PHASE-FIELD SIMULATIONS OF MICORSTRUCTURES
INVOLVING LONG-RANGE ELASTIC, MAGNETOSTATIC AND ELECTROSTATIC INTERACTIONS

A Thesis in
Materials Science and Engineering
by
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ABSTRACT

The phase-field approach is one of the most powerful methods for modeling microstructure evolution processes. In this thesis, phase-field models were developed to study the domain structures and domain structure evolution in ferroelectric materials, ferromagnetic materials (giant magnetostrictive materials), and ferroelectric-ferromagnetic composite materials, i.e. the materials involving long-range elastic, magnetostatic and electrostatic interactions, which provide us a powerful tool for understanding the properties and behaviors of these materials.

The effects of substrate constraint for the epitaxial BiFeO$_3$ thin films were systemically studied by using thermodynamic calculations and phase-field simulations. It was demonstrated that the spontaneous polarizations, domain structures, and domain wall stabilities of BiFeO$_3$ 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 BiFeO$_3$ by heteroepitaxy and strain engineering experimentally.

It was also found that the domain structures of ferroelectric islands could be significantly different from those of continuous ferroelectric films due to the relief of substrate constraint. The dependence of the stress distribution on the aspect ratio of the islands gives us a new tool to control the domain structures and piezoelectric properties of the ferroelectrics.

In this thesis, phase-field simulations were conducted to clarify the role of magnetostatic energy and elastic energy in determining the domain structures of giant
magnetostrictive materials. It was also demonstrated that a compressive pre-stress could efficiently increase the overall magnetostrictive effect. The results agreed well with existing experiment measurements and observations.

We also studied the ferroelectric-ferromagnetic nanocomposite films by using the phase-field model. It was shown that the magnetoelastic coupling effect was highly dependent on the thickness and morphology of the nanocomposite, and substrate constraint.
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Chapter 1

INTRODUCTION

1.1 General Background

1.1.1 Ferroelectric Materials

A ferroelectric is a material that shows, over some temperature range, a spontaneous polarization $P_s$ that is re-orientable between crystallographically defined states upon application of sufficiently high electric fields [1]. The basic element responsible for ferroelectricity is electric dipole $p$. Whenever a separation between charges of equal magnitude but opposite sign exists, there is a dipole defined by $p = qq r$, where $q$ is the magnitude of the charge, and $r$ is the displacement vector pointing from the negative charge to the positive charge. For a typical ferroelectric material that is made up of more than one type of ion, each ion can be considered to have a charge at its center. Above the Curie temperature ($T_c$), as it is illustrated in Figure 1-1(a), the charge centers are arranged in such a way that cancels overall, and there are no dipoles in such a case. However, below the Curie temperature, the ions will change their relative position, as shown in Figure 1-1(b), and the electric dipoles are created by the shift. The second-order Jahn-Teller effects are responsible for the stabilization of the distorted structure [2]. Given the occurrence of electric dipoles, the dipole-dipole interaction is the primary
driving force for the long-range ordering of the dipole moment [2], which yield the net ferroelectric spontaneous polarization. The occurrence of a spontaneous polarization below Curie temperature also results in a change in lattice parameters and therefore is accompanied by the creation of a spontaneous strain, as shown in Figure 1-2. The relationship between the spontaneous polarization and spontaneous strain is given by

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

where $Q_{ijkl}$ are the electrostrictive coefficients [3].

---

Figure 1-1: Schematic diagram of a two-dimensional crystal lattice (a) above Curie temperature; (b) below Curie temperature.
The spontaneous polarization in ferroelectric materials is usually not uniformly aligned throughout the whole crystal along the same direction. The regions with uniformly oriented spontaneous polarization are called ferroelectric domains, while the region between two neighboring domains is called the domain wall. Depending on the crystal structure of the ferroelectrics, the number of possible polarization directions may vary. In a roombohedral ferroelectric crystal, for example, the polarization orients along the eight <111> crystal axes of the paraelectric cubic unit cell, giving rise to 180°, 109° or 71° domain walls. Similarly, in a tetragonal ferroelectric crystal, the polarization is along the six <100> crystal axes, and the available domain walls are 180° or 90° walls. Non-180° domain walls are both ferroelectric and ferroelastic, since they differ in both the spontaneous polarizations and spontaneous strains. While 180° domain walls are purely

Figure 1-2: The perovskite structure ABO₃ that has a cubic structure in the paraelectric phase and tetragonal structure in the ferroelectric phase.
ferroelectric as the two neighboring domains have exactly the same spontaneous strains but different spontaneous strains.

The equilibrium ferroelectric domain structures are determined by the minimizing the total free energy of the system. The electrostatic energy will generate whenever there is a discontinuity in the distribution of the spontaneous polarization, which acts like a charge density, for example the bulk charge density $\rho(r) = -\nabla \cdot P(r)$ as well as the surface charge density $\sigma = P \cdot \hat{n}$, where $\hat{n}$ is the vector normal to the boundary surface. To minimize surface charge density, polarizations are oriented to be parallel to the crystal surface, which introduces the domain walls into the domain structures. The surface charges can also be significantly reduced by the presence of metal electrodes or other free charge carriers that provide the charge compensation at the ferroelectric surfaces. In addition, to keep the mechanical continuity between the ferroelectric domains with different spontaneous strains, elastic strain (also elastic energy) is generated during the phase transition. The existence of external constraints (such as other grains or a substrate in the case of thin films) also significantly changes the elastic energy, and results in the formation of domain structures [4-5]. However, the creation of domains in ferroelectrics implies the creation of domain walls, to which is also associated a free energy. Therefore, the equilibrium ferroelectric domain structures correspond to the minimum of all these energy contributions. It is important to emphasize that the domain wall orientations are not in arbitrary planes. For example, minimization of the interface charges between neighboring domains requires that the domain wall parallel (or anti-parallel) to the polarization vector (for the 180° domain wall) or the domain wall bisects the angle between two domains pointing head-to-tail (for the non-180° domain wall), i.e.
essentially meet the electrostatic compatibility conditions [6]. The orientations of domain walls are also constrained by the elastic compatibility condition [7], which requires that the spontaneous deformations of two neighboring domains match each other along the plane of domain wall.

1.1.2 Ferromagnetic Materials

In analogy to the ferroelectrics, a ferromagnetic material has a spontaneous magnetization that can be reoriented by an external magnetic field [8]. Ferromagnetic materials are one of the oldest functional materials on earth. The metallic meteorites consisting mostly of pure iron, which is ferromagnetic at room temperature, have existed on earth for millions of years. However the origin of ferromagnetism remained as a puzzle until last two hundred years. The spin of an electron, combined with the motion of the electron along its orbit, results in a magnetic moment. In many materials, however, the total magnetic moment of all the electrons is zero (i.e., the spins are in up/down pairs). Only atoms with partially filled shells (i.e., unpaired spins) can experience a net magnetic moment in the absence of an external magnetic field. In a ferromagnetic material, the magnetic moments tend to align spontaneously due to quantum-mechanical exchange interaction, which is called as spontaneous magnetization [9]. Above the Curie temperature, the thermal energy, $kT$ (where $k$ is Boltzmann's constant and $T$ is the temperature), and associated entropic effect overcome the exchange energy, resulting in random orientation of the magnetic moments and paramagnetic bahaviour [10].
Similar to the ferroelectric materials, there is also a shape change associated with the spontaneous magnetization, as shown in Figure 1-3, which is called as magnetostriction [11]. It is an effect observed, to differing degrees, in all ferromagnetic materials. The magnetostrictive coefficients $\lambda_{ijkl}$ relate the spontaneous strains to the square of the spontaneous magnetization, i.e.

$$\varepsilon_{ij}^0 = \lambda_{ijkl} M_k M_l$$  \hspace{1cm} (1.2)

While typical magnetostrictive strains of magnetic materials are of the order of $10^{-5}$~$10^{-6}$, some compounds containing rare earth elements have magnetostriction as high as $10^{-3}$, for example, Terfenol-D ($\text{Tb}_x\text{Dy}_{1-x}\text{Fe}_2$, $x = 0.3$) [11,12]. It has been recently found that large magnetostriction also occurs in FeGa alloys (galfenol) [13-15].

![Diagram](image)

**Figure 1-3**: Schematic diagram illustrating the magnetostriction of a ferromagnetic material. (a) paramagnetic state above Curie temperature; (b) ferromagnetic phase below Curie temperature; and (c) ferromagnetic phase under an external field $\mathbf{H}$. 
One of the most notable common features between the ferroelectric materials and ferromagnetic materials is the occurrence of domain structures. The spontaneous magnetization follows the easy axes determined by the anisotropy energy. Similar to the electrostatic energy, the magnetostatic energy will generate wherever there is a discontinuity of magnetization distribution, i.e. “magnetic charges” exist [16]. But different from the ferroelectrics, the “magnetic charges” that generated on material surfaces cannot be screened, since there is no magnetic "point charges" (so-called magnetic monopoles) exist. The elastic energy usually can be ignored in ferromagnetic materials due to the small magnetostriction effect, but this is not the case for the giant magnetostrictive materials, where large elastic energy will be generated to accommodate the shape changes associated with the spontaneous magnetizations. Therefore, both the magnetostatic energy and elastic energy play an important role in determining the domain structures and domain wall orientations of giant magnetostrictive materials.

1.2 Research Objectives

As we discussed in the last section, the domain structures of ferroelectric and ferromagnetic materials are determined by the minimization of the total free energy of the system, and as a result, they depend on many factors, such as electrical and mechanical boundary conditions, size and shape of the materials, applied fields, the presence of free charge carriers (for ferroelectric materials only), and even the presence and distribution of local defects. Moreover, the elastic energy and electrostatic (magnetostatic) energy are non-local energy contributions, which means that the electric (magnetic) field at certain
position inside the material will depend on the polarization (magnetization) at every other point of the material through these long-range interactions. Therefore, studying the domain structures of the ferroelectric/ferromagnetic materials is turn out to be very complex not only experimentally but also numerically.

Phase-field model is a powerful tool for microstructure simulations and has provided for a considerable insight into the microstructure evolution of various materials [17]. Unlike the classical approaches, phase-field model describes a microstructure, both the compositional/structural domains and the interfaces, as a whole by using a set of field variables. Since there is no need to track the interfaces, phase-field model can be used to study complicated three-dimensional microstructures. Typical examples of field variables used in phase-field models are the concentration and long-range order parameters that characterize the compositional and structural heterogeneities, respectively. The field variables change smoothly from one phase/domain to another across the interfacial regions, and hence the interfaces in a phase-field model are diffuse. The temporal microstructure evolution is described by the temporal evolution of the field variables toward the thermodynamics equilibrium, governed by a pair of well-known continuum equations, namely, the Cahn-Hilliard nonlinear diffusion equation [18] and the Allen-Cahn (time-dependent Ginzburg-Landau) [19] equation.

\[
\frac{\partial c(r,t)}{\partial t} = MV^2 \frac{\delta F}{\delta c(r,t)} \tag{1.3}
\]

\[
\frac{\partial \eta_p(r,t)}{\partial t} = -L_{pq} \frac{\delta F}{\delta \eta_q(r,t)} \tag{1.4}
\]
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 solutions of these equations provide the morphologies as well as kinetic features such as the growth law. Throughout the past decade, the phase-field method has been extensively employed to simulate microstructure evolutions during phase transformations, including spinodal decomposition [20-23], precipitation of an ordered phase from a disordered matrix [24-26], cubic to tetragonal transformation [27], grain growth [28-30], and martensite transformations [31,32].

The goal of this thesis is extending phase-field models to understand and predict the domain structures of ferroelectrics/ferromagnetic materials, which involve the long-range elastic, magnetostatic and electrostatic interactions. The specific objectives are as follows:

(1) To apply phase-field models and corresponding thermodynamic calculations to study the effects of substrate constraint on the spontaneous polarizations, domain structures, and domain wall stabilities of BiFeO$_3$ thin films.

(2) To develop a three-dimensional phase-field model for the study of ferroelectric islands, which simultaneously takes into account the long-range interactions such as electrostatic and elastic interactions, substrate constraint, as well as the stress relaxation effect caused by the edges of islands.

(3) To develop a three-dimensional computational model to study the stability and evolution of magnetic domain structures in giant magnetostrictive materials. It combines the micromagnetic model for ferromagnetic domain evolution [33] and the
phase-field microelasticity theory [34,35] for the elastic solutions in a magnetostrictive material with arbitrary distributions of ferromagnetic domains.

(4) To develop a three-dimensional phase-field model for predicting the magnetoelectric coupling effect in ferroelectric-ferromagnetic nanocomposite thin films. The model simultaneously takes into account the ferroelectric and ferromagnetic domain structures, the electrostrictive and magnetostrictive effects, substrate constraint, as well as the long-range interactions such as elastic, magnetostatic and electrostatic interactions.

1.3 Thesis Structure

This thesis has been organized into 7 chapters.

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

In Chapter 2, the effects of substrate constraint on the spontaneous polarizations of epitaxial BiFeO$_3$ thin films were studied using Landau-type thermodynamic calculations.

In Chapter 3, a phase-field model was applied to study the effects of substrate constraint on the domain structures and domain wall stabilities of BiFeO$_3$ thin films.

In Chapter 4, a phase-field model was developed to simulate the domain structures of ferroelectric islands. The domain structures of PbZr$_{0.2}$Ti$_{0.8}$O$_3$ islands were investigated as an example.

In Chapter 5, a computational model for predicting the stability of domain structures and their temporal evolution in giant magnetostrictive materials was
developed. The domain structures of Fe$_{81.3}$Ga$_{18.7}$ and Terfenol-D were studied by the model.

In Chapter 6, a phase-field model was developed to predict the magnetoelectric coupling in a nanocomposite film made up of ferroelectric and giant magnetostrictive materials. The dependence of magnetic field-induced electric polarization (MIEP) on the film thickness, morphology of the nanocomposite, and substrate constraint in BaTiO$_3$-CoFe$_2$O$_4$ nanocomposite films was analyzed.

Chapter 7 includes final conclusions and discussions on some future directions.
References

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Chapter 2

EFFECT OF SUBSTRATE CONSTRAINT ON THE SPONTANEOUS POLARIZATION OF EPITAXIAL BIFO3 THIN FILMS

2.1 Introduction

Ferroelectric material is a class of functional materials that is attractive for a variety of applications due to its superior piezoelectric, dielectric, and pyroelectric properties. Recently, the research on ferroelectric materials has shifted from bulk materials (ceramics, single crystal) to thin films, due to the potential silicon-based microelectromechanical system (MEMS) sensor and actuator applications [1]. However, 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. Owing to the strong coupling between strain and ferroelectricity, $T_c$ shift of hundred degrees has been observed in strained BaTiO3 thin films [2], and the paraelectric bulk SrTiO3 materials even showed ferroelectricity at room temperature in thin films [3].

The material we are interested in this Chapter and Chapter 3 is BiFeO3. There has been considerable interest in developing BiFeO3 magnetoelectric materials recently, which are simultaneously antiferromagnetic and ferroelectric at room temperature [4-6]. Bulk BiFeO3 single crystals have a Curie temperature of $T_c\approx1103$ K, and a Néel temperature of $T_N\approx643$ K. The ferroelectric phase of BiFeO3 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: 

$r_1^+ = [111]_c$, $r_2^+ = [\overline{1}11]_c$, $r_3^+ = [\overline{1}1\overline{1}]_c$, $r_4^+ = [\overline{1}1\overline{1}]_c$,

$r_1^- = [1\overline{1}1]_c$, $r_2^- = [\overline{1}1\overline{1}]_c$, $r_3^- = [11\overline{1}]_c$, and $r_4^- = [1\overline{1}\overline{1}]_c$. However, for epitaxial BiFeO$_3$ thin films, the existence of a free surface and substrate constraint destroys the macroscopic symmetry of the system and may significantly affect the properties of BiFeO$_3$. Recently, large ferroelectric polarizations have been reported in heteroepitaxially constrained thin films of BiFeO$_3$ [4,7,8]. 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 [4]. However, the substrate strain effect on the spontaneous polarization of BiFeO$_3$ thin films is still unclear. For example, first-principles calculations showed [9,10] 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 [11].

Landau-type phenomenological theory has been extensively used to study the physical properties of single-domain ferroelectric thin films [12-16]. In this chapter, we extend the thermodynamic theory of ferroelectric thin films to variously oriented (i.e. (001)$_c$, (101)$_c$, and (111)$_c$) epitaxial BiFeO$_3$ thin films with general substrate strains. We focus on the spontaneous polarization of BiFeO$_3$ thin films and its dependence on substrate strains at room temperature. Our results are compared to previous experimental and theoretical studies.
2.2 Results and Discussions

We consider a single-domain (001) \(_c\) oriented BiFeO\(_3\) thin film grown on a dissimilar substrate. For a phenomenological description of BiFeO\(_3\) with coexistence of ferroelectric and antiferromagnetic orders, in principle, both the spontaneous polarization \( \mathbf{P} = (P_1, P_2, P_3) \) and spontaneous magnetization \( \mathbf{M} = (M_1, M_2, M_3) \) should be chosen as the order parameters. If we set up a rectangular coordinate system, \( \mathbf{x} = (x_1, x_2, x_3) \) with the \( x_1, x_2, \) and \( x_3 \) axes along the [100]\(_c\), [010]\(_c\), and [001]\(_c\) crystallographic directions of the BiFeO\(_3\) film, respectively, the free energy of BiFeO\(_3\) using a Landau-type of expansion can be written as [17]

\[
F(P, M, \mathbf{\varepsilon}) = \alpha_0 (P_1^2 + P_2^2 + P_3^2) + \alpha_1 (P_1^4 + P_2^4 + P_3^4) + \alpha_{12} (P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2) \\
+ \beta_0 (M_1^2 + M_2^2 + M_3^2) + \beta_1 (M_1^4 + M_2^4 + M_3^4) + \beta_{12} (M_1^2 M_2^2 + M_1^2 M_3^2 + M_2^2 M_3^2) \\
+ \gamma_{ijkl} P_j M_k M_l + \frac{1}{2} \epsilon_{ijkl} \epsilon_{ij} \epsilon_{kl} - \frac{1}{2} q_{ijkl} \epsilon_{ij} P_k P_l - \frac{1}{2} \lambda_{ijkl} \epsilon_{ij} M_k M_l + ..., \tag{2.1}
\]

where \( \epsilon_{ij} \) are the strain components, \( \alpha_0, \alpha_1, \beta_0, \) and \( \beta_1 \) are the phenomenological Landau expansion coefficients, \( \gamma_{ijkl} \) are the magnetoelectric coupling coefficients, \( c_{ijkl} \) and \( q_{ijkl} \) are the elastic constants and electrostrictive constants, respectively, and \( \lambda_{ijkl} \) are the magnetoelastic coupling coefficients. The summation convention for the repeated indices is employed and \( i, j, k, l = 1, 2, 3 \). The electrostrictive coefficients, \( q_{ijkl} \), defined here can be easily obtained from

\[
q_{ijkl} = 2 c_{ijmn} Q_{mkl} \tag{2.2}
\]
where $Q_{mkl}$ are the electrostrictive coefficients typically measured experimentally. Although sixth order terms in polarization are required for a first-order ferroelectric transition in BiFeO$_3$ [18], we only considered terms up to fourth order due to the lack of sufficient experimental data to obtain the numerical values of all the coefficients. Since our focus is on the effect of substrate strains on the spontaneous polarization of BiFeO$_3$ thin films at room temperature, such approximation will not impact the main results of this paper. We also neglect the magnetoelectric coupling term in Eq. 2.1 due to fact that BiFeO$_3$ has a large polarization but a quite small saturated magnetization [5], and the coupling term should have small effect on the spontaneous polarization. With these approximations, the free energy expression of BiFeO$_3$ was reduced to

$$F(P, \varepsilon) = \alpha_1 (P_1^2 + P_2^2 + P_3^2) + \alpha_{11} (P_1^4 + P_2^4 + P_3^4) + \alpha_{12} (P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2)
+ \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} - \frac{1}{2} q_{ijkl} \varepsilon_{ij} P_k P_l,$$

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+ \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} - \frac{1}{2} q_{ijkl} \varepsilon_{ij} P_k P_l,$$

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+ \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} - \frac{1}{2} q_{ijkl} \varepsilon_{ij} P_k P_l,$$

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+ \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} - \frac{1}{2} q_{ijkl} \varepsilon_{ij} P_k P_l,$$

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+ \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} - \frac{1}{2} q_{ijkl} \varepsilon_{ij} P_k P_l,$$

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$$F(P, \varepsilon) = \alpha_1 (P_1^2 + P_2^2 + P_3^2) + \alpha_{11} (P_1^4 + P_2^4 + P_3^4) + \alpha_{12} (P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2)
+ \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} - \frac{1}{2} q_{ijkl} \varepsilon_{ij} P_k P_l,$$
coefficients. The calculated ferroelectric properties of BiFeO$_3$ films at room temperature are compared in Table 2-1 with the available experimentally measured values.

