Computational Simulations of Ferroelectric Domain Structure and Switching Using Phase-Field Approach

A Dissertation in Materials Science and Engineering

by

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Abstract

Ferroelectrics are important functional materials with wide applications in various microelectronic and electrooptical devices such as memories, sensors, and actuators. For the application to information storage devices, the switchability of domains in a ferroelectric by an applied electric field is utilized. The conventional thermodynamic approach to describe switching behavior typically assumes a material to be a perfect crystal while a real ferroelectric material is generally inhomogeneous and contains domains and domain walls, as well as defects such as surfaces, grain boundaries, dislocations and dipolar defects. As a result, prior thermodynamic calculations predicted coercive fields, the minimum applied field to switch a domain, are at least one or more orders of magnitude too high compared to those measured experimentally.

In this work, I developed a three-dimensional (3-D) phase-field model for predicting the domain structures and ferroelectric properties in the presence of structural inhomogenities in both bulk crystals and thin films. The model takes into account realistic polycrystalline grain structures as well as various energetic contributions including elastic energy, electrostatic energy, and domain wall energy. It is shown that the defects such as existing domain walls, and grain boundaries play a critical role in domain switching and in determining the magnitude of coercive field. It will be demonstrated that the phase-field approach is able to predict the coercive fields and remanent polarizations that are in excellent agreement with experimental measurements. The effect of substrate constraint on phase stability and ferroelectric properties is also discussed.
Further, the phase-field model developed has been extended to study the local tip-induced polarization switching in the presence of twin defects. Epitaxial lead zirconate titanate (PbZr_{(1-x)}Ti_{x}O_{3}) thin film were studied as a model system. It was observed that the electric potential required to nucleate new domains during polarization switching in ferroelectric thin films varies spatially within the domain structure. The lowest electric field for nucleation is observed near the twin domain boundaries. The spatial distribution of the nucleation voltage obtained from the phase-field approach shows an excellent agreement with experimental measurements using the switching spectroscopy piezoresponse force microscopy (sspfm) technique.
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Chapter 1

INTRODUCTION

This chapter provides a brief review and general introduction to the thermodynamics of domain switching followed by a discussion of the effect of defects and inhomogeneities on domain switching in ferroelectrics. The final considerations are an introduction of the research objectives and structure of this thesis.

1.1 General Introduction to Ferroelectricity

Ferroelectrics are class of functional materials which exhibit spontaneous electric dipole moment in the absence of an electric field such that the direction of the dipole moment can be switched between equivalent states with the application of an external electric field. The equivalent states share identical crystal structure with different the directions of dipole moment. Since the discovery of ferroelectricity in Rochelle salt (NaKC\textsubscript{4}H\textsubscript{6}O\textsubscript{6}. 4H\textsubscript{2}O) by Valasek (1921), over the last hundred years, ferroelectric materials have emerged as an important material for different engineering applications. During the last four decades, ferroelectrics ceramics and single crystals have been used extensively in bulk capacitors and transducers. However, in the last two decades miniaturization of devices has stimulated research to explore the possibility of using ferroelectrics for a wide variety of novel applications by nano-scale manipulation of the structure of ferroelectrics. For example, ferroelectric in the form of thin film and heterostructures can be used in ultra-high density information storage devices, micromechanical systems (MEMS)\textsuperscript{4,5} as well as in electro-optic devices. In particular, application of ferroelectrics in memory
devices has spurred considerable research attention due to the possibility of reading and writing information on a nano-scale by switching the ferroelectric between two polarization states using a probe. Theoretically, such memory devices can store data at ultra-high densities (~10 Tbit/in\(^2\)) \(^7\) and with long retention times (~70 years). \(^8\)

### 1.2 Thermodynamics of Ferroelectrics Domain switching

The thermodynamic equilibrium of a system can be described by a set of independent variables, together with a set of dependent variables, which are determined by the independent variables. Typically, in a ferroelectric system, the three independent variables are chosen from among three conjugate pairs \((T,S)\), \((\sigma_{ij},\varepsilon_{ij})\), and \((E_i,P_i)\) while the remaining three are dependent variables where, \(T\) is temperature, \(S\) is the entropy of the system, and \(\sigma_{ij},\varepsilon_{ij}, E_i, P_i (i=1,2,3)\) are the components of stress, strain, electric field and polarization, respectively.

From the first law of thermodynamics, an incremental change in the internal energy \((dU)\) can be described as the sum of the infinitesimal heat input to the system from the surrounding \((\delta Q)\) and work done on the system \((dW)\), by both the electric and mechanical forces i.e.:

\[
dU = \delta Q + dW .
\]  

(1.1)

For a reversible process, the second law of thermodynamics describes the heat input \((\delta Q)\) as \(\delta Q = TdS\). For a ferroelectric single crystal subjected to an electric field and a stress field, the incremental work can be written as \(dW = \sigma_{ij}d\varepsilon_{ij} + E_i dP_i\), where repeated indices follows the Einstein convention. Thus, the change in internal energy \((dU)\) can be rewritten as:

\[
dU = TdS + \sigma_{ij}d\varepsilon_{ij} + E_i dP_i .
\]  

(1.2)
Helmholtz free energy is a thermodynamic potential, \( A = U - TS \). Thus, the differential form of the thermodynamic potential is:

\[
dA = -SdT + \sigma_{ij} d\varepsilon_{ij} + E_i dP_i ,
\]

(1.3)

where \( T, \varepsilon_{ij} \) and \( P_i \) are the independent variables. However, experimentally, varying the external stress \( (\sigma_{ij}) \) is easier instead of varying the strain \( (\varepsilon_{ij}) \). Hence, we introduce another set of thermodynamic potentials, i.e. the elastic Gibbs energy, defined as \( G_i = U - TS - \sigma_{ij} \varepsilon_{ij} \). The differential form of the new thermodynamic potential can be written as:

\[
dG_i = -SdT - \varepsilon_{ij} d\sigma_{ij} + E_i dP_i ,
\]

(1.4)

where \( T, \sigma_{ij} \) and \( P_i \) are the independent variables. At this stage, to simplify the theoretical analysis the non-polar phase is assumed to be centro-symmetrical, all the stresses are zero, i.e. \( \sigma_{ij} = 0 \), and the polarization vector lies along one of the crystallographic axes \( (P_i = P) \). Thus the thermodynamic potential, \( G_i \), under stress free conditions can be expressed in a simple polynomial of the polarization:

\[
G_i(P) = (\alpha/2)P^2 + (\gamma/4)P^4 + (\delta/6)P^6 ,
\]

(1.5)

where, although the values of the coefficients, \( \alpha, \gamma \) and \( \delta \), are dependent on temperature, for simplicity, the assumption is that \( \gamma \) and \( \delta \) are independent of temperature. Further, assuming all the coefficients to be positive in the non-polar phase, Eq. (1.5) shows, that as \( \alpha \) becomes negative, \( G_i(P) \) have a maximum for \( P = 0 \) and two minimums for \( P \neq 0 \) as shown schematically in Fig. 1.1(a).

Spontaneous polarization \( (P_s) \) is the magnitude of the polarization for which \( G_i(P) \) has a minimum. Thus, for \( \alpha < 0 \), the ferroelectric system can exhibit two equivalent polarization states that are stable, namely \( +P_s \) and \( -P_s \).
According to phenomenological theory\(^\text{10}\), near the Curie temperature, \(T_c\) (the temperature at which the non-polar phase transforms into a ferroelectric phase), the coefficient, \(\alpha\) varies linearly with temperature:

\[
\alpha = C(T - T_c),
\]

where \(C\) is a positive constant. Using up to a fourth order term, Eq. (1.5) can be rewritten:

\[
G_i(P) = (C(T - T_c)/2)P^2 + (\gamma/4)P^4.
\]

Clearly, from Eq. (1.4), at constant temperature and stress, the electric field can be defined as \(E = \frac{dG_i}{dP}\). Thus differentiating Eq. (1.7) w.r.t \(P\), the electric field can be expressed as

\[
E = C(T - T_c)P + \gamma P^3.
\]

Equating \(E = 0\), the spontaneous polarization can be defined as \(P_s^2 = \frac{C(T_c - T)}{\gamma}\). The variation of spontaneous polarization with temperature is shown in Fig. 1.1(b). The spontaneous polarization decreases continuously with the increase in temperature, and at \(T = T_c\) the spontaneous polarization is zero.
Fig. 1.1(a) Plot of free energy vs. polarization for a second order phase transition for temperatures near the Curie temperature; (b) Plot for spontaneous polarization vs. temperature; (c) A qualitative plot of polarization vs. electric field of a ferroelectric near the Curie temperature.
Fig. 1.1(c) shows a plot of polarization \((P)\) vs. electric field \((E)\) for temperatures near \(T_c\). For \(T < T_c\), the ferroelectric is the stable phase and the relationship between \(P\) and \(E\) can be obtained from Eq. (1.8). The curve A-B-C-D-E-F-G-B demonstrates the change in polarization with the electric field. The region shown by the broken curve represents an unstable state and the ferroelectric jumps from C to E and F to B directly. Two important physical properties characterize the P-E plot. Coercive field \((E_c)\) is defined as the electric field required to switch polarization from positive to negative (DG/2 in Fig. 1.1(c)). The remanent polarization \((P_r)\) is the magnitude of polarization when the electric field is zero.

In deriving Eq. (1.5) the assumption is that in the ferroelectric phase, the polarization vector is directed along one of the crystallographic axes. But in real ferroelectric materials the polarization vector can be along more than one crystallographic axis or even along a non-crystallographic axis. Further, in deriving Eq. (1.5) the assumption is that all the stress components are zero. But in real ferroelectrics stress distributions surrounding defects, like dislocations and grain boundaries can also modify the P-E relationship derived in this section. Thus, the relationship between polarization and electric field, as presented earlier, only gives a simple description of the change in electric field polarization for real ferroelectrics. The next section briefly presents the some of the microstructural features such as defects and inhomogenities present in real ferroelectrics. Later, subsequent chapters, starting with a perfect crystal, describe the effects of each of the defects and inhomoginities on the P-E relationship.
1.3 Typical Microstructure of a Ferroelectric

One of the characteristic features of ferroelectric materials is that they undergo a structural phase transformation from a paraelectric to a ferroelectric phase when cooled through the Curie temperature. The formation of spontaneous polarization in the ferroelectric state accompanies phase transition. In order to avoid a too general description in this section the microstructure of a typical ferroelectric material is described using lead titanate (PbTiO$_3$), as a model system. Lead titanate exhibits a cubic perovskite structure with no spontaneous polarization above 490°C (Fig. 1.2(a)). Below this temperature the material undergoes a phase transition from a cubic to a tetragonal phase and forms a spontaneous polarization ($P_S$) along a definite crystallographic direction, as shown in Fig. 1.2(b). In the figure, $a_c$, $a_T$ and $c_T$ represent the lattice parameters of the parent cubic and tetragonal phase, respectively, such that $a_T < a_c < c_T$. It should be pointed out that in the ferroelectric phase the formation of spontaneous polarization is associated with the formation of strain in the ferroelectric crystal, also known as spontaneous strain ($\varepsilon_{ij}^S$). Spontaneous strain is:

$$
\varepsilon_{ij}^S = \begin{bmatrix}
\frac{(a_T - a_c)}{a_c} & 0 & 0 \\
0 & \frac{(a_T - a_c)}{a_c} & 0 \\
0 & 0 & \frac{(c_T - a_c)}{a_c}
\end{bmatrix}.
$$

(1.9)

In the tetragonal state the spontaneous polarization can form along <100> directions of the parent cubic phase. Thus, the polarization can lie along six equivalent directions (both positive and negative directions) and each of them is called a ferroelectric variant. In absence of any externally applied constraints or fields, all six variants have equal probability of forming in the
Fig. 1.2 (a) Crystal structure of lead titanate (perovskite) above the Curie temperature; (b) The cubic paraelectric phase undergoes phase transition below the ferroelectric transition temperature; (c-e) Schematic diagram of 180° and 90° domain wall. The arrows represent the direction of spontaneous polarization. 180° and 90° domain walls are represented by blue and red lines, respectively.
ferroelectric state.

