given by Equation (1). Here we assume \( e_{12} = e_{21} = 0 \). The over bar indicates an average over the film.

A rectangular coordinate system, \( x = (x_1, x_2, x_3) \) is set up with the \( x_1, x_2 \) and \( x_3 \) axes along the [100], [010] and [001] crystallographic directions, respectively. We employed 64\( \Delta x \) grid size in \( x_1 \) and \( x_2 \) axes, with periodic boundary conditions. \( \Delta x = 1 \) nm is the spacing between two nearest grid points. We vary the thickness of the film from several to hundred of nanometers. The actual strain is calculated using Equation (1) if the thickness is exceeded the critical thickness determined by MB (Equation (2)) or PB (Equation (3)) models. The short-circuit electric boundary condition is employed to compute the dipole-dipole interactions [34].

### 7.3 Results and discussions

#### 7.3.1 Thickness – strain domain stability diagrams

To construct the thickness - strain domain stability diagram for PbTiO\(_3\) thin film, we perform a series of simulations under different strains and thicknesses to obtain the corresponding domain stabilities. Here we present three types of phase diagrams with
different strain relaxation mechanisms: Figure 7.4 is the thickness-strain domain stability diagram without considering the strain relaxation, while Figure 7.5 and Figure 7.6 are the domain stability diagrams using MB and PB models to evaluate the actual misfit strains as a function of film thickness, respectively.

Since a uniform misfit strain without any thickness dependence relaxation is assumed in Figure 7.4, the only reason causes the shift of the phase boundaries as a function of thickness is the effect from electrostatic energies. It is observed that the boundary separating the $c$ domain region and the $c+a_1+a_2$ multi-domain region shifts to the left with increasing thickness, indicating the shrinking of the $c$ domain region in thicker films. This is because this simulation employs the short-circuit boundary condition which favors $c$-domains. When the film is getting thicker, the effect of the boundary condition becomes smaller and the fraction of $c$-domains is getting slightly less. Similar trend is observed at tensile strain regions, where the $c+a_1+a_2/a_1+a_2$ phase boundaries also shift to the left side, indicating a film with small thickness will promote the formation of $c$ domains.

The thickness-strain domain stabilities diagrams presented in Figure 7.5 and Figure 7.6, which include the strain relaxation due to thickness increase, exhibit significant difference with Figure 7.4. In both Figure 7.5 and Figure 7.6, the $x$ axis is the ideal strain due to the lattice mismatch, which could be only maintained below the critical thickness for dislocation formation. When the thickness of the film exceed this critical value, the real or actual strain is determined by Equation (2) or (3), and the corresponding domain stabilities at this thickness could be found at Figure 7.5 or Figure 7.6, depending on either MB or PB criteria for the critical thickness calculation. The MB model predicts very
limited strain regions for the formation of the pure $c$ domain or $a_1+a_2$ domain, as shown in Figure 7.5, indicating all the PbTiO$_3$ films with 20 nm or larger thickness will form the $c+a_1+a_2$ multi domain state. As discussed above, the PB model gives a much larger critical thickness for strain relaxation comparing with the MB model, and results in a much wider region for pure $c$ and $a_1+a_2$ phases as illustrated in Figure 7.6.

7.3.2 Comparison with experiments

The relative domain fractions as a function of film thickness have been measured using various methods for PbTiO$_3$ thin films grown on different substrates. Kwak et.al [35] reported the $c$ domain fraction as a function of film thickness in a wide thickness range from 30 nm to about 700 nm, in PbTiO$_3$ thin films grown on (001) KTaO$_3$ substrates using metal organic chemical vapor deposition. Similarly, Hsu and Raj [36] grew PbTiO$_3$ thin films with thickness from 50 nm to 350nm, on (001) SrTiO$_3$ substrates using pulsed laser ablation, and measured the relative volume fraction of the $a_1+a_2$ domains based on the mapping of the x-ray diffraction intensity distribution in the reciprocal space. From phase-field simulations it’s straightforward to count the populations or volume fractions of different domain variants from the simulated domain structures, which allows us to compare the simulation results with experimental measurements in the two above systems.