<table>
<thead>
<tr>
<th>Properties of BiFeO$_3$ films (on SrTiO$_3$ substrates)</th>
<th>This work$^*$</th>
<th>Experimental measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polarization ($P_3^c$) of (001)$_c$ BiFeO$_3$ film (C/m$^2$)</td>
<td>0.63</td>
<td>0.55 [21], 0.64 [22]</td>
</tr>
<tr>
<td>Polarization ($P_3^c$) of (101)$_c$ BiFeO$_3$ film (C/m$^2$)</td>
<td>0.80</td>
<td>0.80 [21], 0.81 [22]</td>
</tr>
<tr>
<td>Polarization ($P_3^c$) of (111)$_c$ BiFeO$_3$ film (C/m$^2$)</td>
<td>0.96</td>
<td>1.00 [21], 0.96 [22]</td>
</tr>
<tr>
<td>$\varepsilon_{33}$ of (111)$_c$ BiFeO$_3$ film</td>
<td>62</td>
<td>45 [21], 60 [22]</td>
</tr>
</tbody>
</table>

For a general case, strains are imposed along the $x_1$-$x_2$ directions while all the stress components involving the $x_3$ direction are zero due to the existence of the free film surface, i.e.

$$
\varepsilon_{11} = \varepsilon_{11}^0, \varepsilon_{22} = \varepsilon_{22}^0, \varepsilon_{12} = \varepsilon_{21} = \varepsilon_{12}^0, \\
\sigma_{13} = \sigma_{31} = \sigma_{23} = \sigma_{32} = \sigma_{33} = 0,
$$

where the misfit strains $\varepsilon_{ij}^0$ depend on the lattice parameters of the film and substrate. With such specified boundary conditions, the free energy of (001)$_c$ oriented BiFeO$_3$ thin film is given by

* The substrate strains were assumed to be $\varepsilon_{11}^0 = \varepsilon_{22}^0 = -0.015, \varepsilon_{12}^0 = 0$ in the calculations.
The spontaneous polarization can be derived from Eq. 2.5 by solving \( \frac{\partial F}{\partial P_i} = 0 \) \((i = 1, 2, 3)\).

For the case that a \((001)_c\) oriented BiFeO\(_3\) film epitaxially grown on a \((001)_c\) oriented cubic single crystal substrate with an in-plane orientation relationship of [100]\(_c^{BiFeO_3}\) // [100]\(_c\), a constant dilatational plane strain, so-called biaxial strain, is imposed along the \(x_1-x_2\) directions, \(\varepsilon_{11}^0 = \varepsilon_{22}^0\), \(\varepsilon_{12}^0 = 0\).

\[ F = \left[ \alpha_1 - \left( \frac{c_{1111}q_{1111} - c_{1222}q_{1122}}{2c_{1111}} \right) \varepsilon_{11}^0 + \left( \frac{c_{1111}q_{1111} - c_{1222}q_{1122}}{2c_{1111}} \right) \varepsilon_{22}^0 \right] P_1^2 \]

\[ + \left[ \alpha_1 - \left( \frac{c_{1111}q_{1111} - c_{1222}q_{1122}}{2c_{1111}} \right) \varepsilon_{11}^0 + \left( \frac{c_{1111}q_{1111} - c_{1222}q_{1122}}{2c_{1111}} \right) \varepsilon_{22}^0 \right] P_2^2 \]

\[ + \left[ \alpha_1 - \left( \frac{c_{1111}q_{1111} - c_{1222}q_{1122}}{2c_{1111}} \right) \varepsilon_{11}^0 + \left( \frac{c_{1111}q_{1111} - c_{1222}q_{1122}}{2c_{1111}} \right) \varepsilon_{22}^0 \right] P_3^2 - 2q_{1212} \varepsilon_{12}^0 P_1 P_2 
\]

\[ \mathbf{2.5} \]

\[ + \left( \frac{\alpha_{12} - \frac{q_{1212}^2}{4c_{1111}}} \right) P_1^2 P_2^2 + \left( \alpha_{12} - \frac{q_{1111}q_{1122}}{4c_{1111}^2} - \frac{q_{1212}^2}{2c_{1212}} \right) P_1^2 P_3^2 + P_2^2 P_3^2 \]

\[ + \left( \frac{\alpha_{11} - \frac{q_{1212}^2}{8c_{1111}}} \right) P_1^4 + P_2^4 + \left( \alpha_{11} - \frac{q_{1111}^2}{8c_{1111}^2} \right) P_3^4 \]

\[ - \frac{c_{1222}(\varepsilon_{11}^0 + \varepsilon_{22}^0)^2}{2c_{1111}} + \frac{1}{2} c_{1111}[ (\varepsilon_{11}^0)^2 + (\varepsilon_{22}^0)^2 ] + c_{1222} \varepsilon_{11}^0 \varepsilon_{22}^0 + 2c_{1212} (\varepsilon_{12}^0)^2. \]

It should be noted that Eq. 2.5 is essentially the same as that reported in Ref. 15 except for the sixth-order terms and the different notation of coefficients. The dependence of the polarizations on the substrate strains is shown as Figure 2-1. We can see that the in-plane components of polarization \(|P_1| = |P_2|\) are not equal to the out-of-plane component \(|P_3|\) due to the constraint of the...
substrate. As expected, compressive substrate strains lead to an increase in $|P_3|$ and decrease in $|P_1|$ and $|P_2|$, while tensile substrate strains have the opposite effect. Therefore, the direction of the polarization vector deviates from its equilibrium $<111>_c$ directions (towards [001]$_c$/[00¯1]$_c$ directions for compressive strains and [110]$_c$/[11¯0]$_c$/[1¯10]$_c$ directions for tensile strains). As shown in Figure 2-1(b), BiFeO$_3$ becomes the monoclinic $M_A$ phase and $M_B$ phase [23], respectively, which is consistent with prior experimental observations [7,24]. However, the change of the absolution value of the spontaneous polarization ($P_s = |P|$) with the substrate strains is rather small as shown in Figure 2-1(a). For example, a rather large compressive strain of 1.6% leads to an increase of $P_s$ only about 0.3%. It should be noted that all the eight polarization variants are degenerate in energy and hence should exist with the same probability in the (001)$_c$ oriented BiFeO$_3$ thin film.
Figure 2-1: (a) Free energy ($F$) and $P_s$, (b) polarization components of (001)$_c$ oriented BiFeO$_3$ thin films as a function of normal substrate strains. (The free energy and $P_s$ of rhombohedral phase (R) and tetragonal phase (T) were also given for comparison)
For the case that a (001) oriented BiFeO₃ film epitaxially grown on a (110) oriented orthorhombic substrate (for example (110) oriented DyScO₃) with an in-plane orientation relationship of [100]_{BiFeO₃} \|[\bar{1}10]_{o} and [010]_{BiFeO₃} \|[001]_{o} , an anisotropic in-plane strain, is imposed along the \( x_1-x_2 \) directions, while there is no shear strain.

\[
\varepsilon_{11}^0 \neq \varepsilon_{22}^0, \quad \varepsilon_{12}^0 = 0,
\]

where

\[
\varepsilon_{11}^0 = \frac{\sqrt{a_s^2 + b_s^2} - a_{BiFeO₃}}{a_{BiFeO₃}}, \quad \varepsilon_{22}^0 = \frac{c_s - a_{BiFeO₃}}{a_{BiFeO₃}},
\]

and \( a_s, b_s, \) and \( c_s \) are the lattice parameters of the orthorhombic substrate. By fixing the ratio of \( \varepsilon_{11}^0 / \varepsilon_{22}^0 \), we plot the dependence of free energy and \( P_s \) on the substrate strains in Figure 2-2(a). It was interesting to note that all the eight polarization variants have equal energy even under the anisotropy substrate strains. The absolution value of the spontaneous polarization \( P_s \) is insensitive to the normal substrate strains.
Figure 2-2: Free energy ($F$) and $P_s$ of various polarization variants for (001)$_c$ oriented BiFeO$_3$ thin films as a function of (a) anisotropic normal substrate strains and (b) shear substrate strains.
Shear substrate strain may also exist for (001) \textit{c} oriented BiFeO$_3$ films, i.e. \( \varepsilon_{11}^0 = \varepsilon_{22}^0 \neq 0, \varepsilon_{12}^0 \neq 0 \). A potential example would be a (001)$_{c}$ oriented BiFeO$_3$ film constrained by a (001)$_{o}$ orthorhombic substrate with an in-plane orientation relationship of [100]$_{c}^{BiFeO_3}$/[110]$_{o}$ and [010]$_{c}^{BiFeO_3}$/[\(\bar{1}10\)]$_{o}$. The shear strain is \( \varepsilon_{12}^0 = \frac{1}{2} \cos \gamma \), where \( \gamma \) is the angle between [110]$_{o}$ and [\(\bar{1}10\)]$_{o}$ crystallographic axes of the substrate. For simplicity, we assume \( \varepsilon_{11}^0 = \varepsilon_{22}^0 = 0 \) in this work. Unlike previous studied cases, the energies of the eight polarization variants are no longer degenerate under the shear substrate strain as shown in Figure 2-2 (b). Under a negative shear substrate strain, four variants \( (r_2^+, r_2^-, r_4^+, \text{ and } r_4^-) \) have lower energy, while under a positive shear substrate strain the energies of the other four variants \( (r_1^+, r_1^-, r_3^+, \text{ and } r_3^-) \) are lower. From Figure 2-2 (b), one can see that \( P_s \) changes with the shear substrate strain. For example, \( P_s \) (for \( r_1^+, r_1^-, r_3^+, \text{ and } r_3^- \)) increases about 3.6% for a strain \( \varepsilon_{12}^0 = 1.6\% \), which is significant compared to the effect of normal substrate strains. However, the magnitude of change is still dramatically smaller than other traditional ferroelectric systems such as BaTiO$_3$.

For comparison, we also performed calculations by assuming that the symmetry of BiFeO$_3$ was fixed to be rhombohedral \(|P_1| = |P_2| = |P_3| = P_s/\sqrt{3} \) or tetragonal \((P_1 = P_2 = 0, |P_3| = P_s)\) for the case of bi-axial normal substrate strains \( (\varepsilon_{11}^0 = \varepsilon_{22}^0 = e^0, \varepsilon_{12}^0 = 0) \). By reducing Eq. 2.5 with such symmetry relations, the corresponding spontaneous polarization can be obtained by solving \( \frac{\partial F}{\partial P_i} = 0 \). For rhombohedral symmetry,
For tetragonal symmetry,

\[
P_s^2 = \frac{6c_{1212}[-6a_ic_{1111} + 2(c_{1111} - c_{1122})(q_{1111} + 2q_{1122})e^0]}{c_{1212}[24(a_{11} + a_{12})c_{1111} - (q_{1111} + 2q_{1122})^2] - 8c_{1111}q_{1212}^2} \tag{2.8}
\]

For tetragonal symmetry,

\[
P_s^2 = \frac{-4a_ic_{1111} - 4(c_{1122}q_{1111} - c_{1111}q_{1122})e^0}{8a_{11}c_{1111} - q_{1111}^2} \tag{2.9}
\]

From Eq. 2.8, one can see that, when BiFeO₃ has the rhombohedral symmetry, the effect of normal substrate strains on \( P_s \) is highly related to the magnitude of \( (q_{1111} + 2q_{1122}) \), which is given by

\[
q_{1111} + 2q_{1122} = 2(c_{1111} + 2c_{1122})(Q_{1111} + 2Q_{1122}) \tag{2.10}
\]

However, the BiFeO₃ phases with tetragonal symmetry and rhombohedral symmetry are unstable in the range of substrate strains we studied, as the thermodynamic calculations shown in Figure 2-1. For the (001)$_c$ oriented BiFeO₃ thin films, the symmetry reduced to monoclinic, for which the calculations are more complicated. For simplicity, we first ignore the elastic energy term origin from the shear mismatch between the film and substrate. However it should be noted that the shear mismatch also has small effect on the polarization, which will be discussed later. The spontaneous polarization is given by minimizing the total free energy, i.e.

\[
P_s^2 = \frac{1}{2} \frac{-a_i[6a_i(e_{i1} - 3a_i + c_{i1} + 2c_{11})(Q_{11} - Q_{12})] + 2(2a_{11} - a_{12})(c_{11} - c_{12})(c_{11} + 2c_{12}) + 2Q_{11} + 2Q_{12}]}{2a_i^2(e_{i1} - a_{11} + c_{i1} + 2c_{11})(Q_{11} + Q_{12}) + a_i[6a_i(e_{i1} + c_{i1} + 2c_{11})(Q_{11} + Q_{12}) + 2a_{11} - a_{12}(c_{11} + 2c_{12}) + 2Q_{11} + 2Q_{12} + 3Q_{12}²]} \tag{2.11}
\]

We can see that the strain-dependence of spontaneous polarization is also proportional to \( Q_{11} + 2Q_{12} \). However, the value of \( Q_{11} + 2Q_{12} \) is very small for BiFeO₃, therefore the spontaneous polarization does not change much with the strain. Now we
discuss the effect of the shear mismatch on the polarization, which has been ignored so far. As the in-plane shear strain $\varepsilon_{12}^0 = Q_{44} P_1 P_2$, minimizing the shear elastic strain (energy) will result in the decrease of the in-plane components of the spontaneous polarization $|P_1|$ ($|P_2|$), and as a result the spontaneous polarization $P_s$ will also decrease. However, with the increase of normal compressive substrate strains, the effect of the shear elastic strain (energy) will become less important, since the magnitude of $P_1$ ($P_2$) will decrease as we discussed above. Consequently, with the increase of compressive substrate strains, the spontaneous polarization will increase a little bit due to the reduced shear strain effect. On the other side, the effect of the shear elastic strain (energy) will increase under a tensile substrate strain, due to the enhanced magnitude of $P_1$ ($P_2$), as a result the spontaneous polarization will decrease with the increase of tensile substrate strains (as shown in Figure 2-1). From these discussions, we may conclude that the strain-dependence of spontaneous polarizations for (001)$_c$ oriented ferroelectric thin films with monoclinic (distorted rhombohedral) symmetry mainly depends on the values of $(Q_{11} + 2Q_{12})$.

We now discuss (111)$_c$ oriented BiFeO$_3$ thin films grown on a dissimilar substrate. A new coordinate system, $x' = (x'_1, x'_2, x'_3)$, is set up with the $x'_1$, $x'_2$, and $x'_3$ axes along the $[\bar{0}\bar{1}\bar{1}]_c$, $[\bar{2}\bar{1}1]_c$, and $[111]_c$ crystallographic directions of BiFeO$_3$, respectively. The free energy of BiFeO$_3$ in the coordinate system $x'$ is given by:
where \( t_{ij} \) is the transformation matrix from the coordinate system \( x \) to the coordinate system \( x' \). \( P_i' \), \( \varepsilon_{ij}' \), \( c_{ijkl}' \), and \( q_{ijkl}' \) are the polarizations, strains, elastic constants, and electrostrictive constants in the coordinate system \( x' \), which are given by:

\[
P_i' = t_{ij} P_j,
\]
\[
\varepsilon_{ij}' = t_{im} t_{jn} \varepsilon_{mn},
\]
\[
c_{ijkl}' = t_{im} t_{jn} t_{ks} t_{lp} c_{mnop},
\]
\[
q_{ijkl}' = t_{im} t_{jn} t_{ks} t_{lp} q_{mnop},
\]

with the transformation matrix

\[
t_{ij}^{111c} = \begin{pmatrix}
0 & \frac{1}{\sqrt{2}} & \frac{1}{\sqrt{2}} \\
-\frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} \\
\frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}} & \frac{1}{\sqrt{3}}
\end{pmatrix}
\]

For a (111)_c oriented film deposited on a (111)_c oriented cubic crystal substrate with an in-plane orientation relationship of \( [\overline{110}]_c^{\text{BiFeO}_3} // [\overline{110}]_c \), the elastic boundary condition is given by

\[
\varepsilon_{11}' = \varepsilon_{11}'^0, \varepsilon_{22}' = \varepsilon_{22}'^0, \varepsilon_{12}' = \varepsilon_{21}' = 0,
\]
\[
\sigma_{13}' = \sigma_{31}' = \sigma_{23}' = \sigma_{32}' = \sigma_{33}' = 0.
\]
where $\varepsilon_{11}^0 = \varepsilon_{22}^0 = \frac{a_z - a_{BiFeO_3}}{a_{BiFeO_3}}$, $a_z$ and $a_{BiFeO_3}$ are the lattice parameters of the substrate and film respectively. Unlike the (001) c oriented film, under a biaxial substrate strain the polarization variants do not have equal energy except for a critical point at $\varepsilon_{11}^0 = \varepsilon_{22}^0 \sim 0\%$ as shown in Figure 2-3(a). For a large compressive strain, the two polarization variants perpendicular to the film surface ($r_{1}^+$ and $r_{1}^-$) have lower energy than the others, and the compressive substrate strains increase the $P_s$ of the variants, which is consistent with prior first-principles calculations [9,10]. It should be noted that in such a case, BiFeO$_3$ remains the rhombohedral (R) symmetry ($|P_1| = |P_2| = |P_3|$) (as shown in Figure 2-3 (b)), and indeed rhombohedral symmetry is found experimentally in (111)$_c$ epitaxial BiFeO$_3$ film deposited on a (111)$_c$ surface of SrTiO$_3$, which has smaller lattice parameters than BiFeO$_3$ [7,8,25]. At the right side of the critical point in Figure 2-3, the other six polarization variants become more stable energetically. One can see that the substrate strains also increase the spontaneous polarizations of these polarization variants. However, the symmetry of BiFeO$_3$ is no longer rhombohedral, and the stable phases have been marked on Figure 2-3.