The domain structure and the volume fraction of individual variants in real ferroelectric materials are governed by the minimization of the total energy of the system. For example, formation of spontaneous polarization along a particular crystallographic axis leads to build up of charge on the surface. An electric field also known as depolarizing field is produced by the surface charge, which has a direction opposite to the direction of spontaneous polarization. The system minimizes the electrostatic energy associated with the depolarizing field by creating a domain with polarization opposite in direction to that of spontaneous polarization (Fig. 1.2(c)), where a domain is defined as the region within a ferroelectric material with uniform directions of polarization.

Domains are separated by thin walls called the domain walls. In Fig. 1.2(c) the blue line shows a 180° domain wall as the line separates regions of anti-parallel orientation of the polarization vector. A 90° domain wall separates two adjacent domains whose directions of polarization make an angle of 90° to each other (red lines in Fig. 1.2(d) and Fig. 1.2(e)). 90° domain walls are ferroelastic domain walls since the adjacent domains have different orientations of spontaneous strain in addition to different orientations of spontaneous polarization. Unlike 180° domain wall formation, ferroelastic domain walls help to minimize elastic energy of the system. Further, the polarization directions across a ferroelastic domain wall are arranged in head-to-tail fashion to minimize the electrostatic energy. Compared to ferromagnetic domain walls, ferroelectric domain walls are much thinner. Typically for a ferroelectric material, domain wall thickness for 180° and 90° domain walls are on the order of 0.5-2nm and 5-10nm, respectively.
1.4 Domain Switching and Hysteresis Loop

One of the characteristic features of ferroelectric materials is that the spontaneous polarization can be switched with an externally applied electric field. Understanding the switching of spontaneous polarization under the applied electric field is important from both scientific and applications of ferroelectric in microelectronic devices standpoints. Experimentally, the behavior of ferroelectrics under an applied electric field is analyzed using a plot of the electric field and the net polarization measured along the direction of the applied electric field, also known as a hysteresis loop.\textsuperscript{15}

Fig. 1.3(a) shows a schematic diagram of a typical hysteresis loop. Schematic domain structure corresponding to point M in Fig. 1.3(a) appears in Fig. 1.3(b). The gray lines are the grain boundaries, while the arrows indicate the direction of spontaneous polarization in individual grains. The directions of spontaneous polarization are randomly distributed such that the net polarization is zero. As the electric field is increased, polarization directions switch in such a way so that they can align along the direction of the applied electric field. At the maximum electric field, corresponding to point N in Fig. 1.3(a), all the domains are aligned along the applied electric field as shown in Fig. 1.3(c).

As the electric field decreases to zero (point O in Fig. 1.3(a)), only some of the domains back-switched, resulting in a net non-zero polarization (Fig. 1.3(d)). The net polarization without any applied electric field is known as remanent polarization. As the electric field is reversed and increased beyond a critical value, domains with polarization directions reverse such that at the maximum electric field (point P in Fig. 1.3(a)) all the polarization directions try to align along the direction of the applied
Fig. 1.3(a) Schematic diagram of typical hysteresis loop observed in ferroelectric materials; (b-e) Schematic diagram of the domain structure in a polycrystalline ferroelectric corresponding to the electric field at the point M, N, O, P, respectively.
electric field (Fig. 1.3(e)). The coercive field \((E_c)\) is the magnitude of an external electric field, which results in zero net polarization.

Notably, the coercive field calculated using a thermodynamic approach as presented in Section 1.2 is typically two orders of magnitude higher than theoretical measurements. For example, using similar free energy expansion, as in Eq.(1.5), Landauer \textit{et. al.}\textsuperscript{16} found that the calculated coercive field for barium titanate (\(\text{BaTiO}_3\)) is \(2 \times 10^3 \text{Vcm}^{-1}\). The experimentally measured coercive field for barium titanate, single crystal lies between \(500\) and \(2000 \text{Vcm}^{-1}\).\textsuperscript{12} To resolve this discrepancy between experimental and theoretical estimates of the coercive field, a clear understanding the polarization switching mechanism in detail is essential.

To illustrate the polarization switching mechanism in ferroelectric materials, Merz analyzed a simple case of \(180^\circ\) domain switching in barium titanate single crystals.\textsuperscript{17,18} Results showed that \(180^\circ\) polarization switching involves three main stages.\textsuperscript{19,20}

(i) Nucleation of domains with polarization along the direction of applied electric field.

(ii) Forward motion (along the direction of applied field) of the nucleated domain without any substantial growth in the lateral direction

(iii) Growth of the \(180^\circ\) domain in the lateral direction until reaching domain coalescence

Although over the last fifty years substantial research has been conducted to understand the last two stages of polarization switching, not much study has been directed toward understanding the domain nucleation stage. Merz\textsuperscript{18} argued that the nucleation of a new domain during polarization switching occurs due to thermal
fluctuations. However, in a seminal work Landauer\textsuperscript{21} demonstrated that using experimentally observed switching fields negates the possibility of overcoming the activation barrier for nucleation by thermal fluctuation ($\sim 10^3 - 10^5$ kT). Thus, nucleation of a new domain by thermal fluctuations can be ruled out. Recently, Bratkovsky and Lervanyuk\textsuperscript{22} suggested that activation energy is reduced due to interaction between nuclei. But still the nucleation stage of polarization switching is not clearly understood.

After the work by Merz\textsuperscript{18}, various researchers focused their attention on attempting to understand the forward movement of the nucleated domain.\textsuperscript{19,23-30} Similarly, the lateral movement of the domain wall has also been investigated, both theoretically and experimentally. Miller and Weinreich\textsuperscript{31} presented a theory for the sidewise motion of the domain wall under low applied electric field. The results showed that the movement of the $180^\circ$ domain wall takes place by the repeated nucleation of triangular steps on the parent wall due to thermal fluctuations. These researchers found that under low application of an electric field, the temperature and field dependence of the domain wall velocity matches well with experimental observations. Later the theory was extended by Stadler\textsuperscript{32} to analyze domain wall movement under application of a high electric field. Miller\textsuperscript{33} studied the coalescence of the domain wall.

### 1.5 Effect of Inhomogenities and Defects on Polarization Switching

Stability of a polarization state, and consequently polarization switching, are governed by the local distribution of elastic and electrostatic energy distribution. In all the studies referenced in the previous section, in understanding the domain
switching mechanism in ferroelectric single crystal it was assumed that the material is a perfect crystal, free from defects. However, real ferroelectrics, both in the bulk and thin film form contain defects and inhomogenities. Although even in presence of defects, the stages of polarization switching are essentially same as presented in section 1.4, but the stress and electric field surrounding a defect can alter the individual stage. For example, defects can reduce the energy barrier for domain nucleation during polarization switching; thus, nucleation of new domain during polarization switching near a defect becomes easier. Similarly, observations indicate that a defect generally reduces the mobility of the domain-wall, and consequently alters physical properties like the coercive field. Thus, clearly, that any micro-structural features that affect either or both steps of polarization switching should be taken into consideration for a complete understanding of polarization switching. The effect of commonly observed defects on polarization switching in ferroelectric materials is discussed below.

1.5.1 Grain Boundaries

Processing ferroelectrics in single crystal form is difficult. Commonly available ferroelectrics like lead zirconate titanate (PbZr$_{1-x}$Ti$_x$O$_3$) is used in polycrystalline form. Thus, grain boundaries are present in most ferroelectrics. Cao and Randall observed that polarization switching in polycrystalline ferroelectric involves both intergranular and trans-granular cooperation of domains. If that is the case then mis-orientation between grains, presence of non-ferroelectric phases at the grain boundary is expected to affect the polarization switching in polycrystalline ferroelectrics. For example, observation shows that grain orientation plays a
significant role in polarization switching. Further, Randall *et al.*\textsuperscript{36} found that grain boundary severely constrain the domain wall motion due to elastic coupling between the domain wall and the grain boundary. Apart from grain boundary, several researchers report that grain size also plays a significant role in determining the domain structure and polarization switching. Generally, it has been found experimentally that while coercive field increases, remanent polarization decreases with a decrease in grain size.\textsuperscript{36-38}

### 1.5.2 Point Defects

Point defects, like oxygen vacancies, are quite common in ferroelectrics. These defects arise from different processing conditions can significantly affect the behavior of the ferroelectrics under an applied electric field. Research shows that presence of oxygen vacancies in ferroelectric thin films\textsuperscript{39,40} leads to a loss in remanent polarization as these vacancies screen part of the thin film. Similar observation, made by Warren *et al.*\textsuperscript{41} and Anderson *et al.*\textsuperscript{42} found that polarization is suppressed in ferroelectric materials when annealed in a low oxygen atmosphere. Apart from suppressing the polarization, presence of point defects also reduces the mobility of the domain wall by defects segregation into the domain wall region.

### 1.5.3 Domain and domain walls

As mentioned in Section 1.3, ferroelectrics form domain structures below the Curie temperature in order to minimize the energy of the system. Polarization switching occurs by the nucleation of new domains and subsequent displacement of the domain wall under an applied electric field. Thus, the local structure of the domain walls, especially the width and mobility of these walls and interaction of the
domain walls with other defects play a critical role in determining the physical properties in ferroelectric material. Although width of ferroelectric domain wall ranges between 1-5nm, segregation of defects at the domain wall can effectively increase the wall width.\textsuperscript{43,44} For example, Kim \textit{et al.}\textsuperscript{45} reported that such an increase in domain wall width could significantly reduce the coercive fields in single crystals of bulk lithium niobate (LiNbO$_3$).

1.5.4 Interfacial Dislocations in Thin Films

Interfacial dislocations are another kind of defect appears commonly at the interface between thin films and the substrate (~10$^{11}$ dislocations cm$^{-1}$),\textsuperscript{46} in order to accommodate the lattice misfit between the film and the substrate.\textsuperscript{47} It has been observed that the long-range strain field surrounding an interfacial dislocation is inhomogenous.\textsuperscript{48} Such a strain field generally reduces the mobility of a ferroelastic domain wall under an applied electric field.\textsuperscript{49}

1.5.5 Top Free Surface and Substrate Strain in Thin Films

In thin film form, ferroelectrics are subjected to unique mechanical boundary conditions. The film is constrained by a substrate while the top surface of the film is stress free (Fig. 1.4(a)). This mechanical boundary condition, especially the in-plane strain induced by the substrate, can destroy the macroscopic symmetry of the ferroelectric.\textsuperscript{50} For example, if a paraelectric thin film is under a compressive in-plane strain induced by the substrate, the in-plane strain can induce a phase transformation of the cubic paraelectric to a tetragonal ferroelectric phase as shown in
Fig. 1.4(b)). Thus, the in-plane bi-axial strain can play a significant role in determining phase stability in ferroelectrics.