The calculated $c$ domain fractions as a function of thickness in PbTiO$_3$ films on KTaO$_3$ are plotted in Figure 7.7, using both MB and PB models. Experimental data from reference [35] is also included for comparison. The real misfit strain as a function of film thickness in this system is already plotted in Figure 7.3. It is shown that both models
predict the increasing $c$ domain fractions with increasing thickness as observed from experiments. This is because a PbTiO$_3$ thin film grown on a KTaO$_3$ substrate is subjected to a tensile strain state, thus increasing the film thickness will relax the tensile strain and promote the formation of $c$ domains. It is also demonstrated that the simulation results from the PB model even quantitatively agree well with experiments, indicating a better estimation of the critical thickness of dislocation formation than the MB model which gives a much higher $c$ domain fraction in Figure 7.7. It may imply that the MB model overestimates the relaxation of strains, especially for the films with small thickness.

Figure 7.8 is the plot of volume fraction of $a_{1+2}$ domains in PbTiO$_3$ films on SrTiO$_3$ together with experimental data [36]. In this case, PbTiO$_3$ thin film is compressively strained and increasing film thickness will produce more $a_{1+2}$ domains. Again, the PB model demonstrates excellent agreement with experiment data in this system.

### 7.4 Summary

In this chapter, we use a three-dimensional phase-field model for predicting the thickness effect on domain stability in ferroelectric films. The model simultaneously takes into account the ferroelectric domain structures, the electrostrictive effects, as well as the strain relaxation due to the thickness effect. As an example, the thickness - strain domain stability diagram was constructed for PbTiO$_3$ thin films, using both Matthews-Blakeslee (MB) and People-Bean (PB) models for estimating the critical thickness and strain relaxation. The relative domain populations as functions of thickness are plotted for PbTiO$_3$ thin films grown on SrTiO$_3$ and KTaO$_3$ substrates and compared with available experiments. It is shown that the PB model demonstrates a good agreement with experiment measurements in the above two systems. It is expected that this study will
provide guidance for interpreting experimental measurements and observations as well as to the design of PbTiO$_3$ films with specific thickness and domain stabilities.
Figure 7.1 Theoretical MB and PB critical thickness for misfit dislocation formation in PbTiO$_3$ thin film as a function of misfit strain at a room temperature $T=25^\circ$C.
Figure 7.2 Calculated actual misfit strain as a function of thickness using both MB and PB models for PbTiO$_3$ thin film grown on SrTiO$_3$ substrates at $T=25^\circ$C.
Figure 7.3 Calculated actual misfit strain as a function of thickness using both MB and PB models for PbTiO$_3$ thin film grown on KTaO$_3$ substrates at $T=25^\circ$C.
Figure 7.4 Thickness - strain domain stability diagram of PbTiO$_3$ thin films at $T=25^\circ$C, without considering strain relaxation as a function of film thickness.
Figure 7.5 Thickness - strain domain stability diagram of PbTiO$_3$ thin films at $T=25^\circ$C, using Matthews and Blakeslee (MB) model for critical thickness estimation.
Figure 7.6 Thickness - strain domain stability diagram of PbTiO$_3$ thin films, using People and Bean (PB) model for critical thickness estimation.
Figure 7.7 Calculated and experimental $c$ domain fractions [35] as a function of thickness in PbTiO$_3$ thin films grown on (001) KTaO$_3$ substrates.
Figure 7.8 Calculated and experimental $a_1 + a_2$ domain fractions [36] as a function of thickness in PbTiO$_3$ thin films grown on (001) SrTiO$_3$ substrates.
References


8.1 Conclusion

In this thesis, the phase-field models were applied to study the phase transitions, domain stabilities and structures evolution in a series of ferroelectric thin film materials, which involves long-range elastic and electrostatic interactions. The main contributions of the present thesis include:

1. The effects of unequi-biaxial misfit strain for PbTiO₃ and BaTiO₃ thin films were systematically studied by using thermodynamic calculations and phase-field simulations. It was demonstrated that the spontaneous polarizations, domain structures, and domain wall stabilities of PbTiO₃ and BaTiO₃ thin films could be effectively controlled by choosing the substrates with appropriate lattice parameters and orientations. These results provide guidance to modify ferroelectric properties of these films by heteroepitaxy and strain engineering.