It was noted that the remnant polarization (the out-of-plane component of polarization vector $\mathbf{P}$) is less sensitive to the substrate strains for (111)$_c$ oriented BiFeO$_3$ films, compared to the (001)$_c$ oriented films, which is in agreement with previous first-principles calculations [9]. To clarify the origin of such behavior, we plot the free energy profile of the bulk stress-free BiFeO$_3$ crystal as a function of polarizations $P_1 (= P_2)$ and $P_3$ (shown as Figure 2-4). As discussed previously, for (111)$_c$ oriented BiFeO$_3$ thin films, the out-of-plane polarization will increase to relax the compressive substrate strains, and
the rhombohedral symmetry remains unchanged, therefore the change of polarization will follow the route A in the plot (Figure 2-4). While for (001)_c oriented films, \( P_1 \) (\( P_2 \)) will decrease while \( P_3 \) will increase (become distorted rhombohedral symmetry), therefore it will follow the route B in the plot. It is clear to see that there is much larger energy penalty along the route A, which is responsible for the smaller strain-tunablility of (111)_c oriented BiFeO\(_3\) thin film. In fact, this is not a unique property of BiFeO\(_3\), and similar behavior was found in other ferroelectric materials [26]. The good stability of (111)_c oriented films has also been observed experimentally [27], which is a great advantage for application in future FeRAM devices.
Figure 2-3: Free energy ($F$) and $P_s$, (b) polarization components of various polarization variants for (111)$_c$ oriented BiFeO$_3$ thin films as a function of normal substrate strains.
We also study (101)_c oriented BiFeO_3 thin films. The coordinate system x' was set up with the x'_1, x'_2, and x'_3 axes along the [010]_c, [101]_c, and [010]_c crystallographic directions of the BiFeO_3 film, and the free energy of (101)_c oriented BiFeO_3 thin films can be given by Eq. 2.12 with the transformation matrix from the coordinate system x to the coordinate system x':

\[
T^{(100)}_{0} = \begin{pmatrix}
0 & 1 & 0 \\
-\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}} \\
\frac{1}{\sqrt{2}} & 0 & \frac{1}{\sqrt{2}}
\end{pmatrix}
\]  \hspace{1cm} 2.16

For a (101)_c oriented BiFeO_3 film deposited on a (101)_c oriented cubic crystal substrate with an in-plane orientation relationship of [010]_{BiFeO_3} // [010]_c, the elastic boundary condition is given by...
$\varepsilon_{11}^0 = \varepsilon_{22}^0 = \varepsilon_{12}^0 = \varepsilon_{21}^0 = 0,
\sigma_{13} = \sigma_{31} = \sigma_{23} = \sigma_{32} = \sigma_{33} = 0,$

where $\varepsilon_{11}^0 = \varepsilon_{22}^0 = \frac{a_s - a_{\text{BiFeO}_3}}{a_{\text{BiFeO}_3}}$. At a critical point $\varepsilon_{11}^0 = \varepsilon_{22}^0 \sim 0.25\%$, the energies of eight polarization variants are the same, otherwise their energies are different. Polarization variants ($r_1^+$, $r_1^-$, $r_4^+$, and $r_4^-$) have lower energy on the left side of the critical point, while the other four polarization variants are more stable energetically on the right side of the critical point. Consistent with the experimental observation [7,28], the crystal structure of (101)$_c$ oriented BiFeO$_3$ film loses the rhombohedral symmetry as shown in Figure 2-5(b). The substrate strains also change the spontaneous polarizations of these variants as shown in Figure 2-5(a).
Figure 2-5: (a) Free energy ($F$) and $P_s$, (b) polarization components of various polarization variants for (101)$_c$ oriented BiFeO$_3$ thin films as a function of normal substrate strains.
2.3 Summary

In summary, we have extended the Landau-type thermodynamic theory of ferroelectric thin films to a number of different oriented \((001)_c\), \((101)_c\), and \((111)_c\) epitaxial BiFeO\(_3\) thin films with general substrate strains. Our 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 \((001)_c\) oriented BiFeO\(_3\) films, the normal substrate strains only rotate the polarization direction without changing its magnitude. While for \((111)_c\) and \((101)_c\) oriented BiFeO\(_3\) films, normal substrate strains can alter the magnitude of the spontaneous polarization. The relative stabilities of different polarization variants also depend on the orientation of the film and the magnitude of the substrate strains.
References


22. Y. H. Chu (unpublished data)


Chapter 3

EFFECT OF SUBSTRATE CONSTRAINT ON THE DOMAIN STRUCTURES AND DOMAIN WALL STABILITIES OF EPITAXIAL BIFEO3 THIN FILMS

3.1 Introduction

In addition to changing the spontaneous polarization as discussed in Chapter 2, the substrate constraint also play an important role in determining the domain structures of ferroelectric thin films [1-3]. Experimentally, a number of different domain structures have been observed for BiFeO3 films [4-7]. Recent studies have demonstrated the ability to manipulate the ferroelectric domain structures by using vicinal substrates or controlling the growth mode for the bottom electrode [8,9]. Therefore, the study of the ferroelectric domain structures of variously oriented epitaxial BiFeO3 thin film is expected to provide guidance to modify ferroelectric properties by heteroepitaxy and strain engineering.

In this chapter, phase-field models are applied to simulate the domain structures and domain structure evolution of BiFeO3 thin films, which can simultaneously take into account the long-range interactions such as electrostatic and elastic interactions, substrate constraint, as well as the stress relaxation effect caused by the film surface. The effects of substrate constraint on the domain structures and domain wall stabilities of epitaxial BiFeO3 thin films are investigated.
3.2 Phase-field Model of Ferroelectric Thin Films

To study the domain structures of (001)\textsubscript{c}, (101)\textsubscript{c}, and (111)\textsubscript{c} oriented ferroelectric thin films, we introduce two coordinate systems: I: x (x\textsubscript{1}, x\textsubscript{2}, x\textsubscript{3}) with x\textsubscript{1}, x\textsubscript{2}, x\textsubscript{3} along the [100]\textsubscript{c}, [010]\textsubscript{c}, and [001]\textsubscript{c} directions of the pseudocubic cell; and II: x' (x'\textsubscript{1}, x'\textsubscript{2}, x'\textsubscript{3}) with x'\textsubscript{3} out of the film surface, and x'\textsubscript{1} and x'\textsubscript{2} are in plane. For (001)\textsubscript{c} films, x'\textsubscript{1}, x'\textsubscript{2}, and x'\textsubscript{3} are along [100]\textsubscript{c}, [010]\textsubscript{c}, and [001]\textsubscript{c} directions, which are coincident with the coordinate system I. For (101)\textsubscript{c} films, x'\textsubscript{1}, x'\textsubscript{2} and x'\textsubscript{3} are along [010]\textsubscript{c}, [1\bar{0}1]\textsubscript{c}, and [101]\textsubscript{c} directions, respectively. While for (111)\textsubscript{c} films, x'\textsubscript{1}, x'\textsubscript{2} and x'\textsubscript{3} are along [01\bar{1}]\textsubscript{c}, [\bar{2}11]\textsubscript{c}, and [111]\textsubscript{c} directions. The polarization vector in the coordinate system II, P'(P'\textsubscript{1}, P'\textsubscript{2}, P'\textsubscript{3}), is chosen to be the order parameter to describe the ferroelectric domain structures.

The total free energy of a ferroelectric material 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.,

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

3.1

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

$$ F_{\text{bulk}} = \int \left[ \alpha_1 (P_1^2 + P_2^2 + P_3^2) + \alpha_{11} (P_1^4 + P_2^4 + P_3^4) + \alpha_{12} (P_1^2 P_2^2 + P_1^2 P_3^2 + P_2^2 P_3^2) \right] dV $$

3.2

where $\alpha_1$ and $\alpha_{ij}$ are the phenomenological coefficients which determine the transition temperature, the spontaneous polarization, and the dielectric susceptibility in the bulk crystal. $P_j$ are the polarization components in the coordinate system I, which are related to $P'_i$ through
\[ P_i' = t_{ij} P_j \]  \hspace{1cm} 3.3

where \( t_{ij} \) is the transformation matrix from the coordinate system I to the coordinate system II. The transformation matrix for (001)_c, (101)_c, and (111)_c oriented films are given as follows

\[
t_{ij}^{(001)_c} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}, \quad t_{ij}^{(101)_c} = \begin{pmatrix} 0 & 1 \sqrt{2} & -1 \\ -\frac{1}{\sqrt{2}} & 0 & 1 \sqrt{2} \\ \frac{1}{\sqrt{2}} & 0 & 1 \sqrt{2} \end{pmatrix}, \quad t_{ij}^{(111)_c} = \begin{pmatrix} 0 & 1 & 0 \\ -2 & 1 & 1 \\ \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} & \frac{1}{\sqrt{6}} \\ \frac{1}{\sqrt{3}} & 1 & 1 \\ 1 & 1 & 1 \end{pmatrix}. \hspace{1cm} 3.4

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

\[
F_{wall} = \int G_{11}( (P_{i,1})^2 + (P_{i,2})^2 + (P_{i,3})^2 + (P_{2,1})^2 + (P_{2,2})^2 + (P_{2,3})^2 + (P_{3,1})^2 + (P_{3,2})^2 + (P_{3,3})^2 ) dV, \hspace{1cm} 3.5
\]

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:

\[
F_{elec} = -\frac{1}{2} \int \mathbf{E}' \cdot \mathbf{P}' dV, \hspace{1cm} 3.6
\]

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. 3.
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

\[ e'_{ij} = \varepsilon'_{ij} - (\varepsilon^0_{ij})' \]  \hspace{1cm} (3.7)

where \( e'_{ij} \), \( \varepsilon'_{ij} \), and \( (\varepsilon^0_{ij})' \) are the elastic strains, total strains, and stress-free strains in the coordinate system II, respectively. The stress-free strains due to electrostrictive effect can be obtained from

\[ (\varepsilon^0_{ij})' = t_{in} \varepsilon_{jn} (Q_{mnop} P_{op} P_{p}) \]  \hspace{1cm} (3.8)

where \( Q_{mnop} \) are the electrostrictive coefficients in the coordinate system I. The corresponding elastic energy can be expressed as

\[ F_{elas} = \frac{1}{2} \int c'_{ijkl} e'_{ij} e'_{kl} dV = \frac{1}{2} \int c'_{ijkl} [e'_{ij} - (\varepsilon^0_{ij})'][e'_{kl} - (\varepsilon^0_{kl})'] dV \]  \hspace{1cm} (3.9)

where \( c'_{ijkl} \) are the elastic stiffness tensor in the coordinate system II. The calculation of elastic energy for a film-substrate system [2] is obtained using a combination of the Khachaturyan’s mesoscopic elasticity theory [10] and the Stroh formalism of anisotropic elasticity [11].

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

\[ \frac{\partial F'(t)}{\partial t} = -L \frac{\delta F}{\delta P_i(t)} \]  \hspace{1cm} (3.10)
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 [12].

3.3 Results and Discussions

3.3.1 Ferroelectric Domain Structures of Epitaxial BiFeO$_3$ Thin Films

In the simulation, we employed a model of $128\Delta \times 128\Delta \times 32\Delta$ with $\Delta$ 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 $h_f = 16\Delta$. The material constants for the Landau free energy and the nonzero electrostrictive coefficients are from the literature: $^{23}$

$\alpha_1 = 4.9(T-1103) \times 10^5$ (C$^{-2}$m$^2$N), $\alpha_{11} = 5.42 \times 10^8$ (C$^{-4}$m$^6$N), $\alpha_{12} = 1.54 \times 10^8$ (C$^{-4}$m$^6$N),

$\alpha_{Q1111} = 0.032$ (C$^{-2}$m$^4$), $\alpha_{Q1122} = -0.016$ (C$^{-2}$m$^4$), and $\alpha_{Q1212} = 0.01$ (C$^{-2}$m$^4$), where $T$ is temperature in Kelvin. As we focus on the domain structures of BiFeO$_3$ thin films at room temperature, the temperature is chosen to be $T = 300$ K. For the calculation of elastic energy, we take the elastic constants to be isotropic 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 $\Delta = l_0$,

$^a$ The fourth-order coefficients ($a_{11}$ and $a_{12}$) are for the stress-free boundary condition, which are related to those for clamped boundary condition (thermodynamic calculations in Chapter 2) by

$$
\begin{align*}
    a_{11} &= a_{11}^{\text{clamped}} - \frac{1}{2} \left[ C_{1111}(Q_{1111}^2 + 2Q_{1122}^2) + C_{1122}(2Q_{1111} + Q_{1122}) \right] \\
    a_{12} &= a_{12}^{\text{clamped}} - \left[ C_{1111}Q_{1122}(2Q_{1111} + Q_{1122}) + C_{1122}(Q_{1111}^2 + 3Q_{1122}^2 + 2Q_{1111}Q_{1122}) + 8C_{1212}Q_{1122}^2 \right]
\end{align*}
$$
where \( l_0 = \sqrt{\frac{G_{110}}{\alpha_0}} \) 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 71º 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.

Figure 3-1 shows the domain structures of (001)\(_c\) BiFeO\(_3\) thin films from the phase-field simulations, which correspond to different substrate strains: (a) \( \varepsilon_0 = -0.01 \), (b) \( \varepsilon_0 = 0 \), and (c) \( \varepsilon_0 = 0.01 \). Similar twin-like domain structures were obtained in all cases with domain walls that separate the rhombohedral variants along (011)\(_c\) planes, which satisfy the elastic compatibility and charge compatibility conditions [13]. We calculated the volume average of the polarization components over the domain structure (the domain wall regions were excluded) for the three different substrate constraints: (a) \( \overline{P_1} = 0.485, \overline{P_2} = 0.487, \overline{P_3} = 0.601, \overline{P}_s = 0.912 \); (b) \( \overline{P_1} = 0.523, \overline{P_2} = 0.526, \overline{P_3} = 0.530, \overline{P}_s = 0.911 \); and (c) \( \overline{P_1} = 0.560, \overline{P_2} = 0.562, \overline{P_3} = 0.447, \overline{P}_s = 0.910 \) (\( P_s = |\overline{P}_s| \), unit: Cm\(^{-2}\)). It is seen that \( \overline{P_1} \) and \( \overline{P_2} \) are close to each other but different from \( \overline{P_3} \) because of the substrate constraint. The compressive substrate strain increases \( |P_3| \) while tensile strain suppresses it. However, the average spontaneous polarization \( \overline{P}_s \) does not change much with the normal substrate strains, which agree well with the thermodynamic calculations. It should be emphasized that more than one type of twins are available by various combinations of polarization variants, and they are degenerate in energy.
Without any external factor that breaks the degeneracy, all types are equally probable to exist, and they could even co-exist in a film as it has been observed experimentally. [8]

Figure 3-1: Domain structures of (001)$_c$ BiFeO$_3$ thin films. (a) $\overline{\varepsilon}_{11} = \overline{\varepsilon}_{22} = -0.01$, $\overline{\varepsilon}_{12} = 0$; (b) $\overline{\varepsilon}_{11} = \overline{\varepsilon}_{22} = 0$, $\overline{\varepsilon}_{12} = 0$; (c) $\overline{\varepsilon}_{11} = \overline{\varepsilon}_{22} = 0.01$, $\overline{\varepsilon}_{12} = 0$; and (d) $\overline{\varepsilon}_{11} = \overline{\varepsilon}_{22} = 0$, $\overline{\varepsilon}_{12} = 0.005$.

Figure 3-1 also indicates that the (011)$_c$ domain wall deviates from its ideal orientation (for which the angle $\alpha$ between domain wall and the film/substrate interface is equal to $45^\circ$). Following the approach of Streiffer, et al. [13], the domain wall plane satisfying the elastic compatibility conditions can be determined. For example, considering the domain wall plane between variants $r_1^-$ and $r_2^-$, the calculated domain wall planes are (100)$_c$ and (0 h 1)$_c$, where $h = \left| \frac{P_2}{P_3} \right|$. It is noted that Streiffer et al. assumed that $|P_2| = |P_3|$ in their original approach, therefore the corresponding domain wall planes obtained are (100)$_c$ and (011)$_c$. As we discussed above, for a compressive substrate strain, $|P_2|<|P_3|$. Therefore, a compressive substrate strain decreases $\alpha =$
\[\arctan(h)\] whereas a tensile substrate strain increases it, as \(|P_2|>|P_3|\) under a tensile substrate strain, which is consistent with our phase-field simulation results as shown in Figure 3-1 (a-c). However, the angle \(\alpha\) obtained is larger than 45° even for a compressive substrate strain, which cannot be explained using elastic energy consideration only. Another energy contribution that could affect the domain wall orientation is the total domain wall energy of a domain structure, which prefers the domain walls perpendicular to the film/substrate interface (\(\alpha = 90^\circ\)) to minimize the total domain wall area. It should be noted that the electrostatic energy has no effect on the angle \(\alpha\), since the charge compatibility condition is fulfilled for any domain walls that parallel to the [100]c direction. In order to understand the role of the total domain wall energy on the domain wall orientation, we performed simulations with artificially increased gradient coefficient \(G_{11}/G_{110}\). Figure 3-2 (b) and (c) display the domain structures obtained by fixing \(G_{11}/G_{110} = 0.9\) and 1.2, respectively. One can see that \(\alpha\) increases with the gradient coefficients. As comparison, we also conducted a simulation with increased electrostrictive coefficient \(Q_{44}^* = 1.5Q_{44}\) \((G_{11}/G_{110} = 0.6)\). A very small \(\alpha\) was obtained as shown in Figure 3-2 (d), since the elastic energy dominates in this case, which prefer a smaller \(\alpha\) as we discussed above. From these simulations, we may conclude that the equilibrium orientations of the \(\{110\}_c\) type domain walls are determined by the competition between total domain wall energy and elastic energy.
Shear substrate strain may also exist for (001) \textsubscript{c} oriented BiFeO\textsubscript{3} thin films, i.e. $\varepsilon_{11} \neq \varepsilon_{22} \neq 0, \varepsilon_{12} \neq 0$. An example is a (001)\textsubscript{c} oriented BiFeO\textsubscript{3} thin film constrained by a (001)\textsubscript{o} orthorhombic substrate with in-plane orientation relationships of $[100]_c$ BiFeO\textsubscript{3} // $[110]_o$ and $[010]_c$ BiFeO\textsubscript{3} // $[\bar{1}10]_o$. The shear substrate strain $\varepsilon_{12} = \gamma - \frac{\pi}{2}$, where $\gamma$ is the angle between $[110]_o$ and $[\bar{1}10]_o$ crystallographic axes in the substrate. For
simplicity, we assume that $\varepsilon_{11} = \varepsilon_{22} = 0$ in our simulations. The energies of the eight polarization variants are no longer equal under the shear substrate strain. For a positive shear substrate strain, four of them ($r_1^\pm$ and $r_5^\pm$) have lower energy than the rest. However, as pointed out in the reference 13, the twins formed by $r_1^\pm$ and $r_5^\pm$ are not expected to exist in (001)$_c$ oriented films, as they do not relax elastic energy but create additional domain wall energy. Similarly, the variants pairs $r_1^+ / r_1^-$ and $r_3^+ / r_3^-$ separated by 180º domain walls will not exist either. Therefore, with sufficient relaxation time, only one polarization variant will survive, and a single domain structure will be obtained (shown as Fig. 1(d)). For a negative shear substrate strain, the other four variants ($r_2^\pm$ and $r_4^\pm$) have lower energy, and a single domain structure is again the stable state.