To analyze the phase-stability of a thin film under a bi-axial substrate strain Pertsev et al.\textsuperscript{51} introduced a new set of thermodynamic potentials ($\tilde{G}$) for a single-domain thin film deposited on a thick substrate. Using a Legendre transformation of the elastic Gibbs function, presented in (Eq. (1.5)), the new potential is:

$$ \tilde{G} = G_1 + \varepsilon_1 \sigma_1 + \varepsilon_2 \sigma_2 + + \varepsilon_6 \sigma_6 . $$

(1.9)

The assumption was that $\sigma_3, \sigma_4$ and $\sigma_5$ are zero on the surface of the thin film while the in-plane strains are controlled by the substrate such that $\varepsilon_1 = \varepsilon_2 = \varepsilon_0$, where $\varepsilon_0$ is the substrate strain. The phase stability map as a function of substrate strain of a PbTiO$_3$ thin film was constructed. The results showed that the substrate strain not only increases the ferroelectric transition temperature in the thin film but also stabilizes new phases, which are absent in bulk PbTiO$_3$.

Besides, phase stability, the in-plane strain also affects polarization switching in many ways. It has been observed both experimentally and theoretically that strain strongly couples with polarization,\textsuperscript{52} and thus, expectedly substrate strain alters the physical properties in thin film. For example, Pertsev et al.\textsuperscript{53} reported that coercive field in fully coherent ferroelectric PbZr$_{0.52}$Ti$_{0.48}$O$_3$ thin films can be about an order of magnitude higher compared to a thin film exposed to zero substrate strain. Similarly, observations indicate that remanent polarization depends significantly on the strain induced by the substrate.\textsuperscript{54}
Fig. 1.5(a). Schematic diagram showing the mechanical boundary conditions imposed by the substrate in a ferroelectric thin film; (b) Effect on substrate strain on the phase stability of the cubic paraelectric phase.
Clearly, understanding the role of each of these defects and inhomogenities on polarization switching is crucial for designing ferroelectric materials for practical applications. Further, as mentioned in Section 1.4, very little research has been done to understand the role of defects on nucleation of new domains during polarization switching, although considerable work has been done to understand the interaction between defects and domain walls during domain wall propagation. Understanding the nucleation of new domains during polarization switching is important, particularly in thin films. Studies\textsuperscript{55,56} have observed that nucleation of new domains during polarization switching is the rate-controlling step in ferroelectric thin films. However, the exact nature of nucleation centers in ferroelectric materials is still not clearly understood. However, in experiments separating the roles of these individual defects on polarization switching is difficult because one defect often masks the role of another defect.\textsuperscript{36} One possible way to analyze the role of defects individually is through a theoretical approach.

1.6 Theoretical Approaches on Ferroelectric Domain Switching

This section reviews the theoretical approaches used to understand the role of defects in polarization switching and discusses the limitations of each of these approaches.

1.6.1 Finite Element Method

A micro-mechanical model, developed by Hwang and McMeeking\textsuperscript{57}, analyzes the grain-to-grain interactions during polarization switching in bulk polycrystalline ferroelectric. The model assumed that polarization switching occurs when the energy
supplied by the applied electric field exceeds a critical value. Results showed that polarization switching in one grain inhibits the switching of a neighboring grain. A similar approach, used by Garcia et al.\textsuperscript{58}, simulated local grain-to-grain interactions during polarization switching in lead zirconate titanate thin films. The Garcia study showed that grain corners act as a source for nucleation and pinning of new domains during polarization switching. Although, both the approaches provide some qualitative information regarding the role of grain boundary in polarization switching, one of the serious limitations of these approaches is that they assume that each grain consists of a single domain and hence the role of domain structure on polarization switching was completely neglected.

### 1.6.2 Atomistic Simulations Approach

Over the last decade atomistic simulation approaches, in particular, molecular dynamics (MD) approach has been developed for describing ferroelectricity using empirical interatomic potentials. Although MD has been used to study the effect of strain on phase stability in thin film\textsuperscript{59} and superlattices\textsuperscript{60} in different ferroelectric systems, very few studies\textsuperscript{61} explore the behavior of ferroelectric systems under an applied electric field, in particular, the effect of defects on domain switching.\textsuperscript{62} However, recently Shin et al.\textsuperscript{63} in combination with other simulation approaches successfully used MD to reproduce experimentally observed domain wall velocity under an applied electric field in bulk PbTiO\textsubscript{3}.

### 1.6.3 First Principles Approach

Over the last ten years the first principle approach has emerged as an effective tool to study the phase stability and physical properties of various chemical and
structurally complex ferroelectric systems. Using a combination of first principles and an effective Hamiltonian approach, Dieguez et al. calculated the effect of substrate strain on phase stability in epitaxial BaTiO$_3$ thin films. Using a similar approach, Fu and Belliache$^6$ and later Stachiotti$^6$ calculated the polarization and coercive field in BaTiO$_3$ nano particles. Recently, Lee et al. predicted the effect of substrate strain on remanent polarization of PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films. Further, during this period various researchers showed the possibility of incorporating point defects,$^6$,$^7$ domain walls$^6$ as well as planar defects$^7$ effectively in first principle calculations. However, one of the serious limitations of this approach is the limited length scale that can be considered during calculations.$^7$ In particular, the system size that is required to accommodate defects to study polarization switching creates highly intensive computations which limit the applicability of this approach to study the effect of defects on polarization switching.

Apart from the different approaches mentioned earlier some other modeling techniques have been used to study the hysteresis behavior in ferroelectric materials. A majority of these models$^{72-74}$ derived from the Preisach model of hysteresis. In the Preisach model$^{75}$ the ferroelectric is decomposed into a series of primitive domains with a single dipole. This dipole switches direction in presence of an applied electric field. Presence of defects does not allow these dipoles to switch instantaneously, which leads to a hysteresis in ferroelectric materials. The main advantage of this model is that very little computational time is required to calculate the hysteresis loop.$^{76}$ However, this model cannot takes into account the effect of the rate of electric loading on hysteresis behavior as this model is based on the assumption that the switching is rate independent.$^{77}$
1.7 Research Objectives

As discussed in Section 1.5 and Section 1.6, defects and inhomogenities play crucial roles in determining the switching behavior of ferroelectric materials under an applied electric field. Understanding the role of these defects on polarization switching is crucial for application of ferroelectrics in microelectronic devices. However, the different simulation tools mentioned in the previous sections are either computationally intensive or neglect the domain structure in ferroelectrics. Thus, these techniques are inadequate to effectively address the role of defects on polarization switching in realistic ferroelectrics.

Phase-field approach is an effective mesoscale simulation technique widely used to understand microstructure evolution of a range of materials.78 A phase-field approach for a microstructure defines both compositional as well structural domains in terms of a set of field variables also known as order parameters. The field variables change continuously across the domains or interfaces, and thus the interfaces in a phase field model are diffuse. Some of the field variables used in phase-field simulations are concentration and, polarization that define the compositional and heterogeneities in ferroelectrics, respectively. Typical phase field simulations utilize some of the thermodynamic and kinetic parameters as inputs. An initial microstructure is generated by assigning small values of order parameters to each grid point. Later, the driving force for microstructure evolution is calculated and is utilized in the evolution equation to obtain the final microstructure. Depending on the field variables the evolution equation used in phase-field simulations is the Cahn-Hilliard nonlinear diffusion equation79 and the Allen-Cahn80 (time-dependent Ginzburg-Landau) equation:
\[ \frac{\partial \eta_p(r,t)}{\partial t} = -L_{pq} \frac{\delta F}{\delta \eta_p(r,t)} ; \]
\[ \frac{\partial c(r,t)}{\partial t} = M \nabla^2 \frac{\delta F}{\delta c(r,t)} , \]

where \( L_{pq} \) and \( M \) are determined by the mobility of atom or interface, respectively; \( c \) is the conserved field variable; \( \eta_i \) is the non-conserved field variables, and \( F \) is the total free energy of the system. The total energy includes both local as well as long range interaction energies.

Over the years, the phase-field approach has been widely used for studying microstructural evolution in spinodal decomposition\(^8\), Martensitic phase transformations,\(^8\) solidifications\(^8\) and grain growth.\(^8\) Hu and Chen\(^8\) developed a phase field approach to study the evolution of domain structure in bulk ferroelectrics. Later Li \textit{et al.}\(^8\) extended the phase-field model to study the effect of substrate strain on the domain structure in ferroelectric thin films and superlattices. Hu and Chen\(^8\) studied the combined effect of interfacial dislocations and substrate on phase stability in ferroelectric thin films.

The goal of this thesis is to extend the phase-field models developed by previous researchers to predict the role of individual defects on polarization switching in realistic ferroelectric bulk and thin films. The specific objectives are:

(1) To develop a three-dimensional phase-field model for predicting the polarization switching and domain structure evolution under an applied electric field in bulk ferroelectric polycrystals. The model takes into account realistic grain structures as well as various energetic contributions, including elastic energy, electrostatic energy, and domain wall energy.

(2) To develop a phase field model to study the effect of substrate constraint
on phase stability, domain wall mobility and physical properties of ferroelectric thin films.

(3) To develop a phase field model to study polarization switching under a localized electric potential (similar to a piezo force microscope tip) in epitaxial ferroelectric thin films in the presence of ferroelastic domain walls.

1.8 Thesis Structure

The organization of thesis is:

Chapter 1 provides a general background on the domain switching in ferroelectrics, in particular the effects of defects on domain switching. This chapter also presents the research objectives and thesis structure.

In Chapter 2 the effect of grain boundary, grain orientation and presence of non-ferroelectric phases at the grain boundary on polarization switching in bulk polycrystals has been studied.

Chapter 3 presents the effect of the presence of multivariants/multidomains on ferroelectric hysteresis loops. Further, the difference in coercive fields obtained from phase field simulations and thermodynamic calculations are discussed.

The effect of substrate constraint on phase stability of epitaxial PbZr0.53Ti0.47O3 thin film is the subject of analysis in Chapter 4. The difference in the phase stability map obtained from phase field simulation and thermodynamic approach are considered.

Chapter 5 studies the effect of substrate constraint on coercive field and remanent polarization in an epitaxial BaTiO3 thin film. This chapter shows that both coercive field and remanent polarization in ferroelectric thin films can be optimized by judicious use of substrate constraint.
Chapter 6 considers the role of twin defects in polarization switching under a localized electric field.

Finally Chapter 7 includes the conclusion and possible directions for future research.
References:


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19 E. Fatuzzo and W. J. Merz, Ferroelectrics(Amsterdam:North-Holland), 690 (1967).


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Chapter 2

Effect of Grain Boundary on Polarization Switching in

Ferroelectric Polycrystals

As discussed in chapter 1 commonly available ferroelectric like lead zirconate titanate is used in polycrystalline form. It is expected that compared to single crystal presence of grain boundary in ferroelectric ceramics can alter the domain switching mechanism. To analyze the role of grain boundary in polarization switching, in this chapter a phase-field model is developed for predicting the polarization switching and domain structure evolution under an applied electric field in ferroelectric polycrystals. The model takes into account realistic grain structures as well as various energetic contributions, including elastic energy, electrostatic energy, and domain wall energy. A hysteresis loop—average polarization as a function of applied electric field—is computed, and the detailed domain evolution process during switching is analyzed. Phase-field simulations are conducted to understand the effect of grain orientation, grain boundary, and grain size on ferroelectric domain switching, stress distribution and evolution behavior under an applied electric field. In particular, the role of grain boundaries in the nucleation and growth of new domains is studied. A correlation between the domains switching between neighboring grains is analyzed.