2. A modified Landau-Devonshire thermodynamic potential was developed by interpreting phase-field simulations and experimental measurements in several different SrTiO₃ thin film samples. Compared to earlier thermodynamic calculations and phase-field simulation using the previous potential, the predicted transition temperatures and domain stabilities from the new potential have very good agreement with all the existing experiments.

3. Both ferroelectric and antiferrodistortive (AFD) transitions, and corresponding domain stabilities and structures in epitaxial SrTiO₃ thin films are systematically studied using
phase-field model. The strain - temperature domain stability diagram is constructed for equi – biaxially strained SrTiO\textsubscript{3} thin films and typical domain structures are presented. For unequi – biaxially strain films, both ferroelectric and AFD transition temperatures are predicted and agree well with experiments.

4. Phase-field model was extended to study the ferroelectric domain stabilities in epitaxial BiFeO\textsubscript{3} thin films. The strain – driven morphotropic phase boundary in BiFeO\textsubscript{3} thin films is simulated and has very good agreement with experimental measurements in BiFeO\textsubscript{3} thin films grown on LaAlO\textsubscript{3} and YAlO\textsubscript{3} substrates.

5. A three-dimensional phase-field model was developed for predicting the thickness effect on domain stability and Currie temperature in ferroelectric films. The model simultaneously takes into account the ferroelectric domain structures, the electrostrictive effects, as well as the strain relaxation due to the thickness effect. As an example, the thickness – strain domain stability diagram was constructed for PbTiO\textsubscript{3} thin film, and the corresponding domain population as a function of thickness is obtained and compare with available experiments.

8.2  

8.2.1 Coupling of polarization and antiferromagnetic orders in 

multiferroics

In chapter 6, we applied phase-field model to investigate the ferroelectric domain stability in BiFeO\textsubscript{3} thin films. However, BiFeO\textsubscript{3} is simultaneously antiferromagnetic and ferroelectric at room temperature, and it is desirable to develop a phase-field model
which will take into account both spontaneous polarization and antiferromagnetic orders. The model should have a better description of the Landau type free energy functional than the current model which totally ignored the antiferromagnetic order. The model could be used to predict antiferromagnetic transitions and corresponding domain structure in BiFeO₃ thin films.

8.2.2 Modeling of the “super” tetragonal phase in BiFeO₃ thin films

The temperature - strain diagram of BiFeO₃ thin films presented in Chapter 6 shows the strain - driven morphotropic phase boundary is near 4.3% compressive strain, which agrees well with experiments [1] and first - principles calculations [2]. However, experiment measurements for BiFeO₃ thin films on both YAlO₃ and LaAlO₃ substrates [1] suggested the obtained tetragonal phase exhibits a huge polarization (around 150 uc/cm²) as well as a high tetragonality (with c/a ratio about 1.3). This tetragonal phase is different from the one obtained from the current phase-field model, while the magnitude of polarization is around 100 uc/cm² and a much smaller tetragonality. The occurrence of this “super” tetragonal phase with extremely high polarization and c/a ratio is also predicted by first - principles at 0K [2]. However this strain induced increase of the polarization and tetragonality is fundamentally contradictory with previous experiments and theories in relatively small strain regions, which indicate the polarization in BiFeO₃ is intrinsic property and the epitaxial strain will only rotates the direction of the polarization without promote the magnitude of the polarization [3]. A phase-field model with a more complete description of this “super” tetragonal phase is desirable, and a more accurate strain - temperature diagram which includes this “super” tetragonal phase is expected.
References