We also studied the (101)$_c$ BiFeO$_3$ thin film deposited on a (101)$_c$ oriented cubic crystal substrate with an in-plane orientation relationship of $[010]_{c}^{BiFeO_3} / [010]_{c}$. The spontaneous strains of the polarization variants in the coordinate system II can be calculated by Eq. 3.8, which give

$$
\begin{align*}
(e_{yy}^0)_{r_1^\pm} &= \begin{bmatrix} 0 & 0 & 0.0076 \\ 0 & -0.0054 & 0 \\ 0 & 0 & 0.0054 \end{bmatrix},
(e_{yy}^0)_{r_5^\pm} &= \begin{bmatrix} 0 & 0.0076 & 0 \\ 0 & 0.0054 & 0 \\ 0 & 0 & -0.0054 \end{bmatrix},
(e_{yy}^0)_{r_2^\pm} &= \begin{bmatrix} 0 & -0.0076 & 0 \\ 0 & 0.0054 & 0 \\ 0 & 0 & 0.0054 \end{bmatrix},
(e_{yy}^0)_{r_4^\pm} &= \begin{bmatrix} 0 & 0 & -0.0076 \\ 0 & 0 & -0.0054 \\ 0 & 0 & 0.0054 \end{bmatrix}.
\end{align*}
$$

Figure 3-3 shows the domain structures of (101)$_c$ oriented BiFeO$_3$ thin film under different substrate strains. For a large compressive substrate strain, it is clear that polarization variants $r_1^\pm$ and $r_4^\pm$ are favored energetically due to their negative normal
spontaneous strains in (101)$_c$ plane ($x'_1$-$x'_2$ plane). However, the polarization variants $r_1$ and $r_4$ have the same spontaneous deformation in the (101)$_c$ plane, therefore the twin structure formed by these variants will not relax elastic energy and is not expected to exist. As shown in Figure 3-3(a), the equilibrium domain structure is a single domain. On the other hand, for a large tensile substrate strain, the polarization variants $r^\pm_2$ and $r^\pm_3$ are energetically favored. In this case, a twin structure is more stable (shown as Fig. 3-3 (c)), as the spontaneous strains of $r_2$ and $r_3$ have opposite shear components in (101)$_c$ plane. When the substrate strains are close to zero, quite different domain structures were obtained from phase-field simulations, depending on the initial random values used, since the energy difference between various domain structures is quite small in this case. Fig. 3-3 (b) shows one example of the domain structures obtained for $\varepsilon_{11} = \varepsilon_{22} = 0$. We also calculated the volume average of the spontaneous polarization over the domain structure for the three different substrate constraints: (a) $P_s = 0.922$, (b) $P_s = 0.910$, and (c) $P_s = 0.910$ (unit: Cm$^{-2}$). We can see that the effect of the normal substrate strain on the spontaneous polarization is relatively large comparing with the (001)$_c$ films, which is consistent with our previous thermodynamic calculations.
For a (111)\(_c\) oriented BiFeO\(_3\) thin film deposited on a (111)\(_c\) oriented cubic crystal substrate with an in-plane orientation relationship of [\(\bar{1}\bar{1}0\)]\(_c\) \(\text{BiFeO}_3\) //\([\bar{1}\bar{1}0]_s\), the spontaneous strains of the polarization variants in the coordinate system II are given by

\[
\begin{align*}
\varepsilon_{11} &= 0.005, \quad \varepsilon_{12} = 0, \\
\varepsilon_{22} &= 0, \\
\varepsilon_{33} &= \varepsilon_{11} = \varepsilon_{22} = 0.
\end{align*}
\]

Figure 3-3: Domain structures of (101)\(_c\) oriented BiFeO\(_3\) thin films. (a) \(\varepsilon_{11} = \varepsilon_{22} = -0.005, \varepsilon_{12} = 0\); (b) \(\varepsilon_{11} = \varepsilon_{22} = 0, \varepsilon_{12} = 0\); and (c) \(\varepsilon_{11} = \varepsilon_{22} = 0.005, \varepsilon_{12} = 0\).
Figure 3-4 shows the stable domain structures of (111)\textsubscript{c} oriented BiFeO\textsubscript{3} films under different substrate strains. For a large compressive substrate strain, the polarization variants perpendicular to the film surface (\(r_1^\pm\)) have the lowest energy. The stable domain structure is a single domain with either up or down polarization, since existence of both variants will create additional domain wall energy. While for a large tensile substrate strain, the other six polarization variants (\(r_2^\pm\), \(r_3^\pm\), and \(r_4^\pm\)) are more favored energetically, and the domain structure obtained is a twin structure (shown as Figure 3-4 (c)) that relaxes the elastic energy. When the substrate strains are close to zero, the energy differences between various domain structures are relatively small, and domain structures different from Figure 3-4 (b) were obtained from our simulations with exactly same parameters but different initial random polarization distributions. We also calculated the volume average of the spontaneous polarization over the domain structure for the three different substrate constraints: (a) \(\overline{P_s} = 0.915\), (b) \(\overline{P_s} = 0.906\), and (c) \(\overline{P_s} = 0.908\) (unit: Cm\textsuperscript{-2}). We can see that the spontaneous polarization of the BiFeO\textsubscript{3} thin films is enhanced by the normal compressive substrate, and the normal tensile substrate strain to a lesser extent, which is in excellent agreement with the thermodynamic calculations.
Figure 3-4: Domain structures of (111) oriented BiFeO$_3$ thin films. (a) $\varepsilon_{11} = \varepsilon_{22} = -0.005$, $\varepsilon_{12} = 0$; (b) $\varepsilon_{11} = \varepsilon_{22} = 0$, $\varepsilon_{12} = 0$; and (c) $\varepsilon_{11} = \varepsilon_{22} = 0.005$, $\varepsilon_{12} = 0$. 
3.3.2 Strain Control of Domain Wall Stability in (110)$_c$ Oriented BiFeO$_3$ Films

The stability of switched domains against time is one of the critical issues for memory applications of ferroelectrics. It is well understood that favorable domain wall configurations correspond to those having low domain wall energy and satisfying the electrical and mechanical compatibility conditions. A basic understanding of the inhomogeneous distributions of electric and stress fields with domain structures allows one to manipulate the relative stability of domains and domain walls. This section explores the effect of substrate strains on internal stress distributions within domain structures and thus the domain stability and domain wall motion in BiFeO$_3$ thin films.

Recent studies have shown that the magnetic moments of BiFeO$_3$ are coupled ferromagnetically within the (111)$_c$ planes and antiferromagnetically between the (111)$_c$ planes perpendicular to the polarization direction [14]. Consequently, a non-180° rotation of the ferroelectric polarization may change the orientation of the easy magnetization plane. The possibility of coupling the antiferromagnetic sublattice to the ferroelectric polarization has been demonstrated [15]. Specifically, it appears that controlled 109° rotation of the ferroelectric polarization may be useful in terms of stimulating a change in the direction of antiferromagnetic order.

The switching behavior in BiFeO$_3$ films depends on the substrate orientation and the consequent domain structures in the film. For example, only 180° polarization reversal is observed in (111)$_c$ oriented films grown on a SrTiO$_3$ substrate, since polarization variants $r_1^\pm$ are energetically favored under compressive substrate strains. However, the easy plane of magnetization remains unchanged after such a ferroelectric
switching. Conversely, in a (001) \text{c} BiFeO\textsubscript{3} film, all three possible ferroelectric switching mechanisms have been observed \cite{16}, due to the existence of all the eight polarization variants. To simplify the study, we used the (110)\text{c} oriented BiFeO\textsubscript{3} films grown on a SrTiO\textsubscript{3} substrate to demonstrate selectivity of the switching mechanism, for which only four polarization variants ($r_{3}^{\pm}$ and $r_{1}^{\pm}$) are stable as shown in our previous studies. Therefore, if the initial state is $r_{3}^{+}$, we can expect the following two possibilities for switching after an electric field is applied perpendicular to the film surface. The first is that $r_{3}^{+}$ switches to $r_{3}^{-}$, corresponding to a 180° polarization reversal. The other pathway is one in which $r_{3}^{+}$ switches to $r_{1}^{+}$, corresponding to a 109° rotation of the polarization, as shown in Figure 3-5(a).

---

**Figure 3-5:** (a) Schematics of the polarization variants observed in as-grown (110)\text{c} oriented BiFeO\textsubscript{3} film, and corresponding possible switching events. (b) Schematics of as-grown (blue) and poled (orange) film on substrate.
In this section, we will focus on the dynamics of ferroelastic 109° switching within the framework shown schematically in Figure 3-5(b). A square region (shaded yellow) that has been switched by 109° is characterized by four domain walls (I, II, III and IV); I and III correspond to (001)_c-type interfaces while II and IV correspond to (1\bar{1}0)_c-type interfaces. Experimentally, it was observed that this square region begins to relax by a subsequent 71° reversal, which is captured at two different times in Figure 3-6(a); such a 71° relaxation ultimately covers the entire area that was originally switched. It is noteworthy that the relaxation process is not uniform over this area; instead, relaxation progresses rapidly from II, III and IV, while interface I is very stable.

This relaxation process is a consequence of replacing the high elastic energy of the 109° domain walls created during the poling process with less stressed 180° domain walls. As shown by Streiffer, et al. [13], the domain walls satisfying the elastic compatibility condition for the \( r_3^+ / r_1^+ \) variant pairs are (001)_c-type and (110)_c-type planes. Therefore, the domain walls II and IV have large elastic energy due to the mismatched deformation along the walls and are expected to relax rapidly. However, it is interesting to note the difference in the stability of domain walls I and III, even though they correspond to the same (001)_c-type plane.
To clarify the origin, the calculated stress distribution along the A₀-A₁ cross-section of the film is plotted in Figure 3-7(a). This stress in the film can be subdivided into two contributions: a) the lattice mismatch between the film and substrate along the film-substrate interface, and b) accommodation of the differing spontaneous strains of the polarization variants at domain walls [17]. The stress distribution arising from the second
contribution alone is shown in Figure 3-7 (b). Even without the substrate-induced stress, there are still large non-uniform stresses in the film, since it must deform locally to maintain coherency along the domain walls and the film-substrate interface. We note that, at domain walls I and III, the stress distributions are either the same or different only in the sign, therefore, in the absence of epitaxial stress, equal elastic energies are expected for the two domain walls. However, for the BiFeO\textsubscript{3} film studied here, the mismatch between the film and SrTiO\textsubscript{3} substrate adds a significant in-plane compressive stress (\(\sigma_{11}\)), so that the tensile stress near domain wall I was compensated, while the compressive stress near domain interface III was considerably increased. As a result, the elastic energies of domain walls I and III are not equivalent, and domain wall III has larger elastic energy especially near the junction with the film surface. The phase-field simulations show that the relaxation process starts from the domain walls with higher elastic energy, i.e. domain II, IV, and III (Figure 3-6 (b)); all in excellent agreement with experimental observation (Figure 3-6 (a)). This understanding offers a possibility to improve the stability of domain wall III by decreasing the substrate-induced compressive stress (strain). As demonstrated from phase-field simulations, the relaxation process slows down for smaller substrate-induced strains (shown in Figure 3-8 (a)). In order to verify this, BiFeO\textsubscript{3} samples with different thickness (120 nm - 800 nm) were used for relaxation measurements, since we know the strain state is released when the film thickness is increased. The relaxed area as a function of time, plotted in Figure 3-8 (b), clearly shows the relaxation speed for the thicker BiFeO\textsubscript{3} films is much slower.
Figure 3-7: Phase-field simulations of (110) oriented BFO/STO depicting (a) the total stress distribution in the film, and (b) the component of the stress distribution resulting only from the boundary conditions of the domain walls (ignoring substrate lattice mismatch).
In summary, a three-dimensional phase-field model has been applied for studying the domain structures and domain stabilities in BiFeO$_3$ thin films, which simultaneously takes into account the long-range interactions such as electrostatic and elastic interactions, substrate constraint, as well as the stress relaxation caused by film surface.

It was demonstrated that, basing on phase-field simulations, the substrate effect on ferroelectric polarization of BiFeO$_3$ films depends on the film orientations and the types of substrate strains. For (001)$_c$ oriented BiFeO$_3$ films, the normal substrate strains only rotate the polarization direction without changing its magnitude. Twin-like domain structures were observed for the full range of substrate strains, and the orientations of $\{110\}_c$ type domain walls are determined by the competition between elastic energy and

Figure 3-8: a) The relaxed area as a function of time with different strain state. (b) The relaxed area as a function of time with different film thickness (Data from collaborators in UC Berkley).
domain wall energy. On the other hand, under a shear substrate strain, a single domain structure was observed for \((001)_c\) oriented film. For \((101)_c\) and \((111)_c\) oriented BiFeO\(_3\) thin films, it is shown that the normal substrate strains can effectively alter domain structures and the magnitude of the spontaneous polarization. In addition, it was demonstrated that domain wall stability inside the BiFeO\(_3\) thin films also depends on the substrate strains. By decreasing the magnitude of the substrate strains, the stability of \(109^\circ\) switching processes has been significantly increased in \((110)_c\) oriented BiFeO\(_3\) thin films.
References


4.1 Introduction

Ferroelectric materials have found a lot of applications due to their superior piezoelectric properties, for examples, sensors, actuators, and transducers. However, for ferroelectric thin films investigated for piezoelectric applications, substrate clamping suppresses the piezoelectric coefficient significantly compared to their bulk counterpart [1-4]. It has been demonstrated theoretically and experimentally [5-10], the substrate clamping could be reduced, by cutting the ferroelectric thin film into isolated islands using the focused ion-beam patterning [6,7], photolithography [11], or electron-beam lithography [5], and enhanced piezoelectric responses were observed in unclamped islands. Therefore, understanding the domain structures and domain structure evolution under an applied electric field of ferroelectric islands is both academically significant and practically important. While the first step for such study is the variation of ferroelectric domain structures in ferroelectric thin films as they are patterned into discrete islands. Lee, et al. [12,13] studied the lateral size effects on domain structures in epitaxial PbTiO$_3$ islands, and found that the volume fractions of $c$ domain change with the aspect ratio of the islands. While on the other side, Fu et al. [14,15] developed a first-principles-derived effective Hamiltonian approach to study the domain structures in ferroelectric nanostructures, whose focus is on the depolarization effect for stand-free samples. Wang
et al. [16] studied the domain configuration and polarization switching in islands by using a phase-field model, however their model is two-dimensional and can not fully consider the relaxation of isolated islands.

In this chapter, a three-dimensional phase-field model is developed to simulate the domain structures and domain structure evolution of ferroelectric islands. The model can simultaneously take into account the long-range interactions such as electrostatic and elastic interactions, substrate constraint, as well as the stress relaxation effect caused by the edges of islands. As an example, we will study the domain structures of PbZr$_{0.2}$Ti$_{0.8}$O$_3$ islands. Our focus is on the difference of elastic state between isolated islands and continuous films, and its effect on the ferroelectric domain structures. The effect of electric boundary conditions on the domain structures will be also investigated.

### 4.2 Phase-field Model of Ferroelectric Islands

In order to describe the ferroelectric transition and domain structures using the phase-field model, a local spontaneous polarization field $\mathbf{P} = (P_1, P_2, P_3)$ was chosen as the field variable. The temporal domain structure evolution is described by the time-dependent Ginzburg-Landau equation (TDGL),

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

4.1

where $L$ is a kinetic coefficient which is related to the domain evolution, and $F$ is the total free energy of the system, which is expressed by

$$
F = F_{\text{bulk}}(\mathbf{P}) + F_{\text{wall}}(\mathbf{P}) + F_{\text{elec}}(\mathbf{P}) + F_{\text{elast}}(\mathbf{P}),
$$

4.2
where $F_{\text{bulk}}$, $F_{\text{wall}}$, $F_{\text{elec}}$, and $F_{\text{elas}}$ are bulk free energy, domain wall energy, electrostatic energy, and elastic energy, respectively. The mathematical expressions for these energy terms have been given in Chapter 3, so they are not listed here for the sake of conciseness.

To calculate the elastic energy of isolated islands, we discrete the model into three phases, i.e. a gas phase, a film phase, and a substrate phase, as shown in Figure 4-1 (a). Therefore, the elastic energy of the system can be expressed as

$$F_{\text{elastic}} = \int \frac{1}{2} c_{ijkl} e_{ijkl} dV = \int \frac{1}{2} c_{ijkl} (\varepsilon_{ijkl}^* - \varepsilon_{ijkl}^0)(\varepsilon_{ijkl}^* - \varepsilon_{ijkl}^0) dV,$$

where $c_{ijkl}(r)$ is the local elastic modulus tensor given by,

$$c_{ijkl}(r) = \begin{cases} c_{ijkl}^{\text{film}} & \text{in the film phase} \\ c_{ijkl}^{\text{substrate}} & \text{in the substrate phase} \\ 0 & \text{in the gas phase} \end{cases}$$

where $c_{ijkl}^{\text{film}}$ and $c_{ijkl}^{\text{substrate}}$ are the elastic stiffness tensors of the film and the substrate, respectively. The stress-free strains are defined as

$$\varepsilon_{ijkl}^0(r) = \begin{cases} \varepsilon_{ijkl}^{0,\text{sub}} + \varepsilon_{ijkl}^{0,\text{film}} & \text{in the film phase} \\ 0 & \text{in the substrate phase} \\ 0 & \text{in the gas phase} \end{cases}$$

where $\varepsilon_{ijkl}^{0,\text{sub}}$ is the substrate strains due to the lattice mismatch between the film and substrate, and $\varepsilon_{ijkl}^{0,\text{film}}$ are the stress-free strains due to the electrostrictive effect as given in Chapter 3. Following Khachaturyan’s theory [17], the total strain $\varepsilon_{ijkl}(r)$ may be represented as the sum of homogeneous and heterogeneous strains:
The homogeneous strain is defined in such a way so that

\[ \varepsilon_{ij}(r) = \bar{\varepsilon}_{ij} + \eta_{ij}(r) \]  

\[ 4.6 \]

The homogeneous strain represents the macroscopic shape change of a system generated due to the formation of a domain structure. The heterogeneous strain does not affect the macroscopic shape of a system. In order to solve the heterogeneous strain \( \eta_{kl} \) for the inhomogeneous systems, we introduce a set of displacement \( u_k(r) \),

\[ \eta_{kl} = \frac{1}{2} \left[ \frac{\partial u_k}{\partial r_i} + \frac{\partial u_i}{\partial r_k} \right] \]  

\[ 4.8 \]

The mechanical equilibrium condition requires that

\[ \frac{\partial \sigma_{ij}^{el}}{\partial r_j} = 0 \]  

\[ 4.9 \]

where \( \sigma_{ij}^{el} \) are the elastic stress components and are given by

\[ \sigma_{ij}^{el}(r) = [c_{ijkl}^{film} + \delta c_{ijkl}(r)][\varepsilon_{kl}(r) - \varepsilon_{kl}^0(r)] \]  

\[ 4.10 \]

where \( \delta c_{ijkl}(r) = c_{ijkl}(r) - c_{ijkl}^{film} \). Substituting Eq. 4.6, Eq. 4.8, and Eq. 4.10 to equation Eq. 4.9, we obtain

\[ \frac{\partial}{\partial r_j} \left\{ [c_{ijkl}^{film} + \delta c_{ijkl}(r)] \frac{\partial u_k}{\partial r_i} \right\} = \frac{\partial \delta c_{ijkl}(r)}{\partial r_j} (\varepsilon_{kl}^0 - \varepsilon_{kl}) + [(c_{ijkl}^{film} + \delta c_{ijkl}(r))] \frac{\partial \varepsilon_{kl}^0}{\partial r} \]  

\[ 4.11 \]

The determination of the equilibrium elastic field for an elastically inhomogeneous system is reduced to solving the mechanical equilibrium equation (Eq. 4.11) subject to appropriate boundary conditions. Using iteration method [18,19],
we first ignore the elastic inhomogeneity for a zeroth-order approximation, i.e. 
\( \delta c_{ijkl}(r) = 0 \). The mechanical equilibrium equation becomes linear and is given by

\[
\frac{\partial^2 u_k^0(r)}{\partial r_j \partial r_i} = c_{ijkl}^{\text{film}} \frac{\partial \varepsilon_{kl}^0}{\partial r_j}
\]

where \( u_k^0(r) \) represents the \( k \)-th component of displacement with the zeroth-order approximation, which can be readily solved in the Fourier space,

\[
V_k^0(g) = -iG_{ik}(g) g_i [\sigma_{ij}^0]_g
\]

where \( V_k^0(g) \) and \([\sigma_{ij}^0]_g\) are the Fourier transforms of \( u_k^0(r) \) and \( \sigma_{ij}^0 = c_{ijkl}^\text{film} \varepsilon_{kl}^0 \), respectively, \( g \) is a reciprocal lattice vector, \( g_i \) is the \( j \)-th component of \( g \), and \( G_{ik}(g) \) is the inverse tensor to \( (G^{-1}(g))_{ik} = |g|^2 \) \( C_{ijkl}^0 n_j n_i \) with \( n = g/|g| \). The back Fourier transform of \( V_k^0(g) \) gives the real-space solution for the displacement field with the zeroth-order approximation.