2.1 Literature Review

Ferroelectric ceramics are of considerable interest due to applications in various electronic, microelectronic and electrooptical devices,

1 such as acoustic sensors and actuators.2 In microelectronics, the switching behavior of ferroelectrics
under an applied electric field is exploited in the design of nonvolatile random access memories. It has been observed that domain structure and domain-wall mobility play a significant role in determining switching behavior in these materials. \(^3\) Furthermore, dielectric permittivity, coercive field and remanent polarization \(^3\text{-}^7\) are found to be strongly dependent on grain size of ceramics. The change in properties with grain size was primarily attributed to the mechanical stresses developed at the grain boundary. \(^8\) In this context, it is important to understand the role of grain boundary in determining the domain structure and switching behavior in ferroelectric ceramics.

However, experimentally it is often difficult to separate the role of grain boundaries in determining domain structure and ferroelectric properties from other factors, for example, the space charge, grain boundary phases and porosity arising from different processing condition. These factors often mask the role of grain boundaries. \(^3\text{-}^9,^{10}\) In particular, it was observed that the presence of low permittivity, nonferroelectric grain boundary layer decreases the dielectric properties in barium titanate ceramics. \(^10\) Besides the grain boundary and grain boundary phases, grain orientation was found to play a significant role in polarization switching. \(^11\) Preferential orientation of grains has been shown to affect the properties in ferroelectric ceramics. \(^12\) Thus, the objective of this chapter is to examine the roles of grain orientation, grain boundary and presence of low ferroelectric transition temperature at the grain boundary on domain structure, stress distribution and switching behavior in ferroelectric materials during polarization switching.

The most studied and perhaps also the simplest—case is 180° domain switching in single crystals. \(^13\) As presented in Chapter 1, in a single crystal, 180° polarization switching is generally thought to proceed by the nucleation of anti-parallel domains followed by growth via domain wall migration. \(^13,^{14}\) In the high-field
regime, it is believed that nucleation occurs more rapidly, and switching is completed by domain wall migration,\textsuperscript{15} until collision of domains takes place.\textsuperscript{16} For both single-crystal bulk and thin-film systems,\textsuperscript{17-20} a number of computer simulations have been carried out of domain evolution during ferroelectric transitions as well as domain evolution under an applied field. However, switching involving both 180° and 90° domain walls and occurring in polycrystals is less well understood although, there have been several theoretical studies of the switching behavior of ferroelectric polycrystals.\textsuperscript{11,21-25}

Prior models typically assumed that ferroelectric polycrystals are made up of an array of single-domain grains, and the ferroelectric or ferroelastic switching occurs when the energy provided by the applied field exceeds a critical value.\textsuperscript{21} The polarization vs. applied electric field (P-E) loops predicted by such an approach display the main features of those obtained experimentally. An alternative approach is the finite element method of Hwang \textit{et al.}, based on similar switching criteria, which finds that switching in a given grain is inhibited by the presence of neighboring grains.\textsuperscript{23} Arlt\textsuperscript{22} proposed a different model for predicting domain switching mechanism in ferroelectric polycrystal. The model is based on the nucleation of a temporary domain wall by overcoming a certain energy barrier in order to adjust the elastic energy associated by the formation of wall. Kim\textsuperscript{26} proposed a continuum model to investigate the effects of grain boundaries on the switching behavior using a 1-D model. Rodel \textit{et al.}\textsuperscript{27} presented a micro-mechanical model to show the effect of orientations of crystallites in ferroelectric ceramics on switching assuming a laminar domain structure. Recently, Zhang \textit{et al.} presented a computational model for domain switching in single-crystal and bicrystal ferroelectrics.\textsuperscript{11,24} Through two-dimensional
simulations, it was shown that ferroelectric domain switching behavior changes in the bicrystal as the difference in crystallographic orientation between the grains increases.

In this chapter, a three-dimensional phase-field model is presented for studying the domain evolution in a ferroelectric polycrystal under an applied electric field, similar to phase-field models for martensitic transformations in polycrystals.\textsuperscript{28} The temporal evolution of domain structures during polarization switching is studied in a ferroelectric polycrystal using PbTiO\textsubscript{3} as a model system. It is well known that in a real PbTiO\textsubscript{3} polycrystal, the stress induced by the ferroelectric phase transition is so large that it causes cracks to form. The possibility of such crack formation is neglected in the simulations. Since the model is rather computationally intensive in 3-D, as a first attempt simulations in 2-D were conducted. Owing to this 2-D nature and to the neglect of crack formation, the focus of this chapter is on the mechanisms for domain switching and the various energetic contributions to the switching process, rather than on a quantitative comparison with experimentally measured hysteresis loops.

Extensive phase-field simulations was conducted to study the effect of grain orientation, grain boundary and low ferroelectric transition temperature at grain boundary on the domain structure, stress distribution and switching behavior in ferroelectric materials. Hysteresis loops are constructed for a single crystal, a bicrystal and a polycrystal. Coercive fields obtained from phase-field simulations are compared with thermodynamic calculations assuming a single-domain and experimentally observed coercive fields. The chapter is organized as follows: Section 2.2 gives a description of the phase-field model. Methodology of analytical calculations and the choice of the parameters for simulation are given in Section 2.3.
Numerical results and discussions and description of grain structure, are presented in Section 2.4. Finally results are summarized in Section 2.5.

2.2 Phase-field Model of Ferroelectric Domain Structures in Polycrystals

To describe the domain structures in polycrystals, there are two levels of structures, i.e., the grain structure and the domain structure in each individual grain. I employed the phase-field model for grain growth to generate 2-D and 3-D grain structures. The domain structure within each grain is described by the inhomogeneous distribution of the local polarization \( P_i^L \), where \( i = 1,2,3 \), and the superscript \( L \) indicates that the polarization components are expressed in local coordinates within each individual grain. The total free energy of a ferroelectric polycrystal is given by

\[
F = \int \left( f_{\text{bulk}} + f_{\text{elas}} + f_{\text{grad}} + f_{\text{elec}} \right) dV, \tag{2.1}
\]

where \( f_{\text{bulk}} \) denotes the bulk free energy density, \( f_{\text{elas}} \) the elastic energy density, \( f_{\text{grad}} \) the gradient energy density (nonzero only near domain walls and grain boundaries), and \( f_{\text{elec}} \) the electrostatic energy. \( V \) is the volume of the considered polycrystal.

The bulk free energy density in a given grain is expanded in terms of polarization components using the Landau theory, i.e.

\[
f_{\text{bulk}} = \alpha_1 [(P_1^L)^2 + (P_2^L)^2 + (P_3^L)^2] + \alpha_{11}[(P_1^L)^4 + (P_2^L)^4 + (P_3^L)^4] + \alpha_{12}[(P_1^L P_2^L)^2 + (P_2^L P_3^L)^2 + (P_3^L P_1^L)^2] + \alpha_{111}[(P_1^L)^6 + (P_2^L)^6 + (P_3^L)^6] + \alpha_{112}[(P_1^L)^2 (P_2^L)^4] + \alpha_{113}[(P_1^L)^2 (P_3^L)^4] + \alpha_{122}[(P_2^L P_1^L P_3^L)^2], \tag{2.2}
\]

where \( \alpha_1, \alpha_{11}, \alpha_{12}, \alpha_{111}, \alpha_{112}, \alpha_{123} \) are the dielectric stiffness and higher-order stiffness coefficients under stress-free boundary conditions, and \( P_1^L, P_2^L, P_3^L \) are the
polarization components in the local crystallographic coordinate system within each grain.

A ferroelectric material, by definition, develops a spontaneous polarization during its transformation from its paraelectric state to a ferroelectric state when it is cooled below the Curie temperature. This transformation leads to a spontaneous strain that is related to the spontaneous polarization through the electrostrictive coefficient \( Q_{ijkl} \),

\[
e_{ij}^{0L} = Q_{ijkl} P_k^L P_i^L,
\]

where the repeated subscripts imply Einstein summation and this convention is used for the whole chapter except indicated exceptions. In order to solve the elasticity and electrostatic equations, I introduce a common global coordinate system for all grains. The orientation of a particular grain in the polycrystalline structure is described using three Euler angles \((\phi, \theta, \psi)\) that correspond to three consecutive counter clockwise rotations with respect to the global coordinate \((x_1, x_2, x_3)\): \(\phi\) about the \(x_3\) axis, \(\theta\) about the rotated \(x'_1\) axis and \(\psi\) about the newest \(x'_3\) axis. The transformation matrix from the global to local coordinate system is given by

\[
TR = \begin{pmatrix}
\cos(\phi)\cos(\theta) - \cos(\phi)\sin(\theta)\sin(\psi) & \sin(\phi)\cos(\theta) + \cos(\phi)\sin(\phi)\sin(\psi) & \sin(\phi)\sin(\theta) \\
-\cos(\theta)\sin(\phi) - \cos(\phi)\sin(\theta)\sin(\psi) & \cos(\phi)\cos(\theta) - \cos(\phi)\sin(\phi)\sin(\psi) & \cos(\phi)\sin(\theta) \\
\sin(\phi)\sin(\theta) - \cos(\phi)\sin(\theta)\sin(\psi) & -\cos(\phi)\sin(\phi) - \cos(\phi)\sin(\phi)\sin(\psi) & \cos(\phi)\cos(\theta)
\end{pmatrix}.
\]

The polarization in the local coordinate system, \( P_i^L \), is related to that in the global system, \( P_i \), through \( P_i^L = tr_{ij} P_j \), where \( tr_{ij} \) represents the \( ij \)-component of the transformation matrix \( TR \). The local polarization is unique to a particular grain and assumed to remain constant during domain evolution.

The elastic energy density is given by
\[ f_{\text{elas}} = \frac{1}{2} C_{ijkl} e_{ij} e_{kl} = \frac{1}{2} C_{ijkl} (\varepsilon_{ij} - \varepsilon_{ij}^0) (\varepsilon_{kl}^G - \varepsilon_{kl}^0), \]

where \( C_{ijkl} \) represents the elastic stiffness tensor, and \( \varepsilon_{ij} \), \( \varepsilon_{ij} \), and \( \varepsilon_{ij}^0 \) denote the elastic strain, total strain and spontaneous strain, respectively. The spontaneous strain in a given grain can be expressed with respect to the local coordinate system by \( \varepsilon_{ij}^{0L} = Q_{ijkl} P_k^l P_l^L \), where \( Q_{ijkl} \) is the electrostrictive coefficient of the corresponding single crystal. Therefore, the spontaneous strain in the global coordinate system can be obtained from

\[ \varepsilon_{ij}^0 = tr_{kl} tr_{ij} \varepsilon_{kl}^{0L}. \]

The total strain \( \varepsilon_{ij} \) can be written as the sum of the spatially independent homogenous strain, \( \bar{\varepsilon}_{ij} \), and a spatially dependent heterogeneous strain, \( \delta \varepsilon_{ij} \), i.e.,

\[ \varepsilon_{ij} = \bar{\varepsilon}_{ij} + \delta \varepsilon_{ij}. \]

The homogenous strain determines the macroscopic shape deformation of the entire polycrystal resulting from an applied strain, phase transformations or domain structure changes. In this work, the external boundary of the polycrystal is either clamped or stress free. For the clamped boundary condition, the homogenous strain \( (\bar{\varepsilon}_{ij}) \) is zero. By assuming that elastic constants are independent of space, the homogenous strain under the stress-free boundary condition is obtained as the spatial average of eigen strain i.e., \( \bar{\varepsilon}_{kl} = \bar{\varepsilon}_{kl}^{0G} \), where \( \bar{\varepsilon}_{kl}^{0G} = \frac{1}{V} \int_{V} \varepsilon_{kl}^{0G} dV \). The heterogeneous strain is defined in such a way that \( \int_{V} \delta \varepsilon_{ij}^{0G} dV = 0 \). To solve for the equilibrium heterogeneous strain field \( \delta \varepsilon_{ij} \), a set of displacements \( u_i (x) \) is introduced, such that \( \delta \varepsilon_{ij} = 1/2 (u_{i,j} + u_{j,i}) \), with \( u_{i,j} = \partial u_i / \partial x_j \). The mechanical equilibrium
condition is given by $\sigma_{ij,j} = 0$, where $\sigma_{ij}$ denotes the stress, and $\sigma_{ij} = C_{ijkl} e_{kl} = C_{ijkl} (e_{ij} - \epsilon_{ij}^0)$. For simplicity, it is assumed that the elastic modulus is isotropic and homogeneous and thus $C_{ijkl} \epsilon_{kl} = C_{ijkl} e_{kl,ij}^0$. The equilibrium displacement and the heterogeneous strain components can be solved using Fourier transforms.\(^{32}\)

The contribution of the domain walls to the total free energy—i.e., the domain wall energy—is introduced through the gradient of the global polarization field. For the sake of simplicity and because of a dearth of experimental values for the domain wall energies along different directions, it is assumed that the wall energy is isotropic.