PbTiO$_3$ and BaTiO$_3$ (SI Units and $T$ in °C)

<table>
<thead>
<tr>
<th></th>
<th>PbTiO$_3$ $[^{1,2}]$</th>
<th></th>
<th>BaTiO$_3$ $[^3]$</th>
</tr>
</thead>
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### SrTiO$_3$ (in both cgs units and SI units and $T$ in K)

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<th>(SI units, $T$ in K)</th>
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<tbody>
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<td>$\text{cm}^2\text{dyn/esu}^4$ $4.5\times10^{-3} [\coth(54/T) - \coth(54/30)]$</td>
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<td>$10^{29} \text{N} \cdot \text{m}^{-4}$ $1.32 [\coth(145/T) - \coth(145/105)]$</td>
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</table>

APPENDIX B: Materials constants of BiFeO₃

Crystal structure

Rhombohedrally distorted perovskite-like structure

Space group $R3c$

Ferroelectric transition

$T_c \approx 1103K^{[1]}$

$T_c \approx 850ºC^{[2]}$

$T_c \approx 845 \pm 5 ºC^{[3]}$

$T_c \approx 830ºC^{[4]}$

Antiferromagnetic transition

$T_N \approx 643K^{[5]}$

Transition temperatures

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<th>Hexagonal Unit cell (RT)</th>
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<td>$\alpha_T$</td>
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<tr>
<td>3.96$^{[1]}$</td>
<td>89º28'$^{[1]}$</td>
</tr>
<tr>
<td>3.96$^{[2]}$</td>
<td>0.6º$^{[2]}$</td>
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Lattice parameters

Temperature dependence lattice parameters$^{[3]}$

<table>
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<th>$c_{\text{hex}}(\text{Å})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20-325 ºC</td>
<td>$5.5764 + 6.06 \times 10^{-5}T$</td>
<td>$13.8620 + 2.10 \times 10^{-4}T$</td>
</tr>
<tr>
<td>344-838 ºC</td>
<td>$5.5946 + 6.83 \times 10^{-5}T$</td>
<td>$12.503 \times 10^{-7}T^2 + 9.40 \times 10^{-10}T^3 - 3.57 \times 10^{-13}T^4$</td>
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</table>

Liner thermal expansion coefficients$^{[3]}$

<table>
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<th>Temperature range</th>
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<td>25.13-325ºC</td>
<td>$10.9 \times 10^{-6}$</td>
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<tr>
<td>344-838ºC</td>
<td>$12.2 \times 10^{-6}$</td>
<td>$65.0 \times 10^{-6} - 18.0 \times 10^{-8}T + 20.3$</td>
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\[ \alpha_T = \frac{1}{x_0} \left( \frac{\partial x}{\partial T} \right)_p \text{ (deg}^{-1} \text{)} \]

<table>
<thead>
<tr>
<th>Spontaneous polarization ((\mu C/cm^2))</th>
<th>Bulk crystal</th>
<th>Thin films</th>
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<tr>
<td>Single crystal ceramics</td>
<td>3.5 [^7]</td>
<td>8.9 [^8]</td>
</tr>
<tr>
<td>(001)</td>
<td>55</td>
<td>80</td>
</tr>
<tr>
<td>(101)</td>
<td>64</td>
<td>80.5</td>
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<tr>
<td>(111)</td>
<td>73</td>
<td>102</td>
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<table>
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<th>Electrostrictive coefficients ((C^2m^4))</th>
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<th>(Q_{12})</th>
<th>(Q_{44})</th>
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<td></td>
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<td>0.0403</td>
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<table>
<thead>
<tr>
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<th>(U_{\text{eff}}) (Cubic)</th>
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<tr>
<td>Equilibrium volume ((Å^3/atom))</td>
<td>(V_0) 12.74 12.77 12.66</td>
<td>11.49 12.19 12.08</td>
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<tr>
<td>(Expt.) [^5]</td>
<td>12.46 [^{5}]</td>
<td>12.46 [^{5}]</td>
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<tr>
<td>(B_0)</td>
<td>89 96 101</td>
<td>160 153 163</td>
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<tr>
<td>(Expt.) [^{16}]</td>
<td>75.5±15.5[^{16}]</td>
<td>75.5±15.5[^{16}]</td>
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<tr>
<td>(B_0) (Calc.)</td>
<td>130.9 [^{17}]</td>
<td>130.9 [^{17}]</td>
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<tr>
<td>Elastic Constants ((GPa))</td>
<td>(c_{11}) 203 213 222</td>
<td>229 228 279</td>
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<td>(c_{14})</td>
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<td>(c_{33})</td>
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<td>129 139 150</td>
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<td>Shear modulus (GPa)</td>
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<tr>
<td>--------------------</td>
<td>----------------</td>
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<tr>
<td>Bulk modulus (GPa)</td>
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<tr>
<td>$B/G$ ratio $B_{\text{H}}/G_{\text{H}}$</td>
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<td>2.34</td>
</tr>
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</table>