With the zeroth-order solution, one can obtain the solution for the displacement field with higher order approximation using the iteration method. For example, the \( n \)-th order solution for displacement \( u_n(r) \) can be obtained by replacing the non-linear displacement term in the left-hand side of Eq. \ref{eq:4.11} with the \( (n-1) \)-th solution \( (u^{n-1})(r) \) and moving it to the right-hand side,

\[
\frac{\partial^2 u_k^n(r)}{\partial r_j \partial r_i} = \frac{\partial \tilde{c}_{ijkl}(r)}{\partial r_j} (\varepsilon_{kl}^0 - \varepsilon_{kl}) + [(c_{ijkl}^{\text{film}} + \tilde{c}_{ijkl}(r))] \frac{\partial \varepsilon_{kl}^0}{\partial r} - \frac{\partial}{\partial r_j} [\tilde{c}_{ijkl}(r) \frac{\partial u_k^{n-1}(r)}{\partial r_i}]
\]
From which, an analytical solution of displacement with $n^{\text{th}}$ order approximation can be obtained using Fourier transforms. Generally, no more than 10 iterations are needed for static problems, while for the kinetic simulations we are doing here, only one iteration is sufficient per time step. Once the elastic displacement is obtained, the elastic strain and elastic energy can be calculated by Eq. 4.6 and Eq. 4.3, respectively. It should be noted that the stress-free boundary conditions along the edges of the island could be automatically satisfied by such approach [19].

The distribution of the electrostatic energy are also changed by the existence of island’s edges, especially for the case of open-circuit boundary condition, i.e. the charges at the surfaces of the island have not been compensated by the free charge carriers. The electrostatic energy can be calculated from a convolution of the polarization with the three-dimensional LaBonte interaction matrix [20, 21], which can be efficiently evaluated using Fast Fourier Transform (FFT) techniques due to the regular cell.

### 4.3 Results and Discussions

The domain structures of PbZr$_{0.2}$Ti$_{0.8}$O$_3$ islands were studied as an example in this section. In the simulation, we employed a model of $128\Delta \times 128\Delta \times 64\Delta$, and the thickness of the substrate is taken as $h_s = 30\Delta$. The material constants for the Landau free energy and electrostrictive coefficients of PbZr$_{0.2}$Ti$_{0.8}$O$_3$ are from the literature [22]:

\[
\begin{align*}
\alpha_1 &= 3.44(T-456.4) \times 10^5 \text{ (C}^2\text{m}^2\text{N}), \\
\alpha_{11} &= -3.05 \times 10^7 \text{(C}^{-4}\text{m}^6\text{N}), \\
\alpha_{12} &= 6.32 \times 10^8 \text{(C}^{-4}\text{m}^6\text{N}), \\
\alpha_{111} &= 2.48 \times 10^8 \text{(C}^{-6}\text{m}^{10}\text{N}), \\
\alpha_{112} &= 9.68 \times 10^8 \text{(C}^{-6}\text{m}^{10}\text{N}), \\
\alpha_{123} &= -4.90 \times 10^9 \text{(C}^{-6}\text{m}^{10}\text{N}), \\
Q_{11} &= 0.081 \text{(C}^2\text{m}^4), \\
Q_{12} &= -0.024 \text{(C}^2\text{m}^4), \\
Q_{44} &= 0.064 \text{(C}^2\text{m}^4), \\
c_{11} &= 1.75 \times 10^{11} \text{ (Nm}^{-2}), \\
c_{12} &= 0.794 \times 10^{11}
\end{align*}
\]
(Nm$^{-2}$), and $c_{44} = 1.11 \times 10^{11}$ (Nm$^{-2}$), and $T=25^\circ C$. The phase transition for PbZr$_{0.2}$Ti$_{0.8}$O$_3$ is from cubic to tetragonal, and there are three possible orientation variants in the film with the tetragonal axes along the [100], [010], and [001] directions of the cubic paraelectric phase. They are labeled by $a_1$, $a_2$ and $c$, respectively. The cell size in real space is chosen to be $\Delta = l_0$, where $l_0 = \sqrt{G_{110}/\alpha_0}$ and $\alpha_0 = |\alpha_1|_{T=25^\circ C}$. We choose the gradient energy coefficients as $G_{11}/G_{110} = 0.6$. If $l_0 = 1.0$ nm, $G_{110} = 1.73 \times 10^{-10}$ (C$^{-2}$m$^4$N), and the corresponding wall thickness is about 1.5 nm. The initial polarization is created by assigning a zero value at each cell plus a small random noise.

---

Figure 4-1: (a) Schematic illustration of a ferroelectric island. (b) The in-plane stress $\sigma_{11}$ distribution inside ferroelectric islands. (substrate strain $\epsilon^0 = 0.005$)
As the elastic state is believed to be dramatically changed by cutting the film into isolated islands, we will focus on the effect of elastic energy first in our simulation, and the electrostatic energy will be turned off for this purpose. It is well known that, for the continuous thin films, their lateral lengths were constrained by the substrate, and completely relaxation of the average stress requires that $<\varepsilon_{11}^0>\approx<\varepsilon_{22}^0>\approx \varepsilon^0$, where $<\varepsilon_{ij}^0>$ represent the volume average of $\varepsilon_{ij}^0$ over the film, and $\varepsilon^0$ is the bi-axial substrate strain. As a result, the volume fractions of different phase inside the film were essentially determined by the substrate strain. By cutting the film into isolated islands, the substrate constraint will be mostly removed, which is supposed to have significant effect on the ferroelectric domain structures. Figure 4-2 shows the temporal evolution of the domain structures of a ferroelectric island and a continuous thin film with the same thickness and substrate strain ($\varepsilon^0 = 0.005$). In the initial stage, similar domain structures were observed for both the island and film, i.e. nucleation and growth of $a_1/a_2$ domain, since the bi-axial tensile substrate strain (stress) favors the $a_1/a_2$ domain energetically. (A very small amount of $c$ domain was observed near the edges of island, where the tensile stress has been mostly relaxed as shown in Figure 4-1 (b)) However, for the thin film, if there exist $a_1/a_2$ domains only, $<\varepsilon_{11}^0>\approx<\varepsilon_{22}^0>\approx 0.01$, which is much larger than the substrate strain. Therefore, $c$ domain nucleates and forms the $c/a_1/a_2$ polytwins structure to minimize the elastic energy in the later stage. On the other side, for the isolated island, the substrate constraint has been mostly removed, and this is no driving force for the nucleation of $c$ domain. As shown in Figure 4-2(b), we finally obtained a domain structure consisting of $a_1/a_2$ domain only. However, it should be noted that, for the islands, the substrate
constraint still exists along the island/substrate interface. Therefore, a domain structure similar to that of continuous thin film was obtained when we decreased the thickness of the island as shown in Figure 4-3, as the effect of substrate constraint becomes significant for this case.

Figure 4-2: The temporal domain structure evolution of (a) a continuous thin film; and (b) an isolated island. (thickness=16nm and $e^0 = 0.005$) The different ferroelectric tetragonal variants are shown in different colors in this section, i.e., yellow = [100], orange = [001], green = [010], blue = [001], and light blue = [001].
Figure 4-3: The equilibrium domain structure of an isolated island. (thickness=6nm, and $e^0=0.005$)

Another difference between isolated islands and continuous thin films, in term of elastic energy, origins from the stress relaxation caused by the edges of islands. Figure 4-1 (b) shows the stress distribution inside the islands with a bi-axial tensile substrate strain $e^0 = 0.005$. For the stress calculation, the spontaneous polarization of islands was chosen to be zero, corresponding to the paraelectric phase. Dramatic changes in stress state were observed due to relaxation at the edges of the island, and the stress only concentrates in the region near the island/substrate interface. Therefore, with the decrease of the aspect ratio of the island, i.e., lateral dimension over island thickness $w(=l)/h$, the average stress inside the island deceases and could become almost completely stress-free eventually, which provide us a new tool for engineering the domain structures in ferroelectric materials. As shown in Figure 4-4, we can create an anisotropic in-plane stress by controlling the relative in-plane lengths of the island ($l/w$), even under a bi-axial substrate strain. As a result, when the sample was quenched to
room temperature, only $a_1$ domains nucleate (shown as Figure 4-4(a)). Although a small fraction of $a_2$ or $c$ domain nucleates to relax the substrate constraint along the island/substrate interface in the later stage, the volume fraction of $a_1$ domain still dominates in the equilibrium domain structure. As shown in Figure 4-4(b), we can effectively control the volume fraction of $a_1$ domain by the in-plane aspect ratio $l/w$, i.e. the volume fraction of $a_1$ domain is about 50% when the in-plane aspect ratio $l/w = 1$, and it will increase with the decrease of the in-plane aspect ratio. It should be noted that we could also increase the volume fraction of $a_2$ domain by just increasing the aspect ratio. Even the domain structure with 100 percent $a_1$ (or $a_2$) domain can be obtained with the increased substrate strains, which is very important for the piezoelectric applications.

Figure 4-4: (a) The temporal domain structure evolution inside an isolated island. ($l/w = 1/14$, thickness=16nm and $e^0 = 0.015$); (b) The volume fraction of $a_1$ domain as a function as the in-plane aspect ratio $l/w$. 
The electrostatic energy, we have ignored so far, are also expected to play an important role in determining the domain structures of ferroelectric islands, especially for the open-circuit boundary case, large depolarization field will be generated by the uncompensated charges along island surfaces. Figure 4-5 shows the equilibrium domain structure of an island with the open-circuit boundary condition. To minimize the depolarization field induced by the uncompensated charges, the polarization directions try to parallel to the island surface. Therefore, a vortex-like domain structure was obtained.

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Figure 4-5: The equilibrium domain structure of an isolated island. (thickness=16nm and \( e^0 = 0.005 \))

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4.4 Summary

In summary, a three-dimensional phase-field model has been developed for studying the domain structures and their evolutions in ferroelectric islands, which simultaneously takes into account the long-range interactions such as electrostatic and
elastic interactions, substrate constraint, as well as the stress relaxation caused by the edges of the islands. The simulation results demonstrated that the domain structures could be dramatically changed by cutting the continuous films into isolated islands. Moreover, the stress distribution inside islands is highly dependent of the aspect ratio, which provides us a new tool for engineering the domain structures of ferroelectric materials. We can obtain domain structures with 100 percent $a_1$ or $a_2$ domain by controlling the in-plane aspect ratio of the islands. The effect of electrostatic energy on the domain structures of ferroelectric islands was also investigated.
References

5.1 Introduction

Magnetostriiction is a phenomenon in which material changes its physical dimensions when there is a change in its magnetization. The change in magnetization can be induced by the application of a magnetic field or a stress field. Magnetostriiction is observed, to differing degrees, in all ferromagnetic materials. While typical magnetostrictive strains of magnetic materials are of the order of $10^{-5} \sim 10^{-6}$, some compounds containing rare earth elements have magnetostriction as high as $10^{-3}$. Among these, Terfenol-D ($\text{Tb}_x\text{Dy}_{1-x}\text{Fe}_2$, $x = 0.3$) has been extensively investigated for use in sensor and actuator devices because of its high magnetostriction to anisotropy ratio [1,2]. It has been recently found that large magnetostriction (over 200 ppm) at room temperature also occurs in FeGa alloys with disordered bcc $\alpha$-Fe structure [3-5].

Giant magnetostrictive materials often display complex domain structures that arise from the competition of the magnetocrystalline anisotropy energy, exchange energy, magnetostatic energy, external field energy, and elastic energy. The domain evolution under applied fields is directly responsible for the overall strain response of the materials. Therefore, the domain structures and their evolution have been extensively studied experimentally [6-15]. To explain the observed magnetic behavior, there have also been
a number of theoretical developments for magnetostrictive materials, including the works by Brown [16], James and Kinderlehrer [17,18], and DeSimone and James [19]. However, due to the rather complicated elastic solutions associated with an arbitrary domain structure, there has been essentially no simulation of macroscopically inhomogeneous domain patterns and their evolution under external fields in giant magnetostrictive materials.

One type of approach assumed that the magnetizations of domains are constrained by the anisotropy energy to lie along the easy magnetic axes. The ferromagnetic constitutive behavior was then described by the distribution of fixed quantity of available magnetic domains within materials among all the possible directions. The model assumed that each domain is magnetized independently without being affected by the magnetization states of neighboring domains. This type of approach has been used in many works to study the magnetostriction under an external magnetic field [20-24]. But this model is not suitable for describing a material with low magnetocrystalline anisotropy or the system states close to saturation when the magnetic field is applied along directions far away from those of easy axes. Zhu et al. [25] studied the influence of external stress on the cohesive field in magnetic thin films. In their micromagnetic model, without solving the total compatible strain, they use the stress-free magnetostrictive strain caused by the magnetization instead, thus the intrinsic stress resulting from the elastic incompatibility of magnetostrictive strains is not taken into account. The intrinsic stress is critically important for materials with large magnetostriction [26]. Fabian and Heider [27] have calculated the magnetostrictive self-energies of a magnetic particle imbedded in a non-magnetic matrix using the finite
element method and the continuum theory of defects. Recently, Shu et al. [26,28] developed a modified boundary integral formalism to calculate the intrinsic stress induced by incompatible magnetostrictive strains, but their method is confined to some simple two-dimensional (2D) cases due to the complexity of solving the elastic equilibrium equations.

The main purpose of this chapter is to describe a computational approach to model the stability and evolution of magnetic domain structures in giant magnetostrictive materials. It combines the micromagnetic model for magnetic domain evolution [29] and the phase-field microelasticity theory [30,31] for the elastic solutions in a magnetostrictive material with arbitrary distributions of magnetic domains. The model is able to predict the detailed domain structure and their evolution under an applied field without a priori assumptions on domain morphologies. The main limitation of the present model as well as essentially all prior phase-field models for solid-state phase transformations is the assumption of periodic boundary conditions, and hence the results are only valid when the simulation system size is much smaller than the actual sample size. It will be shown that the domain shapes and domain wall configuration in magnetostrictive materials predicted from the model automatically satisfy the condition of magnetic and elastic compatibilities. The domain structure and magnetostriction evolution under a magnetic field will also be studied for samples with different magnitudes of applied pre-stress. The results predicted from our simulations will be compared with existing experimental observation and theoretical predictions.
5.2 Micromagnetic Model and Phase-field Elasticity Theory

In a micromagnetic model, the domain structure is described by the spatial distribution of the local magnetization \( \mathbf{M}(\mathbf{r}) \). The temporal evolution of the magnetization configuration, thus the domain structure, is described by the Landau-Lifshitz-Gilbert (LLG) equation

\[
(1 + \alpha^2) \frac{\partial \mathbf{M}}{\partial t} = -\gamma_0 \mathbf{M} \times \mathbf{H}_{\text{eff}} - \frac{\gamma_0 \alpha}{M_s} \mathbf{M} \times (\mathbf{M} \times \mathbf{H}_{\text{eff}}),
\]

where \( M_s \) is the saturation magnetization, \( \gamma_0 \) is the gyromagnetic ratio, \( \alpha \) is the damping constant, and \( \mathbf{H}_{\text{eff}} \) is the effective magnetic field, which can be represented as a variational derivative of the total free energy of the system with respect to magnetization:

\[
\mathbf{H}_{\text{eff}} = -\frac{1}{\mu_0} \frac{\partial F}{\partial \mathbf{M}}
\]

where \( \mu_0 \) is the permeability of vacuum, the total free energy of magnetostrictive materials is given by

\[
F = F_{\text{anis}} + F_{\text{exch}} + F_{\text{ms}} + F_{\text{external}} + F_{\text{elastic}},
\]

where \( F_{\text{anis}}, F_{\text{exch}}, F_{\text{ms}}, F_{\text{external}}, F_{\text{elastic}} \) are the magnetocrystalline anisotropy energy, exchange energy, magnetostatic energy, external field energy, and elastic energy, respectively.

The magnetocrystalline anisotropy energy of a cubic crystal is

\[
F_{\text{anis}} = \int \left[ K_1 (m_1^2 m_2^2 + m_1^2 m_3^2 + m_2^2 m_3^2) + K_2 m_1^2 m_2^2 m_3^2 \right] dV,
\]
where $m_i$ are the components of the unit magnetization vector, $\mathbf{m} = \mathbf{M}/M_s$. $K_1$ and $K_2$ are the anisotropy constants.

The exchange energy is determined solely by the spatial variation of the magnetization orientation and can be written as:

$$F_{\text{exch}} = A \int (m_{i,1}^2 + m_{i,2}^2 + m_{i,3}^2 + m_{2,1}^2 + m_{2,2}^2 + m_{2,3}^2 + m_{3,1}^2 + m_{3,2}^2 + m_{3,3}^2) dV,$$  \(5.5\)

where $A$ is the exchange stiffness constant. In this paper, a comma in a subscript stands for spatial differentiation, for example, $m_{i,j} = \partial m_i/\partial x_j$, where $x_j$ is the $j^{\text{th}}$ component of position vector in the Cartesian coordinates.

The magnetostatic energy of a system can be written as:

$$F_{\text{ms}} = -\frac{1}{2} \mu_0 M_s \int \mathbf{H}_d \cdot \mathbf{m} dV,$$  \(5.6\)

where $\mathbf{H}_d$ is the stray field that is determined by the long-range interaction among the magnetic moments in the system. The stray field $\mathbf{H}_d$ is governed by [29]

$$H_{d1,1} + H_{d2,2} + H_{d3,3} = -M_s (m_{1,1} + m_{2,2} + m_{3,3})$$  \(5.7\)

where $H_{di}$ are the components of $\mathbf{H}_d$. By introducing magnetic scalar potential $\phi$,

$$H_{di} = -\phi_{,i}$$  \(5.8\)

Eq. 5.7 is thus rewritten as,

$$\Delta \phi = M_s (m_{1,1} + m_{2,2} + m_{3,3})$$  \(5.9\)

The solution of the potential for Eq. 5.9 is given in Fourier space by,

$$\phi(\xi) = -i \frac{M_s [m_1(\xi)\xi_1 + m_2(\xi)\xi_2 + m_3(\xi)\xi_3]}{\xi_1^2 + \xi_2^2 + \xi_3^2}$$  \(5.10\)
where $i = \sqrt{-1}$, $\xi_i$ are the coordinates in Fourier space, and $\phi(\xi)$, $m_i(\xi)$ are the Fourier transforms of $\phi$ and $m_i$ respectively. The value of $\phi$ in real space can be obtained through an inverse Fourier transform of $\phi(\xi)$. The value of $H_d$ can then be calculated by Eq. 5.8.