For isotropic domain wall energy, the gradient energy density can be written as

$$f_{\text{grad}} = \frac{1}{2} G_{11} \left[ (P_{11})^2 + (P_{12})^2 + (P_{13})^2 + (P_{21})^2 + (P_{22})^2 + (P_{23})^2 + (P_{31})^2 + (P_{32})^2 + (P_{33})^2 \right]$$  \(2.8\)

where $G_{11}$ is the gradient energy coefficient, and $P_{i,j}$ represents spatial differentiation of polarization, i.e., $P_{i,j} = \partial P_i / \partial x_j$

Under an applied electric field, the electrical energy density $f_{\text{elec}}$ is comprised of the dipole-dipole interaction energy density due to the inhomogeneous distribution of polarization, $f_{\text{dipole}}$; the depolarization energy density due to surfaces, $f_{\text{depol}}$; and the energy density due to the applied electric field, $f_{\text{appel}}$:

$$f_{\text{elec}} = f_{\text{dipole}} + f_{\text{depol}} + f_{\text{appel}}.$$  \(2.9\)

For an electrically inhomogeneous system the long-range electric dipole-dipole interaction energy density is given by

$$f_{\text{dipole}} = -\frac{1}{2} E_i P_i.$$  \(2.10\)
where $E_i$ denotes the inhomogeneous electric field due to dipole-dipole interactions.

It is obtained by solving the electrostatic equilibrium equation given by $D_{i,j} = 0$, where $D_i$ is the electrical displacement represented by $D_i = \varepsilon_0 \kappa_i E_j + P_i$, where $\varepsilon_0 = 8.85 \times 10^{-12}$ Fm$^{-1}$ represents the dielectric permittivity of vacuum and $\kappa_i$ the relative dielectric permittivity, assumed to be independent of space. Spatially differentiating the electric displacement and using the electrostatic equilibrium equation, we find

$$D_{i,j} = 0 = \varepsilon_0 (\kappa_i E_{j,i}) + P_{i,j}.$$  \hspace{1cm} (2.11)

The electric field $E_i$ is related to the electric potential $\phi$ through $-\phi_i = E_i$. Hence, by assuming $\kappa_{ij} = 0$ for $i \neq j$ and rearranging the terms in Eq. (2.11), we obtain

$$(\kappa_{11} \phi_{11} + \kappa_{22} \phi_{22} + \kappa_{33} \phi_{33}) = \frac{1}{\varepsilon_0} (P_{1,1} + P_{2,2} + P_{3,3}).$$ \hspace{1cm} (2.12)

Transforming Eq. (2.12) to Fourier space yields

$$\phi(\zeta) = -\frac{1}{\varepsilon_0} \frac{I(\zeta_1 P_1 (\zeta) + \zeta_2 P_2 (\zeta) + \zeta_3 P_3 (\zeta))}{(\kappa_{11} \zeta_1^2 + \kappa_{22} \zeta_2^2 + \kappa_{33} \zeta_3^2)}.$$ \hspace{1cm} (2.13)

where $\zeta_i$ is the positional co-ordinate in the Fourier space, and $I = \sqrt{-1}$. The symbols $\phi(\zeta)$ and $P_i (\zeta)$ denote the Fourier transforms of the electric potential and polarization component, respectively, and are given by

$$P_i (\zeta) = \frac{1}{(2\pi)^{3/2}} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P_i (x) e^{-i\zeta \cdot x} d^3 x.$$
\[ \phi_i(\zeta) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \phi_i(x)e^{-j\zeta x}d^3x, \quad (2.14) \]

The electric field and electric potential are related by \( E_i(\zeta) = -i\zeta/\phi(\zeta) \). Therefore, the real-space electric field arising from dipole-dipole interactions is given by

\[ E_i(x) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} E_i(\zeta)e^{j\zeta x}d^3\zeta. \quad (2.15) \]

It should be noted that the point \( \zeta = 0 \) is excluded when calculating the dipole-dipole interaction energy. The average depolarization field in global coordinates due to the presence of surface charges can be approximated as

\[ E_{i,\text{depol}} = -\frac{1}{\varepsilon_i} \bar{P}_i, \quad (2.16) \]

where \( \bar{P}_i \) is the spatial average of the \( i \)th component of polarization, and \( \varepsilon_i = \varepsilon_0 \kappa_{ii} \) (no summation implied by the repeated index). Hence, the depolarization energy density is

\[ f_{\text{depol}} = -\frac{1}{2} E_{i,\text{depol}}P_i. \quad (2.17) \]

Finally, when an externally electric field \( E_{i,\text{appel}} \) is applied in the global \( i \)th direction, an additional contribution \( f_{\text{appel}} \) should be taken into consideration:

\[ f_{\text{appel}} = -E_{i,\text{appel}}P_i. \quad (2.18) \]

With the total free energy \( F \) expressed as a functional of the global polarization, the temporal evolution of the domain structure can be obtained by solving the time-dependent Ginzburg-Landau (TDGL) equation,

\[ \frac{\partial P_i(x,t)}{\partial t} = -M \frac{\delta F}{\delta P_i(x,t)}i = 1, 2, 3, \quad (2.19) \]

whereby \( M \) is a kinetic coefficient related to the domain mobility, and \( t \) is time.
2.3 Numerical Simulations

Although the model described in the last section is applicable to 3-D polycrystalline systems, for computational reasons and simplicity 2-D simulations are performed to study the qualitative features and mechanisms of domain evolution during polarization switching in polycrystalline ferroelectrics.

The temporal evolution of the global polarization vector fields is obtained by numerically solving Eq. (2.19) using the semi-implicit Fourier spectral method. The Landau energy coefficients in Eq. (2.2) and the electrostrictive coefficients for PbTiO$_3$ are found in Ref. 20 and Ref.30 and were given originally by Haun et al. In the simulations I employed 512×512 discrete grid points and periodic boundary conditions applied along the $x_1$ and $x_2$ axes. The grid spacing was chosen to be $\Delta x_1 = 1.5\Delta x_1$, and the domain wall energy densities at $T = 25^\circ C$ are evaluated to be about $0.60 \alpha_0 l_0 P_0^2$ for $90^\circ$ domain walls and $1.26 \alpha_0 l_0 P_0^2$ for $180^\circ$ domain walls. The spontaneous polarization is $P_0 = |P|_{T=25^\circ C} = 0.757 \text{Cm}^2$. If $l_0 = 2.0 \text{nm}$, $G_{110} = 7.12 \times 10^{-10} \text{C}^2\text{m}^4\text{N}$. The corresponding specific domain wall energy is about $0.12 \text{Jm}^2$ for $90^\circ$ domain walls, and the wall width is around 3.0 nm, which is similar to experimentally observed domain wall energies and widths in single crystals. The time step in Eq. (2.19) is taken to be $\Delta t/t_0 = 0.05$, where $t_0 = 1/(\alpha_0 M)$. For the calculation of elastic energy, the elastic constants are assumed to be isotopic and homogeneous, with shear modulus $\mu=0.476\times10^{11}$ Nm$^{-2}$ and Poisson’s ratio $\nu=0.312$, in order to avoid having to solve inhomogeneous elastic equations in a polycrystal.
Clamped boundary conditions were used. For the dipole-dipole interaction energy calculations, $\kappa_{11} = \kappa_{22} = 100$ is used in simulation. It should be pointed out that although it is assumed constant dielectric constants, there is a spatial dependence of the apparent dielectric constant due to the spatial dependence of the spontaneous polarization. However, a more accurate calculation should use spatially varying dielectric constant tensor with the dielectric constant locally evaluated from the inverse of the second derivative of free energy with respect to polarization, which would significantly complicate the solution of the electrostatic equilibrium equation since the dielectric constant tensor would have tetragonal symmetry with tetragonal axes along different directions in different domains.

Assuming a single tetragonal domain for the ferroelectric state, the hysteresis loops under clamped boundary conditions can be computed analytically for a single crystal at different orientations. For a single domain system, the dipole-dipole interaction energy, depolarization energy and the gradient energy vanish. Thus, under a clamped boundary condition and assuming a single domain state, the total energy of the system can be defined as the sum of the bulk, the elastic energy and electric energy due to applied electric field. The hysteresis loop is computed analytically by minimizing the total energy with respect to $P_i$. Thus, the applied electric field along the $x_i$ direction is expressed as a function of $P_i$ and is calculated as

$$E_{i,appel} = \frac{\partial F^0}{\partial P_i},$$

where $F^0$ is the sum of the bulk and the elastic energies.

A domain structure was first generated by performing the simulations without an applied electric field, starting from an initial paraelectric state with small random perturbations. A depolarizing field was assumed to exist along both $x_1$ and $x_2$ directions. To compute the PE loop, an electric field is applied to the generated
domain structure in the $x_1$ direction, while a depolarizing field is assumed to exist along the $x_2$ direction. At each increment of the electric field, the domain structure from the previous simulation is used as the starting configuration. The PE loop is obtained by plotting the normalized average polarization $(\overline{P}_1 / P_0)$ vs. the normalized electric field in the $x_1$ direction $(E_1 / E_0)$, where $E_0=\alpha_0 P_0=1.306\times10^8 \text{Vcm}^{-1}$.

2.4 Results and Discussion

2.4.1 Ferroelectric domain switching in single crystals

For calculating the hysteresis loop of a 2-D single crystal of different orientation with respect to the applied electric field two different co-ordinate systems are used, are shown schematically in Fig. 2.1(i). Hysteresis loops of a single crystal under clamped boundary conditions is calculated analytically for two different orientations, 0° and 45°, with respect to the applied electric field, and the corresponding loops are shown by the broken lines in Fig. 2.2. As expected, the coercive field along the 45° orientation is $\sqrt{2}$ times larger than the 0° orientation. However, as it is well known that multi domains form during a ferroelectric phase transition, and it can be expected that the switching of a single crystal with multidomains is very different from that of a single-domain crystal. The solid lines in Fig. 2.2 show the hysteresis loops for single crystals under the clamped boundary condition at different orientations obtained from simulations as an electric field is applied along the $x_1$ direction. Each point in the PE loop represents
Fig. 2.1. (i) Schematic diagram of a single crystal with the two different coordinate systems. The global coordinate system is fixed. The orientation angle $\phi$ varies between $0^\circ$ and $45^\circ$; (ii) Schematic diagram of a bi-crystal. The considered orientations of grain 1 and 2 are listed; (iii) Schematic diagram of a bi-crystal with reduced transition temperature at the grain boundary. The transition temperature is varied linearly between the grain boundary and grain. The lowest transition temperature at the grain boundary is maintained either at $25^\circ$C or $150^\circ$C for PbTiO$_3$. The grain boundary width is same for all bi-crystals with reduced transition temperature at the grain boundary.
the average polarization at the end of 10000 iterations at a given electric field. It is shown that as the angle $\varphi$ increases, coercive field increases.