* All the elastic properties, if not specifically cited, are calculated by GGA i.e. $U_{\text{eff}} = 0$ eV and GGA+$U$ with cubic ($Pm\bar{3}m$) and G-type AFM ($R3c$) structures [18]. Bulk modulus ($B$) and shear modulus ($G$) are estimated by Hill approach.

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<th>Band gap (eV)</th>
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<table>
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<tr>
<th>Domain wall energies (J/m$^2$)</th>
<th>First-principle$^{[25]}$</th>
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<th>Bc 0.205</th>
<th>Bd 0.896</th>
<th>c 0.829</th>
<th>Fd 1.811</th>
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</table>

B and F indicated the BiFeO- and FeO$_2$- centered planes, c and d label the continuous or
discontinuous oxygen octahedral rotations[25]

| Phase-field simulations | 0.09[26], 0.1[27] | 0.16[27] | 0.21[27] |

<table>
<thead>
<tr>
<th>Bulk</th>
<th>Thin film</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>(101)</td>
</tr>
</tbody>
</table>

200 nm BFO on TiO_2 / SiO_2 / Si (Calc.) 62[32]

215~250[31]

GHz dielectric constant at RT

Dielectric constants

Low temperatures

90~110[33]

45[34]

90~110[33]

45[34]

100 nm BFO on quartz[36]

Real part 200~325

Imaginary part 0~80

Landau coefficients

\[ f = \alpha_1 \left( p_1^2 + p_2^2 + p_3^2 \right) + \alpha_{11} \left( p_1^4 + p_2^4 + p_3^4 \right) + \alpha_{12} \left( p_1^2 p_2^2 + p_2^2 p_3^2 + p_3^2 p_1^2 \right) \]

\[ \alpha_1 = 8.78(T-830) \times 10^5 \text{ C}^{-2}\text{m}^6\text{N}, \alpha_{11} = 4.71 \times 10^8 \text{ C}^{-4}\text{m}^6\text{N}, \alpha_{12} = 5.74 \times 10^8 \text{ C}^{-4}\text{m}^6\text{N} \]

(under stress free condition)

Gradient energy coefficients

In cubic system, gradient energy density has the following expression:

\[ f_{\text{null}} = \frac{1}{2} G_{11} \left( P_{1,1}^2 + P_{1,2}^2 + P_{1,3}^2 + P_{2,2}^2 + P_{2,3}^2 + P_{3,3}^2 + P_{3,1}^2 + P_{3,2}^2 + P_{3,3}^2 \right) \]

\[ P_{i,j} = \frac{\partial P_i}{\partial x_j}, G_{11} \cdot G_{110} = 0.6 \Delta x = \sqrt{G_{110}/\alpha_0} \alpha_0 = |\alpha|_{T = 25^\circ C} \]

If \( \Delta x = 1 \text{ nm}, \ G_{110} = 0.465 \times 10^{-10} \text{ C}^{-2}\text{m}^4\text{N} \] [15] [27]


VITA

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