Note that the origin of the Fourier space $(\xi_1 = \xi_2 = \xi_3 = 0)$ is a singularity point in Eq. 5.10 and its contribution corresponds to the demagnetization field caused by the average magnetization of the system. This can easily be seen by writing the local magnetization field as

$$M(\mathbf{r}) = \overline{M} + \delta \mathbf{M}(\mathbf{r}) \quad 5.11$$

where $\overline{M}$ is spatially independent average magnetization and $\delta \mathbf{M}$ is the spatially dependent heterogeneous part of the magnetization field. The average field $\overline{M}$ is defined in such a way that $\int \delta \mathbf{M}(\mathbf{r}) dV = 0$. Since the contribution from $(\xi_1 = \xi_2 = \xi_3 = 0)$ is excluded in Eq. 5.10, it only includes the contribution from the heterogeneous part of the magnetization field $\delta \mathbf{M}$. Therefore, in order to consider the demagnetization field caused by the average magnetization in this work, we approximate the demagnetization field by

$$H_d(\overline{M}) = N \overline{M} \quad 5.12$$

where $N$ is the demagnetizing factor, which depends only on the shape of the specimen. It should be pointed out since we assume periodic boundary conditions for the heterogeneous magnetization, Eq. 5.12 is an approximation for incorporating the effect of sample shape on domain structures. Such an approximation is, in principle, only valid if the simulation system size is much smaller than the real sample size to be simulated.
Although the demagnetization factor, $N$, is known for certain specific shapes, in general, it has to be computed numerically.

The effect of an external applied magnetic field $H_{ex}$ on the system energy can be taken into account through the interaction between the magnetization and the external field:

$$F_{\text{external}} = -\mu_0 M_s \int H_{ex} \cdot m \, dV .$$ \hfill 5.13

For a cubic magnetostrictive material, the deformation associated with the local magnetization is described by the stress-free strain,

\begin{align*}
\varepsilon_{11}^0 &= \frac{3}{2} \lambda_{100} (m_1^2 - \frac{1}{3}), \\
\varepsilon_{12}^0 &= \frac{3}{2} \lambda_{111} m_1 m_2 , \\
\varepsilon_{22}^0 &= \frac{3}{2} \lambda_{100} (m_2^2 - \frac{1}{3}), \\
\varepsilon_{13}^0 &= \frac{3}{2} \lambda_{111} m_1 m_3 , \\
\varepsilon_{33}^0 &= \frac{3}{2} \lambda_{100} (m_3^2 - \frac{1}{3}),
\end{align*} \hfill 5.14

where $\lambda_{100}$ and $\lambda_{111}$ are the magnetostrictive constants of a cubic crystal.

To accommodate the local deformations arising from the magnetostrictive effect, the elastic strains $e_{ij}$ and thus elastic energy $F_{\text{elastic}}$ are generated in a magnetic domain structure,

$$e_{ij} = \varepsilon_{ij} - \varepsilon_{ij}^0 ,$$ \hfill 5.15

where $\varepsilon_{ij}$ is the total strain. The corresponding elastic energy can be expressed as

$$F_{\text{elastic}} = \int \frac{1}{2} c_{ijkl} e_{ij} e_{kl} \, dV = \int \frac{1}{2} c_{ijkl} (e_{ij} - e_{ij}^0)(e_{kl} - e_{kl}^0) \, dV ,$$ \hfill 5.16
where $c_{ijkl}$ is the elastic stiffness tensor. The summation convention for the repeated indices is employed and $i, j, k, l = 1, 2, 3$. For a cubic material with its three independent elastic constant $c_{11}, c_{12}$ and $c_{44}$ in the Voigt’s notation, the elastic energy can be rewritten as

$$F_{\text{elastic}} = \int \left\{ \frac{1}{2} c'_{11} (\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2) + c'_{12} (\varepsilon_{11} \varepsilon_{22} + \varepsilon_{22} \varepsilon_{33} + \varepsilon_{11} \varepsilon_{33}) + 2c'_{44} (\varepsilon_{12}^2 + \varepsilon_{23}^2 + \varepsilon_{13}^2) \right\} dV$$

$$= \int \left\{ \frac{1}{2} c'_{11} [(\varepsilon_{11} - \varepsilon_{11})^2 + (\varepsilon_{22} - \varepsilon_{22})^2 + (\varepsilon_{33} - \varepsilon_{33})^2] + c'_{12} [(\varepsilon_{11} - \varepsilon_{11})(\varepsilon_{22} - \varepsilon_{22}) + (\varepsilon_{22} - \varepsilon_{22})(\varepsilon_{33} - \varepsilon_{33}) + (\varepsilon_{11} - \varepsilon_{11})(\varepsilon_{33} - \varepsilon_{33})] + 2c'_{44} [(\varepsilon_{12} - \varepsilon_{12})^2 + (\varepsilon_{23} - \varepsilon_{23})^2 + (\varepsilon_{13} - \varepsilon_{13})^2] \right\} dV$$

which can be separated into three contributions,

$$F_{\text{elastic}} = F_{\text{elastic}1} + F_{\text{elastic}2} + F_{\text{elastic}3}$$

with

$$F_{\text{elastic}} = \int \left\{ \frac{1}{2} c'_{11} (\varepsilon_{11}^2 + \varepsilon_{22}^2 + \varepsilon_{33}^2) + c'_{12} (\varepsilon_{11} \varepsilon_{22} + \varepsilon_{22} \varepsilon_{33} + \varepsilon_{11} \varepsilon_{33}) + 2c'_{44} (\varepsilon_{12}^2 + \varepsilon_{23}^2 + \varepsilon_{13}^2) \right\} dV$$

$$F_{\text{elastic}2} = \int \left\{ (2c'_{44} \left( \frac{3}{2} \lambda_{1111} \right)^2 - (c'_{11} - c'_{12}) \left( \frac{3}{2} \lambda_{1100} \right)^2 \right\} \left( m_1^2 m_2^2 + m_2^2 m_3^2 + m_1^2 m_3^2 \right) dV$$

$$F_{\text{elastic}3} = \int \left\{ -\frac{3}{2} \lambda_{1000} (c'_{11} - c'_{12}) (\varepsilon_{11} m_1^2 + \varepsilon_{22} m_2^2 + \varepsilon_{33} m_3^2) - 6\lambda_{1111} (c'_{44} (\varepsilon_{12} m_1 m_2 + \varepsilon_{23} m_2 m_3 + \varepsilon_{13} m_1 m_3) \right\} dV$$

Following Khachaturyan’s theory [31], the total strain $\varepsilon_\eta (\mathbf{r})$ may be represented as the sum of homogeneous and heterogeneous strains:

$$\varepsilon_\eta (\mathbf{r}) = \bar{\varepsilon}_{ij} + \eta_\eta (\mathbf{r})$$
The homogeneous strain is defined in such a way so that

$$\int \eta_g(r) dV = 0 \quad 5.23$$

The homogeneous strain represents the macroscopic shape change of a system generated due to the formation of a domain structure. The heterogeneous strain does not affect the macroscopic shape of a system.

The equilibrium heterogeneous strain satisfies the mechanical equilibrium condition given by the Euler equation with respect to the elastic displacement

$$\sigma_{ij,j} = 0, \quad 5.24$$

where $\sigma_{ij}$ are the stress components and given by $\sigma_{ij} = c_{ijkl} e_{kl} = c_{ijkl} (e_{kl} - e_{kl}^0)$.

For the case of homogeneous modulus approximation, the equilibrium heterogeneous strain can be calculated by solving the equation Eq. 5.24 in Fourier space. First, we introduce a set of displacements $u_i(r)$,

$$\eta_g = \frac{1}{2} (u_{i,i} + u_{j,j}) \quad 5.25$$

The equations of equilibrium 5.24 are thus rewritten as

$$c_{ijkl} u_{k,j} = c_{ijkl} e_{kl}^0 \quad 5.26$$

The general solution of the displacement field for Eq. 5.26 is given in Fourier space by

$$u_j(\xi) = X_j N_{ij}(\xi) / D(\xi) \quad 5.27$$
where \( X_i = -ic_{ijkl} e^0_{kl}(\xi) \xi_j \), \( u_i(\xi) \) and \( e^0_{kl}(\xi) \) are the Fourier transforms of \( u_i \) and \( e^0_{kl} \) respectively, \( N_{ij}(\xi) \) are cofactors of a 3 \( \times \) 3 matrix \( K[\xi] \),

\[
K[\xi] = \begin{bmatrix}
K_{11} & K_{12} & K_{13} \\
K_{21} & K_{22} & K_{23} \\
K_{31} & K_{32} & K_{33}
\end{bmatrix}
\]

and \( D(\xi) \) is the determinant of matrix \( K[\xi] \). Note that \( K_{kl} = c_{ijkl} \xi_j \xi_l \).

For cubic crystals, the explicit expressions of \( D(\xi) \) and \( N_{ij}(\xi) \) are

\[
D(\xi) = \mu^2(\lambda + 2\mu + \chi) \xi^6 + \mu\chi(2\lambda + 2\mu + \chi) \xi^2(\xi_1^2 \xi_2^2 + \xi_1^2 \xi_3^2 + \xi_2^2 \xi_3^2) + \chi^2(3\lambda + 3\mu + \chi) \xi_1^2 \xi_2^2 \xi_3^2 \]

\[
N_{11}(\xi) = \mu^2 \xi_4^4 + \mu(\lambda + \mu + \chi) \xi_2^2(\xi_2^2 + \xi_3^2) + \chi(2\lambda + 2\mu + \chi) \xi_2^2 \xi_3^2
\]

\[
N_{12}(\xi) = -(\lambda + \mu) \xi_1 \xi_2 (\mu \xi_2^2 + \chi \xi_3^2)
\]

and other components are obtained by the cyclical permutation of 1, 2, 3, where

\[
\lambda = c_{12}, \mu = c_{44}, \chi = c_{11} - c_{12} - 2c_{44}, \text{ and } \xi^2 = \xi_1 \xi_2.
\]

The displacement field \( u_i(\mathbf{r}) \) in the real space can be obtained through an inverse Fourier transform of \( u_i(\xi) \). Consequently, the heterogeneous strain can be calculated by Eq. 5.25.

The value of the homogeneous strain depends on the boundary conditions. For a clamped boundary condition, the system as a whole is not allowed to deform. Therefore, the homogeneous strain is zero. When a system is subject to a constant homogeneous applied strain \( e^0_{kl} \), the homogeneous strain is simply equal to the applied strain. If there is no external stress applied and the system is unconstrained with respect to the
macroscopic deformation, the homogeneous strain is obtained by minimizing the total elastic energy respect to the homogeneous strain. Substitute Eq. 5.22 into the total elastic energy given in Eq. 5.16 and use the fact of Eq. 5.23, we obtain

\[ F_{\text{elastic}} = \frac{1}{2} \sum_{ijkl} C_{ijkl} (\varepsilon_{ijkl}^0 + \eta_{ij} \varepsilon_{kl} - \varepsilon_{ijkl}^0) dV \]

\[ = \frac{V}{2} \sum_{ijkl} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} - c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} dV + \frac{1}{2} \sum_{ijkl} \eta_{ij} \varepsilon_{kl} dV + \frac{1}{2} \sum_{ijkl} \eta_{ij} (\varepsilon_{kl}^0 - \varepsilon_{ijkl}^0) dV \]

where \( V \) is the total volume of the system. Minimize it with respect to the homogeneous strain, i.e.

\[ \frac{\partial F_{\text{elastic}}}{\partial \varepsilon_{ij}} = 0 = Vc_{ijkl} \varepsilon_{kl} - c_{ijkl} \int \varepsilon_{kl}^0 dV \]

we have

\[ \varepsilon_{kl} = \frac{1}{V} \int \varepsilon_{kl}^0 dV \]

Using the stress-free strain given in Eq. 5.14, the homogeneous strain is given by

\[ \varepsilon_{11} = \frac{3}{2} \lambda_{100} \varepsilon_{11}^0 (m_1^2 - \frac{1}{3}), \quad \varepsilon_{12} = \frac{3}{2} \lambda_{111} m_1 m_2, \]

\[ \varepsilon_{22} = \frac{3}{2} \lambda_{100} \varepsilon_{22}^0 (m_2^2 - \frac{1}{3}), \quad \varepsilon_{13} = \frac{3}{2} \lambda_{111} m_1 m_3, \]

\[ \varepsilon_{33} = \frac{3}{2} \lambda_{100} \varepsilon_{33}^0 (m_3^2 - \frac{1}{3}), \quad \varepsilon_{23} = \frac{3}{2} \lambda_{111} m_2 m_3, \]

where \( m_i^2 \) and \( m_i m_j \) represent the volume average of \( m_i^2 \) and \( m_i m_j \) over a system containing a domain structure, respectively.

When a system is subject to a homogeneous applied stress \( \sigma_{ij}^a \), the total potential energy is given by the sum of elastic energy of the system and the potential of the mechanical loading,
\[ F_p = F_{\text{elastic}} - V\sigma^a_{ij} \tilde{e}_{ij} \]

Minimizing the total potential energy with respect to the homogeneous strain, we have

\[ \frac{\partial F_p}{\partial \tilde{e}_{ij}} = \frac{\partial F_{\text{elastic}}}{\partial \tilde{e}_{ij}} - \frac{V\sigma^a_{ij} \tilde{e}_{ij}}{\partial \tilde{e}_{ij}} = Vc_{ijkl} \tilde{e}_{kl} - c_{ijkl} \int \tilde{e}_{ij}^0 dV - V\sigma^a_{ij} = 0 \]

Therefore

\[ \tilde{e}_{kl} = \frac{1}{V} \int \tilde{e}_{ij}^0 dV + s_{ijkl} \sigma^a_{ij} \]

where \( s_{ijkl} \) is the elastic compliance tensor. Using the Eq. 5.14, we obtain the homogeneous strain

\[
\begin{align*}
\tilde{e}_{11} &= s_{11}\sigma^a_{11} + s_{12}(\sigma^a_{22} + \sigma^a_{33}) + \frac{3}{2}\lambda_{100}(m_1^2 - \frac{1}{3}), \\
\tilde{e}_{22} &= s_{11}\sigma^a_{22} + s_{12}(\sigma^a_{11} + \sigma^a_{33}) + \frac{3}{2}\lambda_{100}(m_2^2 - \frac{1}{3}), \\
\tilde{e}_{33} &= s_{11}\sigma^a_{33} + s_{12}(\sigma^a_{11} + \sigma^a_{22}) + \frac{3}{2}\lambda_{100}(m_3^2 - \frac{1}{3}), \\
\tilde{e}_{12} &= \frac{1}{2}s_{44}\sigma^a_{12} + \frac{3}{2}\lambda_{111}m_1m_2, \\
\tilde{e}_{13} &= \frac{1}{2}s_{44}\sigma^a_{13} + \frac{3}{2}\lambda_{111}m_1m_3, \\
\tilde{e}_{23} &= \frac{1}{2}s_{44}\sigma^a_{23} + \frac{3}{2}\lambda_{111}m_2m_3,
\end{align*}
\]

where \( s_{11}, s_{12}, \) and \( s_{44} \) are the three independent compliance constants for a cubic material in the Voigt’s notion.

The total strain can be calculated by Eq. 5.22. Consequently, the elastic energy can be obtained for a magnetostrictive material with an arbitrary magnetic domain structure by Eq. 5.16.

### 5.3 Results and Discussions

The magnetic domain structures are obtained by the numerically solving the LLG equation using the Gauss-Seidel projection method in this work [32]. The LLG equation
can be rewritten in dimensionless form, by employing the following set of dimensionless variables.

\[
M = M_s m \\
H_{\text{eff}} = M_s h_{\text{eff}} \\
t = 1 + \frac{2}{\gamma_0 M_s} \tau
\]

The equation becomes,

\[
\frac{\partial m}{\partial \tau} = -m \times h_{\text{eff}} - c m \times (m \times h_{\text{eff}}) \tag{5.40}
\]

We can rewrite the effective magnetic field as

\[
h_{\text{eff}} = \frac{1}{M_s} (H_{\text{eff}} + H_{\text{ext}}) \\
= \frac{1}{M_s} \left[ \left( -\frac{1}{\mu_0} \frac{\partial E_{\text{exch}}}{\partial M} \right) + \left( -\frac{1}{\mu_0} \frac{\partial E'}{\partial M} \right) \right] \\
= A^* \Delta m + \frac{1}{M_s} \left( -\frac{1}{\mu_0} \frac{\partial E'}{\partial M} \right) \\
= A^* \Delta m + h[m]
\]

Where \( E' \) is the total free energy excluding the exchange energy part. \( A^* \) is defined as

\[
A^* = \frac{2A}{\mu_0 M_s^2 l_d^2}, \text{ where } l_d \text{ is the cell size in the model.}
\]

Following reference 32, we solve the equation

\[
\frac{\partial m}{\partial \tau} = -m \times (A^* \Delta m + h[m]) - c m \times (A^* \Delta m + h[m]) \tag{5.42}
\]

in three steps:

Step 1:

\[
g_i'' = (1 - A^* \Delta \tau \Delta)^{-1} (m_i'' + \Delta \tau z_{i} [m'']) \\
g_i' = (1 - A^* \Delta \tau \Delta)^{-1} (m_i' + \Delta \tau z_{i} [m']) \tag{5.43}
\]

i = 1, 2, 3
Step 2:

\[
\begin{pmatrix}
    m_1^* \\
    m_2^* \\
    m_3^*
\end{pmatrix} =
\begin{pmatrix}
    m_1^n + (g_3^n m_3^n - g_5^n m_5^n) \\
    m_2^n + (g_3^n m_3^n - g_5^n m_5^n) \\
    m_3^n + (g_3^n m_3^n - g_5^n m_5^n)
\end{pmatrix}
\]  \hspace{1cm} 5.44

Step 3:

\[
\begin{pmatrix}
    m_1^{**} \\
    m_2^{**} \\
    m_3^{**}
\end{pmatrix} =
\begin{pmatrix}
    m_1^* + \alpha \Delta \tau (A^* \Delta m_1^{**} + h_i [m^*]) \\
    m_2^* + \alpha \Delta \tau (A^* \Delta m_2^{**} + h_i [m^*]) \\
    m_3^* + \alpha \Delta \tau (A^* \Delta m_3^{**} + h_i [m^*])
\end{pmatrix}
\]  \hspace{1cm} 5.45

We solve Eq. 5.43 and Eq. 5.45 by employing the Fourier transform. For example, by Fourier transforming both sides of Eq. 5.43, the equation becomes

\[
g_i^n(\xi) = \frac{m_i^n(\xi) + \Delta \tau \tilde{h}_i [m^n]}{1 + (\xi_1^2 + \xi_2^2 + \xi_3^2) A^* \Delta \tau}
\]  \hspace{1cm} 5.47

where \( g_i^n(\xi) \), \( m_i^n(\xi) \), and \( \tilde{h}_i [m^n] \) are the Fourier transforms of \( g_i^n \), \( m_i^n \), and \( h_i [m^n] \), respectively. The value of \( g_i^n \) in real space can be obtained by doing an inverse Fourier transform of \( g_i^n(\xi) \). Eq. 5.45 can be solved in a similar way.

5.3.1 Domain Structures and Magnetostriction in FeGa

We first consider Fe_{81.3}Ga_{18.7} as an example for the numerical simulations. The corresponding material parameters are from the literatures [3-5]: \( M_s = 1.432 \times 10^6 \) A/m,
$K_1 = 2 \times 10^4 \text{ J/m}^3$, $K_2 = -4.5 \times 10^4 \text{ J/m}^3$, and $\lambda_\text{iso} = 2.64 \times 10^{-4}$, $\lambda_{111} = 0$. The bulk cubic elastic constants are $c_{11} = 1.96 \times 10^{11} \text{ N/m}^2$, $c_{12} = 1.56 \times 10^{11} \text{ N/m}^2$, and $c_{44} = 1.23 \times 10^{11}$ N/m$^2$. To save the computational time and since the magnetic easy axes are along $<100>$ directions, we performed the simulations with $(512 \times 512 \times 1$ or $256 \times 256 \times 1$) discrete cells, i.e. essentially two-dimensional systems. Periodic boundary conditions are applied along the $x_1$, $x_2$, and $x_3$ axes. The magnetization is assumed to be uniform in each cell, but it is allowed to rotate in three dimensions (3D). For the damping constant, a value of $\alpha = 0.5$ is used in the simulation. In reduced variables, the exchange stiffness constant is chose be $A^* = 0.0625$, and the time step is $\Delta \tau = 0.1$.