It is interesting to observe that there is a significant jump in the coercive field between $\varphi = 20^\circ$ and $30^\circ$. The reason for such a jump can be found by examining the domain structures in Fig. 2.3. In a typical tetragonal domain structure simulated in 2D, there are four tetragonal variants. The four variants are labeled as $a_1$ positive, $a_2$ positive, $a_1$ negative, $a_2$ negative with polarization $\left( P_{1L}^L > 0, P_{2L}^L = P_{3L}^L = 0 \right)$, $\left( P_{2L}^L > 0, P_{1L}^L = P_{3L}^L = 0 \right)$, $\left( P_{1L}^L < 0, P_{2L}^L = P_{3L}^L = 0 \right)$, and $\left( P_{2L}^L < 0, P_{1L}^L = P_{3L}^L = 0 \right)$, respectively. The four variants are represented with the different shades as shown in Fig. 2.3. The arrows represent the directions of polarization vectors. Fig. 2.3(i) represents the domain structure for $\varphi = 0^\circ$ at the maximum electric field corresponding to position A in Fig. 2.2. As one can see, the domain structure consists of three types of domains, $a_1$ positive, $a_2$ positive, and $a_2$ negative. Fig. 2.3(ii) shows the domain structure for $\varphi = 0^\circ$ that corresponds to point B in Fig. 2.2. It shows the nucleation of new domains at the twin boundary through $90^\circ$ domain switching (marked by the circles). Similarly, the domain structures for $\varphi = 15^\circ$ and $20^\circ$ at the maximum applied electric fields (points C and D in Fig. 2.2) also display three types of domains (Fig. 2.3 (iii) and (iv)).
Fig. 2.2. Hysteresis loops of single crystals with different orientations obtained from the phase-field simulations and the analytical calculations. The solid and the dotted lines indicate the hysteresis loops obtained from phase-field simulations and analytical calculations, respectively. Angles in the legend denote the orientations of the single crystals with the applied electric field.
Fig. 2.3. Domain structures of the single crystals with different orientations for various stages of polarization switching presented in Fig. 2.2 (i) for $\varphi = 0^\circ$ at point A; (ii) for $\varphi = 0^\circ$ at point B; (iii) for $\varphi = 15^\circ$ at point C; (iv) for $\varphi = 20^\circ$ at point D; (v) for $\varphi = 30^\circ$ at point E; (vi) for $\varphi = 45^\circ$ at point F.
By comparing Fig. 2.3(i), (iii) and (iv), it is found that $\varphi = 20^\circ$ has smaller volume fraction of $a_2$ positive domain. On the other hand, when $\varphi$ is greater than $30^\circ$, there are only two types of domains at the maximum applied electric field, namely $a_1$ positive and $a_2$ negative (Fig. 2.3(v) and (vi)). Absence of the third type of domains is the main reason for the significantly increase in the coercive field for $\varphi$ greater than $30^\circ$ (Fig. 2.2).

To study the effect of external mechanical boundary conditions on the switching behavior, two single crystals with different orientations under stress-free boundary conditions is considered and the PE loops are shown in Fig. 2.4. The dotted and solid lines show the hysteresis loops obtained from thermodynamic calculations and phase-field simulations, respectively. For comparison, hysteresis loops of single crystals obtained from thermodynamic calculation under clamped boundary condition are also presented. The figure shows that similar to the clamped boundary condition the coercive field obtained from thermodynamic calculation increases as the angle $\varphi$ increases. Contrary to the thermodynamic calculation the coercive field obtained from the phase-field simulation under a stress-free condition decreases as the angle $\varphi$ increases. This can be explained from the domain structure corresponding to the maximum electric field as shown in Fig. 2.5. The figure shows that for $\varphi = 0^\circ$ the single crystal comprised of a single domain while for $\varphi = 45^\circ$ the domain structure comprised of two kind of domains, which facilitates the formation of new domains during polarization switching. This observed decrease in coercive field with the presence of more than one tetragonal variant in a single crystal is similar to the trend observed under a clamped boundary condition as presented above.
Fig. 2.4. Hysteresis loops of the single crystals with different orientations under stress-free condition.
Fig. 2.5. Domain structures of the single crystals obtained from simulations under stress-free condition corresponding to the maximum electric field. (i) for single crystal with $\phi = 0^\circ$ corresponding to point K; (ii) for single crystal with $\phi = 45^\circ$ corresponding to point L in Fig. 2.4.
Comparison of the domain structures obtained under the stress-free and clamped boundary conditions shows that it is easier to stabilize more than one tetragonal variant under the clamped boundary condition. Since a crystalline grain is clamped by neighboring grains in a polycrystal, a clamped boundary condition is assumed for the rest of the chapter.

2.4.2 Switching in bicrystals

Fig. 2.1(ii) shows a schematic diagram of two bi-crystals. In both bi-crystals, the orientation ($\phi$) of grain 1 is 0° while that of grain 2 is 15° for bi-crystal 1 and 45° for bi-crystal 2.

Fig. 2.6(i) and (ii) show the hysteresis loops for bi-crystal 1 and bi-crystal 2, respectively. For comparison, I have also included the hysteresis loops for the corresponding single crystals at different orientations. It is shown that the hysteresis loop for bi-crystal 1 lies in-between those for corresponding single crystal values with the coercive field approximately the average of the single crystal values, i.e., the effect of grain boundary is minimal. However, for bi-crystal 2, the coercive field is much lower than the average of the corresponding single crystals as shown in Fig. 2.6(ii).

To understand the difference between the switching behaviors of the two bi-crystals, I examine the domain structure (Fig. 2.7(i)) of bi-crystal 1 at the maximum applied electric field (point M in Fig. 2.6(i)). It is shown that each grain consists of three domains, similar to their corresponding single crystals at the same orientations.
Fig. 2.6. Hysteresis loops of the bi-crystals shown in Fig. 2.1(ii). The hysteresis loops of the single crystals obtained from simulation for $\phi=0^\circ$ and $15^\circ$, $\phi=0^\circ$ and $45^\circ$ are presented in Fig. 2.6(i) and Fig. 2.6(ii) respectively for comparison. Plots in (iii) show the comparison of the hysteresis loops of bi-crystal 2 and bi-crystal 3.
Fig. 2.7 Domain structures of bi-crystals at various stages of polarization switching presented in Fig. 2.6. Domain structures in (i) and (ii) are, respectively, corresponding to point M and point N of bi-crystal 1 in Fig. 2.6(i). Domain structures in (iii) and (iv) are, respectively, corresponding to point X and point Y of bi-crystal 2 in Fig. 2.6(ii). The circles represent the nucleated new domains near the grain boundaries. Domain structure in (v) is corresponding to points Z of bi-crystal 3 in Fig. 2.6(iii).
Fig 2.7(ii) is a domain structure during initiation of switching in the bi-crystal corresponding to point N in Fig. 2.6(i). A new domain is shown to nucleate at the grain boundary. For comparison, the domain structure of bi-crystal 2 at the maximum applied electric field is shown in Fig. 2.7(iii) (point X in Fig. 2.6(ii)). It is seen that though the domain structure in grain1 has three types of domains, grain2 with $\phi = 45^\circ$ contains only two types of domains. However, in this case, nucleation of a new domain occurs during switching at the grain boundary (Fig. 2.7(iv)) which corresponds to point Y in Fig. 2.6(ii) and it propagates towards the grain interior. Hence, although grain2 in bi-crystal 2 consists of only two domains at the maximum applied field, presence of the grain boundary acts as a source for nucleating new domains. As a result, the coercive field is much lower than the average of the corresponding single crystals (Fig. 2.6(ii)).

In the above two examples, both of them have one of the two half crystals oriented along $\phi$ equal to 0. As another example, the switching behavior of a bi-crystal with $45^\circ$ misorientation between the two half crystals is examined. One half crystal is oriented at $\phi = 22.5$ and the other half is with $\phi = -22.5^\circ$. I call this example bi-crystal 3. Fig. 2.7(v) shows the domain structure at the maximum applied electric field (point Z in Fig. 2.6(iii)). It is shown that both grains contain three types of domains. Thus, when the electric field is reversed, new domains can nucleate at twin boundaries, and consequently, the coercive field in bi-crystal 3 is less than the coercive field for bi-crystal 2 (Fig. 2.6(iii)). Furthermore, a comparison between the slopes of the hysteresis loops from the two bi-crystals shows that nucleation of a new domain during switching initiates at a much lower field at a twin boundary in bi-crystal 3 than at the grain boundary as in bi-crystal 2.
Fig. 2.8 Normalized global elastic stress distribution near the grain boundary of bicrystal1 and bicrystal2 during switching. The normalization factor \((\sigma_0)\) is \(9.8 \times 10^6\) MPa. Figure (i-iii) shows the distributions of stress components \(\sigma_{11}^G / \sigma_0\), \(\sigma_{22}^G / \sigma_0\) and \(\sigma_{12}^G / \sigma_0\) of bicrystal1 corresponding to the domain structure in Fig. 2.7(ii) while figure (iv-vi) shows the distribution of similar stress components in bicrystal2 corresponding to the domain structure in Fig. 2.7(iv). A thick line shows the grain boundary while the domain walls are schematically shown by dotted line. The location of concentration of stress near the grain boundary is marked.
To study the effect of grain boundaries on the stress distribution during polarization switching, the distribution of normalized global elastic stress near the grain boundary in bi-crystal 1 and bi-crystal 2 is plotted. The corresponding stress distributions are shown in Fig. 2.8. The elastic stress components $\sigma_{ij}$ are calculated from the elastic strains using the relation $\sigma_{ij} = C_{ijkl} e_{kl}, i, j, k, l = 1, 2, 3$. Fig. 2.8(i-iii) displays the distribution of stress components in bi-crystal 1 corresponding to the domain structure presented in Fig. 2.7(ii). Solid lines mark the grain boundary while the domain walls are schematically shown by dotted lines. The high-stress location near the grain boundary is marked. The fact that high stresses occur near the grain boundary can be related to the nucleation of the new domain. Shown in Fig. 2.8(iv-vi) are the distributions of stress components in bi-crystal 2 (based on the domain structure presented in Fig. 2.7(iv)). Similar to bi-crystal 1, high stress is generated near the grain boundary during polarization switching. Comparing the stress distribution for the two bi-crystals, the magnitude of the stress components is higher in bi-crystal 2 with a larger misalignment between the two grains. Nucleation of a new domain at a grain boundary creates intersections between domain boundaries and a grain boundary. The domains around the intersections have different transformation strains as a result of different crystallographic orientations. The incompatibility of the deformation among these domains near the grain boundary results in high stress concentration at the intersections.