5.3.1.1 Energetic Contributions and Domain Structures

Giant magnetostrictive materials usually exhibit rather complicated domain structures resulted from competing energetic contributions such as elastic energy and magnetostatic energy. To understand the relation of each energetic contribution to the resulting domain structure, we performed simulations taking into account different energy contributions.

The obtained domain structures are shown in Figure 5-1, 3-5. Figure 5-1 shows the temporal evolution of a domain structure in the presence of elastic energy but without the magnetostatic energy. Mechanical clamped boundary conditions were used, which means that the overall dimensions of the system do not change. At the beginning, the random initial configuration evolves to domains as shown in Figure 5-1 (a). All the six
different kinds of orientation domains determined by the cubic anisotropy energy, including the domains with magnetization along positive $x_1$ direction ([100] domain), negative $x_1$ direction ([010] domain), positive $x_2$ direction ([001] domain), negative $x_2$ direction ([010] domain), positive $x_3$ direction ([001] domain), and negative $x_3$ direction ([001] domain), are present with almost equal fractions. Figure 5-1 (b) illustrates the domain structure after 40000 steps of evolution, indicating domain growth and coarsening. The domains are separated by 180º or 90º domain walls. A schematic diagram showing the 180º domain and 90º domain walls separating the domains is given in Figure 5-2. The 90º domain walls tend to align along the [110] or [011] directions separating [100] domain (or [001] domain) and [010] domain (or [010] domain). The alignment becomes increasingly strong at the later stage of evolution as shown in Figure 5-1 (c) and (d). Since in this case, the magnetostatic energy is not included and the exchange energy is isotropic, the domain wall alignment must be entirely due to the anisotropic elastic interactions. For 90º domain walls, the condition of elastic compatibility between the associated domain pairs requires that the tangential components of the stress-free strain must be equal in both domains for the given wall orientation. For a pair of [100] (or [100]) and [010] (or [010]) domains, the corresponding wall plane is (110) (or [001]), which is automatically predicted by the simulations without a priori assumptions. For 180º domain walls, since the magnetizations are anti-parallel on either side of the wall and correspond to identical strains, there is no preferred orientation of the 180º domain walls as shown in Figure 5-1 (b) and (c). It is interesting to note that the 180º domain walls become straight and
perpendicular to the neighboring 90° domain walls as shown in Figure 5-1 (d). The directional alignment for the 180° walls can be easily understood as a result of domain wall minimization associated with the straight domain walls. Periodic segments were observed in some 180° domain walls as shown in Figure 5-1. Similar substructures along 180° domain walls have been observed and studied experimentally [33], in which case the subdivision of domain wall was explained as a result of magnetostatic energy minimization. To reveal the origin of the subdivision of the 180° domain wall observed here, we simulated the domain structure without considering both the magnetostatic energy and elastic energy. As Figure 5-3 shows, the substructures along 180° domain walls still exist, which indicates that neither the magnetostatic energy nor elastic energy is responsible for the formation of the substructure. They are formed due to degeneracy of the domain wall with four different orientations that have equal energy. It is also noted, as expected, that since the magnetostatic energy is absent, both the head to tail and head to head (tail to tail) domain walls exist in the domain structure.
Figure 5-1: Domain evolution in the presence of elastic energy but the absence of magnetostatic energy: (a) 4000 steps; (b) 40000 steps; (c) 200000 steps; (d) 400000 steps. Black = [100] and [T00] domains, light gray = [010] and [0 T0] domains, and dark gray = [001] and [00 T] domains.
One may also notice that in Figure 5-1 the fraction of [001] domain and [00\bar{T}] domain decreases with time. Eventually as shown in Figure 5-1(c) and Figure 5-1(d), only those [100] (or [\bar{T}00]) and [010] (or [0\bar{T}0]) domains survive. This is easily understandable since this is a quasi 2D simulation, and hence the domain walls between [001] (or [00\bar{T}]) domains and the other four domains with magnetization perpendicular to the $x_3$ axis are parallel to the [001] direction instead of the energetically favorable (011)/(01\bar{T}) or (101)/(\bar{T}01) planes.

Figure 5-2: Schematic diagram of the 180° domain wall and 90° domain wall separating the domains: (a) 180° domain wall; (b) 90° domain wall.
Experimental results [3-5] showed that the magnetostrictive constant of FeGa alloy is sensitive to the material composition and temperature. Therefore, it is useful to study the domain structure of magnetostrictive materials with different magnetostriction constants. Figure 5-4 shows the simulated domain structure with varying magnetostrictive constants: $\lambda_{100} = 1.32 \times 10^{-4}$, $2.64 \times 10^{-5}$ ($\lambda_{111} = 0$), which are 0.5 and 0.1 times of that for Fe$_{81.3}$Ga$_{18.7}$, respectively. With the decrease of magnetostrictive constant, the domain walls become less aligned, since the contribution of elastic energy becomes increasingly insignificant. We also note that the [00$\bar{T}$] domains survive for the case of low magnetostrictive constants, which confirm the responsibility of the elastic

Figure 5-3: Simulated domain structure in the absence of both magnetostatic and elastic energies. Black = [100] and [1$\bar{T}$00] domains, light gray = [010] and [0$\bar{T}$0] domains, and dark gray = [001] and [00$\bar{T}$] domains.
energy for the disappearance of [001] (or [00\overline{1}]) domains in materials with high magnetostrictive constants in our 2D simulations as shown in Figure 5-1.

Figure 5-4: Simulated domain structure with varying magnetostrictive constants: (a) $\lambda_{100} = 1.32 \times 10^{-4}$, $\lambda_{111} = 0$; (b) $\lambda_{100} = 2.64 \times 10^{-5}$, $\lambda_{111} = 0$ (In the presence of elastic energy but the absence of magnetostatic energy). Black = [100] and [\overline{1}00] domains, light gray = [010] and [0\overline{1}0] domains, and dark gray = [001] and [00\overline{1}] domains.

It should be noted that some other material parameters of FeGa alloy beside magnetostriction constants were also found to depend on composition and temperature, such as saturation magnetization and cubic anisotropy constant. They should also affect the domain structure of FeGa alloy, which was not studied in this work. Thus, complicate behaviors of domain structures in FeGa are expected depending on composition and temperature.

Figure 5-5 shows the temporal evolution of domain structure when the magnetostatic energy and elastic energy are both taken into account. In this case, the
domain wall orientation is constrained by both the elastic compatibility and the magnetic compatibility. Two adjacent domains are magnetically compatible if the normal components of the magnetization vectors of both domains with respect to their common domain wall are equal. Therefore, only head to tail domain walls survive. Since the discontinuities in the strain do not occur for 180° domain walls, the 180° domain walls are only constrained by the magnetic compatibility. It is shown that the 180° domain walls are found to be parallel to the magnetization direction of associated domain pair (Figure 5-5(d)). Finally, a twin-like domain structure was obtained as shown in Figure 5-5 (d), which is similar to that described in a prior theoretical prediction [17]. If the exchange stiffness constant of Fe_{81.3}Ga_{18.7} has a similar magnitude as Fe (A \sim 10^{-11} J/m), the system studied here is around 3 \times 3 \mu m.
5.3.1.2 Magnetization Process

Figure 5-5: Domain evolution in the presence of both elastic energy and magnetostatic energy: (a) 4000 steps; (b) 40000 steps; (c) 200000 steps; (d) 500000 steps. Black = [100] and [1000] domains, light gray = [010] and [0 T0] domains, and dark gray = [001] and [001 T] domains.
The overall strain response of a magnetostrictive material is directly related to the domain evolution in the material under applied fields. The field-induced magnetostriction under a certain applied field depends on the initial demagnetized domain structure in a crystal. The largest magnetostriction appears only when an ideal initial domain structure is formed, i.e., all the domains align perpendicular to the applied magnetic field direction. Such an alignment can be obtained by an applied pre-stress. From Eq. 5.21, it can easily been seen that the elastic energy contribution can alter the anisotropy energy. For the positive $\lambda_{100}$ used here, a tensile stress, that produces an elongation in the $x_1$ axis (and hence contraction in $x_2$ and $x_3$ axes), energetically favors the domains with magnetization along the $x_1$ axis while a compressive stress will favor domains with magnetization perpendicular to the $x_1$ axis. Figure 5-6 shows the domain structures of samples with different applied pre-stresses. As expected, while a tensile stress increases the fraction of domains along $x_1$ axis, a compressive stress applied along $x_1$ axis decreases it.
The magnetostriction and associated domain structure evolution under an applied magnetic field for the samples with different applied pre-stress were shown in Figure 5-7 and Figure 5-8. In prior experiments [3-5], to obtain large magnetostriction at a relatively low magnetic field, the samples were usually prepared in the shapes of a thin disk or a rod to decrease the demagnetization effect. To approximate this case, in our simulation we use the demagnetizing factor of infinite thin sheet ($N_x = N_y = 0, N_z = 1$). A magnetostriction vs. $M/M_s$ curve for the magnetization process was given in Figure 5-7 (c). The initial flat stage of the curve show that the initial increase of magnetization is accompanied by a small magnetostrictive change. As Figure 5-8 shows, such an initial magnetization stage mainly consist of 180° domain wall movement (such as region A in Figure 5-8(a) and (b)), which does not produce any magnetostrictive change in dimensions. 90° domain wall movement also occurred by switching from [100] to [010](or [010]) domains or from [010](or [010]) to [100] domains (such as region B in Figure 5-8(c)).

Figure 5-6: Simulated domain structure with different applied pre-stress (along $x_1$ axis): (a) 5 MPa (61% domain with magnetization along $x_1$ axis); (b) 0 MPa (49%); (c) −5 MPa (32%). Dark gray = [100] domains, black = [1̅00] domains, light gray = [0̅01] domains, and white = [010] domains.
Figure 5-8 (a) and (b)). As magnetostriction vs. $M/M_s$ curve measuring the average behavior of the system, the effect of such two distinct $90^\circ$ domain wall motion is equal to a $180^\circ$ domain switching from $[\bar{1}00]$ to $[100]$ domain, which does not produce magnetostrictive change. With further magnetization, the fraction of the $[\bar{1}00]$ domain deceases, and the associated $180^\circ$ domain switching decreases too. As shown in the magnetostriction vs. $M/M_s$ curve, the slope increases with magnetization. Finally, a single domain with saturated magnetization and magnetostriction along the applied field was obtained as shown in Figure 5-8 (d). It is shown that a pre-stress can indeed have a significant effect on the magnetostriction. A larger saturation magnetostriction was obtained for systems with a compressive pre-stress, while a smaller magnetostriction was obtained when a tensile pre-stress was applied.

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**Figure 5-7**: The field dependence of magnetization and magnetostriction for the giant magnetostrictive material with different pre-stress applied: (a) $M/M_s$ vs. Applied field curves; (b) Magnetostriction vs. Applied field curves; (c) Magnetostriction vs. $M/M_s$ curves.
Figure 5-8: The domain structure evolution under applied field along [100] (without pre-stress): (a) 0 kA/m; (b) 0.80 kA/m; (c) 4.38 kA/m; (d) 7.96 kA/m. Dark gray = [100] domains, black = [T00] domains, light gray = [0T0] domains, and white = [010] domains.
5.3.2 Three-dimensional Domain Structures in Terfenol-D

As Terfenol-D has a negative magnetocrystalline anisotropy with easy directions along <111>, it is not possible to approximate the domain structures in 2D. Therefore, we chose a 3D system with \(128 \times 128 \times 128\) cells. The periodic boundary conditions are applied along all three Cartesian axes. The material parameters are [26]: \(M_s = 8.0 \times 10^5\) A/m, \(A = 9 \times 10^{-12}\) J/m, \(K_1 = -6 \times 10^4\) J/m\(^3\), \(K_2 = 0\) J/m\(^3\) and \(\lambda_{100} = 0, \lambda_{111} = 1.64 \times 10^{-3}\). The bulk cubic elastic constants are \(c_{11} = 1.41 \times 10^{11}\) N/m\(^2\), \(c_{12} = 6.48 \times 10^{10}\) N/m\(^2\), and \(c_{44} = 4.87 \times 10^{10}\) N/m\(^2\). Because of the extensive computational time required for 3D simulations, in this paper we only focused on the prediction of 3D domain structures without an applied field. An example of 3D domain structure is shown in Figure 5-9. Domains with magnetization along the 8 possible <111> easy directions were observed. The obtained domain wall orientations of non-180º walls, which constrained by the elastic compatibility, agree with those predicted by theory of James and Kinderlehrer [17,18] and with prior experimental observations [6, 11]. It should be emphasized that these domain wall orientations were predicted without \textit{a priori} assumptions. The orientations of 180º domain wall are not exactly along those planes determined by the magnetic compatibility, which comes from the competition between magnetostatic and exchange energy, since the exchange energy prefers a flat domain wall with minimization of wall. Extensive studies on the magnetic behavior of Terfenol-D such as the magnetic process with applied magnetic field or stress will be carried out using extensive 3D simulations.
5.4 Summary

A computational model for predicting the stability of domain structures and their temporal evolution in giant magnetostrictive materials is developed by combining a micromagnetic model with the phase-field microelasticity of Khachaturyan for arbitrary
domain structures. It takes into account both the inhomogeneous stress and magnetic field distributions in a domain structure. Its applications to FeGa and Terfenol-D demonstrated that the model correctly predicts the domain wall orientations as well as the domain structure evolution and the magnitude of magnetostriction during a magnetization process. It is shown that the elastic energy minimization results in an alignment of 90° domain wall orientation while the magnetostatic energy is responsible for the orientation of 180° domain walls and the head-tail magnetization configuration across a domain wall. Subdivision of 180° domain walls was observed, which was attributed to the degeneracy of the domains with different magnetic easy directions rather than the elastic interactions or the magnetostatic interactions that were believed to be responsible previously. Under an applied magnetic field, the domain structure evolution starts with the 180° domain switching, which does not produce any magnetostriction. It is also demonstrated that pre-stress can be efficiently used to increase the magnetostriction changing the initial magnetic domain structure in the demagnetization state.
References


Chapter 6

A PHASE-FIELD MODEL FOR EPITAXIAL FERROELECTRIC AND FERROMAGNETIC NANOCOMPOSITE THIN FILMS

6.1 Introduction

Magnetoelectric materials, which are simultaneously magnetic and ferroelectric, have drawn increasing interest due to their multifunctionality [1,2]. However, natural magnetoelectric single-phase crystals are rare and exhibit weak magnetoelectric coupling [3]. As a result, there have been many efforts to prepare synthetic magnetoelectrics, i.e., composites or solid solutions of ferroelectric and magnetic materials [4-7]. In addition to possessing the ferroelectricity and ferromagnetism in each individual phase, composites are shown to exhibit an extrinsic magnetoelectric coupling. Recently, epitaxial BaTiO$_3$-CoFe$_2$O$_4$ [8] and BiFeO$_3$-CoFe$_2$O$_4$ [9] nanocomposite films have been deposited by using pulsed laser deposition (PLD), and magnetoelectric coupling phenomena have been observed directly. Calculations by Nan et al. [10] and Liu et al. [11,12] have shown that large magnetic field-induced electric polarization (MIEP) could be produced in nanocomposite film due to the enhanced elastic coupling interaction.

The main purpose of this chapter is to develop a phase-field model for predicting the magnetoelectric coupling effect for ferroelectric and ferromagnetic nanocomposite thin films. The model simultaneously takes into account the ferroelectric and ferromagnetic domain structures, the electrostrictive and magnetostrictive effects, substrate constraint, as well as the long-range interactions such as elastic, magnetostatic
and electrostatic interactions. As an example, we will study the magnetoelectric response in the BaTiO$_3$-CoFe$_2$O$_4$ nanocomposite films, i.e. the magnetic field-induced electric polarization. The effects of film thickness, morphology of nanocomposite, and substrate constraint on the magnetoelectric coupling will be investigated.

### 6.2 Phase-field Model

In the model, a given microstructure state is described by three fields: a local magnetization field $\mathbf{M} = M_s \mathbf{m} = M_s (m_1, m_2, m_3)$, a local polarization field $\mathbf{P} = (P_1, P_2, P_3)$, and an order parameter field $\eta$, which describes the spatial distributions of the two phases in the composite with $\eta = 1$ for the magnetic phase and $\eta = 0$ for the ferroelectric phase. $M_s$ is the saturation magnetization. The total free energy of a ferroelectric-ferromagnetic composite is, then, expressed by

$$F = F_{\text{anis}}(\mathbf{M}) + F_{\text{exch}}(\mathbf{M}) + F_{\text{ms}}(\mathbf{M}) + F_{\text{external}}(\mathbf{M}, \mathbf{H}^e)$$
$$+ F_{\text{bulk}}(\mathbf{P}) + F_{\text{wall}}(\mathbf{P}) + F_{\text{elec}}(\mathbf{P}) + F_{\text{elas}}(\mathbf{P}, \mathbf{M}),$$

where $F_{\text{anis}}$, $F_{\text{exch}}$, $F_{\text{ms}}$, $F_{\text{external}}$, $F_{\text{bulk}}$, $F_{\text{wall}}$, $F_{\text{elec}}$, and $F_{\text{elas}}$ are the magnetocrystalline anisotropy energy, magnetic exchange energy, magnetostatic energy, external magnetic field energy, ferroelectric bulk free energy, ferroelectric domain wall energy, electrostatic energy, and elastic energy, respectively. $\mathbf{H}^e$ is the externally applied magnetic field.

The magnetocrystalline anisotropy energy of a cubic crystal is

$$F_{\text{anis}} = \frac{1}{2} \left[ K_1 (m_1^2 m_2^2 + m_2^2 m_3^2 + m_3^2 m_1^2) + K_2 m_1^2 m_2^2 m_3^2 \right] V$$

where $K_1$ and $K_2$ are the anisotropy constants.
The magnetic exchange energy is determined solely by the spatial variation of the magnetization orientation and can be written as

$$F_{\text{exch}} = A \int (\text{grad} \; m)^2 \, dV,$$

where $A$ is the exchange stiffness constant.

The magnetostatic energy of a system is given by

$$F_{\text{ms}} = \frac{1}{2} \mu_0 M_s \int \mathbf{H}_d \cdot \mathbf{m} \, dV,$$

where $\mathbf{H}_d$ is the demagnetization field that is determined by the long-range interaction among the magnetic moments in the system and $\mu_0$ is the permeability of vacuum.

The effect of an externally applied magnetic field $\mathbf{H}^e$ on the system can be taken into account through the interaction between the magnetization and the external field,

$$F_{\text{external}} = -\mu_0 M_s \int \mathbf{H}^e \cdot \mathbf{m} \, dV.$$

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

$$F_{\text{bulk}} = \int \left[ \alpha_i \left(P_i^2 + P_2^2 + P_3^2\right) + \alpha_{ij} \left(P_i^4 + P_j^4 + P_k^4\right) + \alpha_{ijk} \left(P_i^2 P_j^2 + P_2^2 P_3^2 + P_3^2 P_1^2\right) + \alpha_{ijkl} \left(P_i^2 P_j^2 P_3^2 + P_2^2 P_3^2 P_1^2 + P_3^2 P_1^2 P_2^2\right) \right] \, dV,$$

where the coefficients $\alpha_i$, $\alpha_{ij}$, $\alpha_{ijk}$ and $\alpha_{ijkl}$ are fitted to single crystal properties under stress-free boundary condition.
The contribution of ferroelectric domain walls to the total free energy is introduced through the gradients of the polarization field. For the sake of simplicity, we assume the domain wall energy to be isotropic,

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

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

The electrostatic energy of a ferroelectric domain structure is

\[ F_{\text{elec}} = -\frac{1}{2} \int \mathbf{E} \cdot \mathbf{P} dV \]

where the electric field \( \mathbf{E} \) depends on the polarization distribution and the electric boundary conditions.