2.4.2.1 Effect of reduced transition temperature at grain boundaries

In order to study the effect of the nonferroelectric phase of a grain boundary on switching, I assumed a reduced transition temperature at the grain boundary of a bi-crystal (Fig. 2.1(iii)). I studied two cases where the lowest transition temperatures
at the grain boundary are assumed to be 150°C and 25°C, respectively. The transition temperature within the grain is 479°C, the same as the transition temperature of bulk lead titanate under the clamped boundary condition. It is assumed that the transition temperature varies linearly near the grain boundary as shown in Fig. 2.1(iii). The grain boundary width is maintained at four simulation grid points i.e. the width of the grain boundary is $4\Delta x$. The orientation of the bi-crystal is the same as described in Fig. 2.1(ii). For the rest of the chapter, bicrystal1 and bicrystal2 with a reduced transition temperature at the grain boundary will be referred as bi-crystal 1' and bi-crystal 2', respectively.

Fig. 2.9(i) and (ii) show the hysteresis loops for bi-crystal 1' and bi-crystal 2'. It can be seen that, in both the cases, the coercive field increases as the transition temperature at the grain boundary decreases. For bi-crystal1' in which the transition temperature at the grain boundary is decreased from 479°C to 25°C, the increase in the coercive field is small. This can be explained from the switching behavior in bi-crystal 1 in Fig 2.6(i), which was found to be similar to the single crystal with the coercive field approximately the average of the single crystal values. As the grain boundary does not play a significant role in the switching behavior of bi-crystal 1, reducing the transition temperature at the grain boundary only has a small effect on the coercive field. For the case of bi-crystal 2, the situation is quite different. As it is shown above, nucleation of new domains in bi-crystal 2 occurs primarily at the grain boundary for bi-crystal 2 (Fig. 2.7(iv)), a significantly lower transition temperature at the grain boundary greatly decreases the coupling across the grain boundary, and thus increases the coercive field (Fig. 2.9(ii)). Therefore, if this is the general case, a
Fig. 2.9. Hysteresis loops of bi-crystals for two different orientations of grain 2 shown in Fig. 2.1(iii). (i) for bi-crystal 1; (ii) for bi-crystal 2’. In each of the figures the lowest transition temperature at the grain boundary is varied.
decrease in the ferroelectric transition temperature at the grain boundary will increase the coercive field.

2.4.3 Domain switching in a polycrystal

To simulate the polarization switching in polycrystal a 2-D grain structure is generated employing the grain-growth model developed by Krill and Chen. Figure 2.10 shows an example of a 2-D grain structure generated by the 2-D version of the 3-D grain-growth model. In this work, it is assumed that the grain structure is static—i.e. it does not evolve with time. The simulated polycrystal is comprised of 91 grains, with each grain assumed to be oriented along a different crystallographic direction. In two dimensions the orientations of different grains can be specified by the rotation angle $\varphi$ about the $x_3$ axis; hence, the angles $\theta$ and $\psi$ are assumed to be zero in Eq. (2.3). The grain orientations vary between $0^\circ$ and $45^\circ$ because of symmetry. The orientation of each individual grain ($\varphi$) was assigned randomly and does not change with time during domain switching.

Figure 2.11 shows an example of the domain structure in a polycrystal at zero applied electric field following 50000 iterations beginning from a paraelectric state. There are four tetragonal variants, labeled as $a_1$ positive, $a_2$ positive, $a_1$ negative, and $a_2$ negative, with polarization components $(P_{1}^{L} > 0, P_{2}^{L} = P_{3}^{L} = 0)$, $(P_{2}^{L} > 0, P_{1}^{L} = P_{3}^{L} = 0)$, $(P_{1}^{L} < 0, P_{2}^{L} = P_{3}^{L} = 0)$, and $(P_{2}^{L} < 0, P_{1}^{L} = P_{3}^{L} = 0)$, respectively. The four variants are represented by different shading. As expected, the polarization directions for the domains vary from one grain to another, with both $90^\circ$
Fig. 2.10. Grain structure generated using the 2-D phase-field model for grain growth.

The dotted and solid pairs of arrows illustrate the global and local coordinate systems, respectively, with $0^\circ \leq \phi \leq 45^\circ$. 
Fig. 2.11: Domain structure after 50000 iterations without applied electric field. The four tetragonal variants are shaded according to the legend at top left.

Fig. 2.12. Hysteresis loop computed for lead titanate ceramic
and 180° domain walls existing in the simulation cell. Figure 2.12 shows the $\overrightarrow{P}_1$ vs. $E_{\text{appel}}$ loop (PE loop) as an electric field is applied along the $x_1$ direction. Each point in the PE loop represents the average polarization at the end of 5000 iterations at the given electric field. As the applied electric field increases, the volume fractions of the tetragonal $a_1$ and $a_2$ domains change. The polarization directions in different grains try to orient along the direction of the electric field. Therefore, for the maximum positive applied electric field, corresponding to point b in Fig. 2.12, the $a_1$ domains with negative polarization vanish, as seen in Fig. 2.13. The domain structure is predominantly comprised of just two types of domains—namely, $a_1$ positive and $a_2$ negative. A small volume fraction of $a_2$ positive domains is present in the grains having an orientation close to that of the applied field.

Fig. 2.13: Domain structure corresponding to the point b in the PE loop of Fig. 2.12. The tetragonal $a_1$ negative variant is completely absent, and the majority of the simulation cell is comprised of two tetragonal variants.
To illustrate the domain evolution process in more detail, in Figs. 2.14(i–iv) the evolution of the polarization configurations within the dotted rectangular box of Fig. 2.11 is plotted for various iteration numbers $N_{itr}$ at point $c$ of Fig. 2.12, where $E_{appel} = 104.48 \text{kV/cm}$. The small arrows in Fig. 2.14 indicate the local polarization direction. Figure 2.14(i) shows the domain structure in grain A after the first iteration. As the number of iterations increases, an $a_1$ domain with positive polarization nucleates at the grain boundary where the twin boundary and the grain boundary meet [Fig. 2.14(ii)]. A solid circle marks the location of the nucleated domain. The domain then grows towards the center of grain A, with the large arrow in Fig. 2.14(ii) indicating the direction of domain growth. From Fig. 2.14(iii) it is evident that switching in grain A propagates to the neighboring grain B, resulting in the nucleation a new domain in grain B. The nucleated domain then grows toward the center of grain B, as shown in Fig. 2.14(iv). Switching occurs by a similar mechanism in other grains as well, suggesting that this is a rather general mechanism for switching in a polycrystal. To analyze the energetic contributions to local domain switching, the changes in the local energy densities in grain A as switching progressed are determined. Figures 2.15 and 2.16 show the contours of the change in electric and elastic energy density distributions, respectively, at different stages of the switching process. The difference in the energy densities is calculated with reference to the domain structure presented in Fig 2.14(i). For example, Fig. 2.15(i) represents the distribution of the difference in electrical energy density between the domain structures presented in Figs. 2.14(ii) and 2.14(i); the darker the color of the contour,
Fig 2.14: Domain structure during switching at an applied electric field of $E_1 = 104.48$ kV/cm. Figures correspond to the point c in the PE loop of Fig. 2.12 at different iteration steps: (i) $N_{itr}=1$; (ii) $N_{itr}=500$; (iii) $N_{itr}=1000$ and (iv) $N_{itr}=3700$. The filled lines represent grain boundaries, while the dashed and thin lines denote 90° and 180° domain walls, respectively. The nucleated 90° domain is marked by a circle. The big arrow shows the direction of growth of the nucleated 90° domain.
Fig. 2.15. Difference in electrical energy density of the domain structure presented in Figs. 2.14(ii–iv) with respect to that of the unswitched domain structure of Fig. 2.14(i). It can be seen that the electrical energy density decreases with the nucleation and growth of the 90° domain.
Fig. 2.16. Difference in elastic energy density of the domain structure presented in Figs. 2.14(ii–iv) with respect to that of the unswitched domain structure of Fig. 2.14(i).
the higher the magnitude of energy density. The iteration steps were chosen to be identical to those presented in Figs. 2.14(ii–iv). The stability of domain structures in ferroic materials is governed by competing energetic contributions. In the case of a ferroelectric material, the total energy includes the bulk free energy, domain wall energy, electrostatic energy, and elastic energy densities. Under an applied electric field, the changes in these energies determine the nucleation of a new domain at a particular site and growth by domain wall migration during polarization switching.

According to Fig. 2.15(i), the nucleation of a new domain near the grain boundary in grain A reduces the electrical energy density locally. The figure shows that the nucleated domain marked by the circle is bounded by contour lines of –0.05 and –0.02. Figures 2.15(ii–iii) illustrate how the growth of the 90° domains is also accompanied by a decrease in the electrical energy density with respect to the unswitched energy state. The decrease in electrical energy density during nucleation and growth can be attributed to the difference in polarization direction across the grain boundary between grains A and B. Nucleation and growth of a 90° domain in grain A helps to maintain a head-to-tail configuration across the grain boundary. The switching in grain A seems to promote the nucleation of a 90° domain within grain B near the grain boundary, indicating that switching in one grain influences the occurrence of switching in neighboring grains.

The elastic energy density changes during switching are shown in Figs. 2.16(i–iii). All contour lines near the switched domain have positive values, indicating that switching increases the elastic energy density locally compared to the unswitched state. Comparing Figs. 2.15 and 2.16, it is concluded that the switching-induced increase in elastic energy density is more than offset by the decrease in electrical energy density; hence, the total energy density of the system decreases.
Therefore, it can be concluded that nucleation and growth of 90° domains is primarily driven by the decrease in the electrical energy density.

The observation of polarization switching by nucleation and growth of 90° domains has already been found in experiment. For example, Chen et al. 37 observed that polarization switching in PZT thin films occurs by nucleation of new 90° domains at twin boundaries and subsequent growth along the twin boundaries. This confirms the behavior seen in Fig 2.14(ii) that a new 90° domain nucleates at the twin boundary in grain A and grows toward the center of the grain along the twin boundary marked by the large arrow. Using a finite element model, Hwang et. al. 23,25 suggested that the change in dielectric interaction energy arising from neighboring grains was the primary cause for 90° switching in ferroelectric polycrystals. In addition, the prediction that the polarization switching in one grain is facilitated by the polarization switching in a neighboring grain is consistent with prior observations by Cao et al. 38, which indicated that the domain switching process involves both intergranular and trans-granular cooperation.

It should be noted that the model takes into account the random orientation of grains in a polycrystalline structure, the complicated local elastic and electrostatic interactions between neighboring grains in a polycrystalline ferroelectric. However, the developed phase-field model does not take in to consideration the energetic contribution from the grain boundary also known as grain boundary energy. Phase-field model are available to incorporate the grain boundary energy 39 as a function of mis-orientation between the grains and can be introduced to make the model more realistic. Moreover, it is possible to introduce other defects into the model, such as inhomogeneous compositional distributions, dislocations and second-phase precipitates.40-42 Further, in future effect of point defects on polarization switching
should also be taken into consideration as these defects are known to play a significant role in determining remanent polarization when the ferroelectric is subjected through repeated electric cycles. In addition, in this work it is assumed that the elastic coefficients are homogenous and isotopic, although real polycrystalline materials are always inhomogeneous. Further, it was shown by Li et al.\textsuperscript{20} using phase-field simulations of lead titanate thin films as a model system that the anisotropy in elastic modulus can also affect the domain structure. Numerical algorithms are now available for taking into account the anisotropy\textsuperscript{20} and inhomogeneity\textsuperscript{41,43} in elastic modulus and its effect can be included on ferroelectric domain switching. Finally, it should be emphasized at this point that dielectric constants can be calculated from the expression of landau energy. Thus a close inspection of landau energy will reveal that the anisotropy in dielectric constants is in-built in the model. Hence for a precise phase-field simulations one should assume a vacuum dielectric constant in calculating the electrostatic energy density. However, my observation shows that using vacuum dielectric constants may lead to some numerical instability. Hence in these simulations I assumed the dielectric constant to be equal to 100. Although the emphasis of this chapter is on the domain switching mechanisms under an electric field, the model can be applied to domain evolution under an applied stress or to the simultaneous application of stress and an electric field. Furthermore, the present model can be applied directly to switching and domain evolution in a 3-D system; as a matter of fact, a parallel version of the current computer code is being developed for the study of domain switching mechanisms and hysteresis loops in 3D.
2.4.3.1 Grain size effect on domain switching in a polycrystal

To study size effects on the domain structure and polarization switching I used six grain structures with different grain sizes and $512 \times 512$ discrete grid points, such that the average grain radius varies between 11 to 89 nm.