The elastic energy can be calculated with

\[ F_{\text{elas}} = \frac{1}{2} \int c_{ijkl} e_{ij} e_{kl} dV = \frac{1}{2} \int c_{ijkl} (\epsilon_{ij} - \epsilon_{ij}^0) (\epsilon_{kl} - \epsilon_{kl}^0) dV \]

where \( e_{ij} \) is the elastic strain, \( \epsilon_{ij}^0 \) is the total strain, and \( c_{ijkl} \) is the elastic stiffness tensor.

The summation convention for the repeated indices is employed and \( i, j, k, l = 1, 2, 3 \). \( \epsilon_{ij}^0 \) is the stress-free strain due to the electrostrictive effect or magnetostrictive effect, and is given by

\[ \epsilon_{11}^0 = \eta \left( \frac{3}{2} \lambda_{100} (m_1^2 - \frac{1}{3}) \right) + (1 - \eta) [Q_{11} P_1^2 + Q_{12} (P_2^2 + P_3^2)], \]

\[ \epsilon_{22}^0 = \eta \left( \frac{3}{2} \lambda_{100} (m_2^2 - \frac{1}{3}) \right) + (1 - \eta) [Q_{11} P_2^2 + Q_{12} (P_1^2 + P_3^2)], \]

\[ \epsilon_{33}^0 = \eta \left( \frac{3}{2} \lambda_{100} (m_3^2 - \frac{1}{3}) \right) + (1 - \eta) [Q_{11} P_3^2 + Q_{12} (P_1^2 + P_2^2)], \]

\[ \epsilon_{ij}^0 = \eta \left( \frac{3}{2} \lambda_{111} m_i m_j \right) + (1 - \eta) Q_{44} P_i P_j, (i \neq j), \]

\[ \epsilon_{12}^0 = \eta \left( \frac{3}{2} \lambda_{112} m_i m_j \right) (1 - \eta) [Q_{11} P_1 P_2 + Q_{12} (P_1 P_3 + P_2 P_3)], \]

\[ \epsilon_{13}^0 = \eta \left( \frac{3}{2} \lambda_{113} m_i m_j \right) + (1 - \eta) Q_{11} P_1 P_3, (i \neq j) , \]

\[ \epsilon_{23}^0 = \eta \left( \frac{3}{2} \lambda_{113} m_i m_j \right) + (1 - \eta) Q_{11} P_2 P_3, (i \neq j) . \]
where $Q_{ij}$ are the electrostrictive coefficients, $\lambda_{100}$ and $\lambda_{111}$ are the magnetostrictive constants. The calculation of elastic energy for a film-substrate system [13] is obtained using a combination of the Khachaturyan’s mesoscopic elasticity theory [14] and the Stroh formalism of anisotropic elasticity [15].

The temporal evolution of the magnetization configuration is described by the Landau-Lifshitz-Gilbert (LLG) equation,

\[
(1 + \alpha^2) \frac{\partial \mathbf{M}}{\partial t} = -\gamma_0 \mathbf{M} \times \mathbf{H}_{\text{eff}} - \frac{\gamma_0 \alpha}{M_s} \mathbf{M} \times (\mathbf{M} \times \mathbf{H}_{\text{eff}}),
\]

where $\gamma_0$ is the gyromagnetic ratio, $\alpha$ is the damping constant, and $\mathbf{H}_{\text{eff}}$ is the effective magnetic field, which is given by $\mathbf{H}_{\text{eff}} = -\frac{1}{\mu_0 M_s} \frac{\partial F}{\partial \mathbf{m}}$.

The temporal evolution of the polarization field is described by the time-dependent Ginzburg-Landau equation (TDGL),

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

where $L$ is a kinetic coefficient which is related to the domain evolution.

### 6.3 Results and Discussions

We used a BaTiO$_3$-CoFe$_2$O$_4$ nanocomposite film as an example for our numerical simulations. The coefficients employed in the simulations are listed in Ref. 16 [17-21]. The system was modeled by discretizing it into a three-dimensional array of cubic cells of $64\Delta x \times 64\Delta x \times 128\Delta x$ and periodic boundary conditions were applied along the $x_1$ and $x_2$ axes. The cell size in real space was chosen to be $\Delta x = l_0$, where
\[ l_0 = \sqrt{G_{110}/\alpha_0} \] and \[ \alpha_0 = |\alpha_1|_{\theta=25^\circ C}. \] We chose the gradient energy coefficient as \[ G_{11}/G_{110} = 0.6. \] If \[ l_0 = 1 \text{ nm}, \] \[ G_{110} = 3.71 \times 10^{-11} \text{ (C}^{-2}\text{m}^4\text{N}), \] and the domain wall energy density is about \[ 5 \times 10^{-3} \text{ (Jm}^{-2}) \] for \( 180^\circ \) domain wall, which is in line with existing experimental measurement and theoretical calculation [22]. In this work, we ignored the misfit strain along the ferroelectric-ferromagnetic interface due to the lattice constant difference between the two phases for simplicity.

One measure of magnetoelectric response is the appearance of electric polarization upon applying an external magnetic field. The initial polarization of BaTiO\(_3\) phase was chosen to be along \( x_3 \) axis (\( P_1 = P_2 = 0, P_3 > 0 \)), which corresponds to the epitaxially grown single tetragonal \( c \)-phased BaTiO\(_3\) under in-plane compressive substrate strain [23]. An external magnetic field \( \mathbf{H}_e \) is applied, which is large enough to saturate the magnetic phase. By rotating the magnetic field from \( x_1 \) axis to \( x_3 \) axis, we simulated the evolution of the polarization in the ferroelectric phase, from which the magnetic field-induced electric polarization (MIEP), i.e., \[ \Delta \overline{P}_3 = \overline{P}_3 - \overline{P}_3(\mathbf{H}_e/|x_1|) \], was calculated, where \( \overline{P}_3 \) is the effective (average) polarization of the entire composite film.
We started with 1-3 type BaTiO$_3$-CoFe$_2$O$_4$ nanocomposite film with CoFe$_2$O$_4$ pillars embedded in the BaTiO$_3$ matrix as shown in Figure 6-1 (a). The volume fraction of CoFe$_2$O$_4$ is chosen to be $f = 0.35$ (similar to those studied in the experiments in Ref. 8), the thickness of film is $h = 16$ nm, and only one magnetic pillar was included in our model, therefore the distance between neighboring magnetic phases is $d = 64$ nm and the radius of the pillar is $r = 21.4$ nm. The constraint strains from the substrate were $\varepsilon_{11}^s = \varepsilon_{22}^s = -0.005$. The calculated effective (average) polarization of the composite was $\bar{\mathbf{P}}_3(\mathbf{H}_e//x_1) = 0.180$ Cm$^{-2}$ when the applied magnetic field was along $x_1$ axis, which is
larger than that of a bulk single-crystal sample (0.65 × 0.260 Cm² = 0.169 Cm²) due to the compressive substrate strains. As shown in Figure 6-1 (b), with the rotation of the applied magnetic field, the effective (average) polarization of the composite increases gradually. To clarify the origin of MIEP, the stress distributions in the nanocomposite film were calculated. Since the film consists of single ferroelectric/magnetic domains, stress components $\sigma_{11}$ and $\sigma_{22}$ are almost constant along the film thickness direction. However, as it can be seen in Figure 6-2 (a), component $\sigma_{33}$ varies significantly with the film thickness as it has to be zero at the film surface to satisfy the stress-free boundary condition. The change of the stress along the cross-section at one half of the film thickness with the applied magnetic field rotating from $x_1$ axis to $x_3$ axis is plotted in Fig. 2(b-d). It is seen that the rotation of the applied magnetic field changes the stress distribution in the ferroelectric phase. As a result of the magnetostrictive effect, the magnetic phase deforms its shape with a change in magnetization. As $\lambda_{100}$ is negative for CoFe$_2$O$_4$, the length of the magnetic phase increases along $x_1$ axis and decreases along $x_3$ axis after the rotation of the applied magnetic field, and consequently the stress distribution in the neighboring ferroelectric phase changes through the elastic interaction between the two phases. Because of the piezoelectric effect, the change in stress distribution leads to a change in the polarization of the ferroelectric phase. For the electrostrictive constants we used, the decrease of $\sigma_{11}$ ($\sigma_{22}$) ($\Delta\sigma_{11},\Delta\sigma_{22} < 0$) in the ferroelectric phase increases the polarization along $x_3$ axis ($P_3$), while the decrease of $\sigma_{33}$ ($\Delta\sigma_{33} < 0$) reduces it. Therefore, $\Delta\overline{P_3}$ is determined by the competition of $\Delta\sigma_{11}$ ($\Delta\sigma_{22}$)
and $\Delta \sigma_{33}$. In this example, $\Delta \sigma_{11}$ is dominant in enhancing the polarization of the nanocomposite film.

Figure 6-2: (a) The stress distribution ($\sigma_{33}$) when $H_e$//$x_1$ and (b-d) the change of stress distributions ($\Delta \sigma_{11}, \Delta \sigma_{22},$ and $\Delta \sigma_{33}$) when the applied magnetic field rotates from $x_1$ axis to $x_3$ axis ($\Delta \sigma_{ii} = \sigma_{ii}(H_e$//$x_3)$-$\sigma_{ii}(H_e$//$x_1)$, $f = 0.35$, $h = 16$ nm, $d = 64$ nm, and $\varepsilon_{11}^* = \varepsilon_{22}^* = -0.005$).

The dependence of MIEP on the film thickness was studied and the results of $\Delta \overline{P}_3 = \overline{P}_3(H_e$//$x_3) - \overline{P}_3(H_e$//$x_1)$ were presented in Figure 6-3(a). With the increase of the film thickness, the effect of $\Delta \sigma_{33}$ becomes more important as the influence of film
surface is less significant. It was seen that the $\Delta P_3^*$ decreases with the increase of the film thickness, and even becomes negative above certain critical film thickness, since the decrease of $\sigma_{33}$ ($\Delta \sigma_{33} < 0$) reduces $P_3$ as we discussed above. Recent studies [24-26] have shown that different morphologies of epitaxial nanocomposite films could be obtained by controlling the volume fractions of the phases, or substrate’s thickness and orientation. Therefore, we studied as well the MIEP for two stripe-like nanocomposites as shown in the inset of Figure 6-3 (a) (The volume fraction of CoFe$_2$O$_4$ was fixed to be $f = 0.35$). From Figure 6-2 (b) we can see that the change of $\sigma_{11}$ is mostly along the sides of the magnetic phase in the $x_1$ direction. The stripe-like morphologies could enhance or decrease the effect of $\Delta \sigma_{11}$ depending on orientation of its periodic distribution. As shown in Figure 6-3 (a), compared to the 1-3 type nanocomposite with magnetic pillars in a ferroelectric matrix, $\Delta P_3^*$ becomes larger for the stripe-like morphology that distributes periodically along $x_1$ axis, while $\Delta P_3^*$ is smaller for the stripe-like morphology that distributes periodically along $x_2$ axis. The difference is more significant for thin films for which the effect of $\Delta \sigma_{11}$ dominates.
It is expected that the constraint of the substrate will also play an important role in the MIEP since it can affect the stress distribution in the film dramatically. Figure 6-3 (b) shows $\Delta P^*_3$ obtained under various compressive substrate strains for 1-3 type nanocomposite films with two different thickness. With the increase of the magnitude of compressive substrate strains, the magnitude of $\Delta P^*_3$ decreases for both films. This indicates that under a large substrate compressive strain, it becomes difficult to change the stress distribution in the neighboring phase through the elastic coupling.

In addition to changing the magnitude of electric polarization, it is also possible to switch the polarization orientation in the ferroelectric phase by rotating the applied magnetic field. Recent phase-field simulations [13] have showed that the equilibrium
domain structures of ferroelectric films would be different under various substrate strains (stresses). To make the switching of polarization more easily, we chose that the substrate strain \( \varepsilon_{11} = \varepsilon_{22} = 0 \), and temperature \( T = 100^\circ C \). The temperature dependence of the magnetostrictive constants and electrostrictive constants was not considered for simplicity. As shown in Figure 6-4, by rotating the applied magnetic field, the polarization switching occurs locally and the equilibrium domain structure in the ferroelectric phase changes. It should be noted that for the potential application in data storage requires that the ferroelectric phase has single domain with up/down orientation, which can be obtained by controlling the morphology of the nanocomposite, for example, small ferroelectric pillars in a magnetic matrix. The magnetic field-induced polarization switching in such structures is currently underway.

Figure 6-4: Magnetic field-induced polarization switching (\( f = 0.35, h = 16\text{nm}, \) and \( d = 64\text{nm} \)). The different ferroelectric tetragonal variants are shown in different colors, i.e., yellow = [100], orange = [\( \bar{1} 00 \)], green = [010], blue = [001], and light blue = [00\( \bar{1} \)].
6.4 Summary

We have developed a phase-field model to predict the magnetoelectric coupling in a nanocomposite thin film made up of ferroelectric and ferromagnetic materials. The magnetic field-induced electric polarization (MIEP) in BaTiO$_3$-CoFe$_2$O$_4$ nanocomposite films was analyzed. The simulations showed that the MIEP is highly dependent of the film thickness, morphology of the nanocomposite, and substrate constraint, which provides a number of degrees of freedom in controlling coupling in nanocomposite films. It should be emphasized that the phase-field approach presented here is three-dimensional and considers the microstructure of nanocomposite that is proved to be critical to the magnetoelectric coupling in the nanocomposite. The elastic energy in the constrained thin film was incorporated, including the effect of free film surfaces and the constraint from the substrate. All prior studies essentially considered two-dimensional structures and the effect of thin film boundary condition was included only approximately.
References


16. For BaTiO$_3$, $\alpha_1 = 4.124(T-115) \times 10^5$, $\alpha_{11} = -2.097 \times 10^8$, $\alpha_{12} = 7.974 \times 10^8$, $\alpha_{111} = 1.294 \times 10^9$, $\alpha_{112} = -1.950 \times 10^9$, $\alpha_{123} = -2.500 \times 10^9$, $\alpha_{1111} = 3.863 \times 10^{10}$, $\alpha_{1112} = 2.529 \times 10^{10}$, $\alpha_{1122} = 1.637 \times 10^{10}$, $\alpha_{1123} = 1.367 \times 10^{10}$, $Q_{11} = 0.10$, $Q_{12} = -0.034$, and $Q_{44} = 0.029$. For CoFe$_2$O$_4$, $M_s = 4 \times 10^5$, $\lambda_{100} = -590 \times 10^{-6}$, $\lambda_{111} = 120 \times 10^{-6}$, $K_1 = 3 \times 10^5$, $K_2 = 0$, and $A = 7 \times 10^{-12}$. $T = 25^\circ$C. For simplicity, we assumed elastic homogeneity in this work, the elastic constants of BaTiO$_3$ are used, i.e., $c_{11} = 1.78 \times 10^{11}$, $c_{12} = 0.96 \times 10^{11}$, $c_{44} = 1.22 \times 10^{11}$ (in SI units).


Chapter 7

CONCLUSIONS AND FUTURE DIRECTIONS

7.1 Conclusions

In this thesis, the phase-field models were applied to study the domain structure evolution in ferroelectric materials, ferromagnetic (giant magnetostrictive) materials, and ferroelectric-ferromagnetic nanocomposite films, which involves long-range elastic, magnetostatic and electrostatic interactions. The main contributions of the present thesis include:

1. The effects of substrate constraint for BiFeO$_3$ thin films were systemically studied by using thermodynamic calculations and phase-field simulations. It was demonstrated that the spontaneous polarizations, domain structures, and domain wall stabilities of BiFeO$_3$ 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 BiFeO$_3$ by heteroepitaxy and strain engineering experimentally.

2. A three-dimensional phase-field model was developed to study the domain structures of ferroelectric islands. Compared to previous phase-field models of ferroelectrics in bulk and thin film system, the model can take into account the stress relaxation caused by the edges of the islands, and the electrostatic energy generated by
the uncompensated charges at the island surfaces. The PbZr_{0.2}Ti_{0.8}O_{3} islands were studied by using the model, which show drastic changes in the domain structures compared to the corresponding continuous thin films. The stress distribution inside the island depends on its aspect ratio, which gives us a new tool for controlling the domain structures and piezoelectric properties of the ferroelectrics.

3. A three-dimensional computation model was developed to study the stability and evolution of ferromagnetic domain structures in giant magnetostrictive materials. It combines the micromagnetic model for ferromagnetic domain evolution and the phase-field microelasticity theory for the elastic solutions in a magnetostrictive material with arbitrary distributions of magnetic domains. The model was applied to study the domain structures and magnetostriction effect of Fe_{81.3}Ga_{18.7} and Terfenol-D. It was demonstrated that the elastic energy and magnetostatic energy play an important role in determining the domain structures of giant magnetostrictive materials. The simulations results also showed that a compressive pre-stress could efficiently increase the overall magnetostrictive effect.

4. A three-dimensional phase-field model was developed for predicting the magnetoelectric coupling effect in ferroelectric-ferromagnetic nanocomposite films. The model simultaneously takes into account the ferroelectric and ferromagnetic domain structures, the electrostrictive and magnetostrictive effects, substrate constraint, as well as the long-range interactions such as elastic, magnetostatic and electrostatic interactions. As an example, the magnetic field-induced electric polarization in BaTiO_{3}-CoFe_{2}O_{4} nanocomposite film was analyzed. It was demonstrated that the magnetoelectric
coupling effect was highly dependent of the film thickness, morphology of the nanocomposite, and substrate constraint.

7.2 Future Directions

7.2.1 Morphologies of Ferroelectric-Ferromagnetic Nanocomposite Films

As shown in Chapter 6, the morphologies of the ferroelectric-ferromagnetic nanocomposite films are a critical factor in determining the magnetoelectric coupling effect. In order to obtain desirable magnetoelectric properties, it is very important that the fundamental thermodynamic driving forces and kinetic mechanisms that control the two-phase morphology be understood. There are a number of factors that determine the two-phase morphologies, including the volume fractions of each individual phase, the elastic constants of the two phases, the lattice mismatch between the two phases, the substrate constraint, the interphase energies between the two phases, the surface energies of the two phases, as well as the presence of defects such as interfacial dislocations. In fact, quite different morphologies have been observed experimentally in nanocomposite films [1-3], however, the underlying energetic contributions and kinetic mechanisms that are responsible for the difference are still not clear.

Therefore, it is desirable to develop a phase-field model for predicting the two-phase morphologies of ferroelectric-ferromagnetic nanocomposite films, taking into account the elastic inhomogeneity, coherency strain energy, the lattice misfit between the film and substrate, and various interfacial energies.
7.2.2 Role of Point Defects in the Ferroelectrics

Unlike other imperfections in ferroelectrics, such as dislocations, grain boundaries, and inclusions, point defects cannot be eliminated at all temperatures above 0 K basing on the thermodynamic considerations. As a result, the role of point defects in ferroelectrics has received considerable attention in recent years. Previous experimental works have shown that the distribution and migration of point defects have great effect on the degradation, imprint, and fatigue behavior of ferroelectrics [4-6].

Therefore, it is desirable to develop a phase-field model for studying the role of point defects (for example, oxygen vacancies) in determining domain structures, ferroelectric properties, electric fatigue, and other related behaviors in ferroelectric materials. The key step is introducing point defect densities into the phase-field model to describe the diffusion process of the point defects. The model will provide us a new understanding to many practical problems related to the point defects.
References


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