Fig. 2.17 shows the domain structures of the six polycrystals without any applied electric field. Comparison of the domain structures in Fig. 2.17(i-vi) shows that the larger the average grain size, the higher the total number of tetragonal variants present in each grain. As the grain size decreases, the number of tetragonal variants present in each grain decreases. This prediction matches well with experimentally observed domain structures by Randall et. al.$^{38}$ in PZT. Furthermore, it is observed that as average grain radius decreased to 11 nm, most of the grains become single domains.

To study the effect of grain size on the switching behavior, the hysteresis loops for three-grain sizes ($R_{\text{ave}}=11, 32, 52$ nm) is constructed as shown in Fig. 2.18. It is shown that the polycrystalline structure with a smaller grain size has smaller magnitude of coercive field. It has been shown in Fig.2.16 (ii) and (iv), grain boundaries act as sources for the nucleation of new domains during switching. As a result, a polycrystal with smaller grain size provides more nucleation sites for new domains during switching, and thus results in a lower coercive field. The remanent polarization for different grain sizes almost remains the same.
Fig. 2.17 Domain structure of lead titanate polycrystal in decreasing grain size. The system size is kept fixed in all the six cases at 512x512. The average grain radii are 88nm, 52nm, 43nm, 32nm, 17nm and 11nm, respectively.
Although the predicted effect of grain size on the domain structure is consistent with experimental observation, but the decrease of coercive field with grain size from phase-field simulations seems to contradict to the experimental observations where it was observed that the coercive field increases with the decrease of grain size. This difference in the grain size dependence on switching is possibly due to the much smaller grain size (of the order of few tens of nanometers) considered in my simulations as compared to those studied experimentally which of the order of microns. Hence, for a grain structure with experimental grain size, each grain typically contains more than two different types of domains. As my simulation results on switching behavior of bicrystals show that the number of domains present within each grain affects the domain switching behavior of individual grains, it appears that the range of grain size considered in this work may not be sufficient enough to explain experimental observation. Thus, it is difficult to draw a clear conclusion on the effect of size on coercive fields based on 2-D simulations.
Fig. 2.18. Effect of grain size on hysteresis loop obtained from phase-field simulations.
2.5 Summary

A 3-D phase-field model has been developed for predicting domain structure evolution under an applied electric field in ferroelectric polycrystals. Phase-field simulations were performed to understand the role of grain orientations and boundaries in domain switching in ferroelectric single-, bi- and poly-crystals. It was found that switching behavior in a single crystal is strongly dependent on the orientation of the grain with respect to the applied electric field for both clamped and stress-free boundary conditions. It was observed that in single crystals, the number of tetragonal variants in the domain structure at the maximum applied electric field determines the coercive field during polarization switching. The switching behavior of a bi-crystal was found to be similar to that in single crystals when the mis-orientation between the grains of a bicrystal is less than $15^\circ$. Grain boundary was found to play a significant role in determining the switching behavior for bicrystals with larger mis-orientations between the grains of the bicrystal. Furthermore, it was observed that reducing the transition temperature at the grain boundary might change the switching behavior of a bi-crystal. The effect of reduction of transition temperature at grain boundary on coercive field depends on the orientation of the grains with respect to the applied electric field direction. Based on the simulation of ferroelectric domain evolution in polycrystal, it was found that polarization reversal takes place by the nucleation and migration of $90^\circ$ domain walls instead of by direct $180^\circ$ domain switching. It was observed that these $90^\circ$ domains nucleate at the grain boundaries and then grow toward the grain interior. The electrical energy was found to be the main driving force for both the nucleation and growth of $90^\circ$ domains. Finally, it was demonstrated that polarization switching between neighboring grains is correlated.
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Chapter 3

Effect of Multi Ferroelectric Variants on Coercive Field

In this chapter the effect of number of ferroelectric variants on domain switching and coercive fields in bulk PZT single crystals has been studied. The study is performed using a combination of the continuum phase field approach, microelasticity and electrostatics. Further, the values of coercive fields predicted from the phase field simulations are compared with the corresponding values obtained from phenomenological thermodynamic theory assuming a single ferroelectric domain.

3.1 Literature Review

A common feature for all ferroelectrics is the formation of domains upon cooling below the ferroelectric transition temperature. The coercive field is defined as the magnitude of an external electric field, which results in zero net polarization. Theoretically, the coercive field calculated from a phenomenological thermodynamic theory assuming a perfect crystal with a single domain, corresponds to the critical field that drives a homogeneously polarized ferroelectric to instability. The values of coercive field predicted from such an approach is typically one or more orders of magnitude too high compared to those measured experimentally. On the other hand, Landauer showed that it was impossible to nucleate domains through the homogeneous nucleation mechanism; the estimated nucleation energy barrier (~10^8 kT) at an electric field of 1 kV/cm is much too high compared to the available thermal energy. Therefore, to explain the experimentally measured coercive fields, various
materials inhomogeneities have been suggested to be responsible for lowering the domain nucleation barrier, including surfaces, grain boundaries, dislocations and dipolar defects. For example, it has been shown that structural and/or dipolar defects can reduce the energy barrier for domain nucleation during polarization switching, and thus lead to a much smaller coercive field than thermodynamic estimates.

While it is realistic to expect the coercive field of a ferroelectric to be dependent on the defect and defect densities, the existence of defects alone is not sufficient to explain experimentally observed coercive field and the disagreement in the coercive fields between theory and experiments. For example, the experimentally reported coercive fields for a given ferroelectric are within a relatively narrow range, e.g. 9 – 20 kVcm\(^{-1}\) for PbZr\(_{1-x}\)Ti\(_x\)O\(_3\) (PZT) polycrystal at the morphotropic phase boundary (MPB) composition. If structural or dipolar defects are the critical structural features that control the coercive field, one would expect much larger variations of coercive fields measured on ferroelectric samples prepared under different processing conditions but with the same chemistry since defect densities are expected to be strongly processing-dependent. On the other hand, in the absence of external constraints, the number of ferroelectric domain variants for a ferroelectric is solely determined by the transformation crystallography and is independent of processing conditions, where a variant is defined by the direction of the spontaneous polarization along a definite crystallographic direction. The main focus of this chapter is to discuss the relationship between the number of domain variants in a ferroelectric domain structure and the magnitude of coercive fields in an attempt to shed light on the main factors that determine the coercive field.
In this chapter bulk PbZr\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{3} (PZT) single crystals is considered as the model system for phase field simulations. I employ two-dimensional (2-D) and three-dimensional (3-D) phase field simulations as well as thermodynamic calculations. Phase field approach has previously been used to predict ferroelectric transition temperatures and domain structures in bulk ferroelectric and thin films.\textsuperscript{8-10} Unlike the thermodynamic approach, the phase-field approach does not make any \textit{a priori} assumptions with regard to the possible domain structure that might appear under a given condition. It is able to predict the detailed domain structures and their temporal evolution when an uniform external electric field is applied.\textsuperscript{10} In this chapter, I will demonstrate that with the systematic increase of the number of ferroelectric variants, the predicted coercive field approaches to the experimental measurements.

### 3.2 Phase-field model

To describe a proper ferroelectric transition, the spontaneous polarization 
\( \mathbf{P} = (P_1, P_2, P_3) \) is chosen as the order parameter. The total free energy of an inhomogeneous ferroelectric single crystal is given by

\[
F = \int_V \left( f_{\text{bulk}} + f_{\text{elas}} + f_{\text{grad}} + f_{\text{elec}} \right) d\mathbf{V},
\]

where \( f_{\text{bulk}} \) is the bulk free energy density, \( f_{\text{elas}} \) is the elastic energy density, \( f_{\text{grad}} \) is the gradient energy density which is only nonzero around domain walls, and \( f_{\text{elec}} \) is the electrostatic energy density. \( V \) is the volume of the simulated system. The mathematical expressions of all the free energies are given in chapter 2 and hence they are not listed here.
3.3 Numerical Simulations

In the simulations, the simulation cell is discretized as $256\Delta x_1 \times 256\Delta x_2 \times 1\Delta x_3$ and $128\Delta x_1 \times 128\Delta x_2 \times 128\Delta x_3$ grid points, respectively. Periodic boundary conditions are applied along the all $x_1$, $x_2$ and $x_3$ directions. The grid spacing was chosen to be $\Delta x_1 = \Delta x_2 = \Delta x_3 = l_0$, where $l_0 = \sqrt{G_{110}/\alpha_0}$ and $\alpha_0 = |\alpha_1|_{T=25^\circ C}$. The gradient energy coefficient was assumed to be $G_{11}/G_{110} = 0.6$ which resulted in a domain wall width about $1.5\Delta x_1$. For elastic energy calculation, the elastic constants were assumed to be homogenous and isotopic with shear modulus $\mu = 0.476 \times 10^{11}$ Nm$^{-2}$ and Poisson’s ratio $\nu = 0.312$. Clamped boundary condition was used. For the dipole-dipole interaction energy calculations, $\kappa_{11} = \kappa_{22} = 100$ was used, where $\kappa_{ij}$ the relative dielectric permittivity, assumed to be independent of space.

In order to construct a polarization versus applied electric field (PE) loop, an initial domain structure was generated by performing the simulations without an applied electric field, starting from a paraelectric state with small random perturbations. Depolarizing fields along all $x_1$, $x_2$ and $x_3$ directions were considered. Then, an electric field is applied to the domain structure along the $x_1$ direction while depolarizing fields were assumed to exist along the other $x_2$ and $x_3$ direction. At each increment of the electric field, the domain structure from a previous simulation was used as the input, where the increment in the electric field between two consecutive points in the PE loop is maintained at 0.001 kV/cm.

3.4 Results and Discussion

As the first example, PZT with composition of $x = 0.80$ was considered. Its stable ferroelectric phase is of tetragonal symmetry. The polarization vs electric field
Fig. 3.1. Hysteresis loops for bulk PZT single crystal of composition x=0.80 and x=0.575. The black and the blue dotted lines are the hysteresis loops obtained from 2-D and 3-D phase-field simulations for PZT (x=0.80) bulk single crystal, respectively. For comparison, the hysteresis loop obtained from thermodynamic calculation assuming a single domain is presented, as shown by green solid line. The red solid line shows the hysteresis loop obtained from a 3-D phase-field simulation for PZT (x=0.575) bulk single crystal.
(PE) loops obtained in the 2-D and 3-D simulations were given by dotted lines in Fig. 3.1. In the 2-D simulations, the domain structure consists of four possible tetragonal variants, namely $a_1$ positive, $a_2$ positive, $a_1$ negative, and $a_2$ negative, with polarization components $(P_1 > 0, P_2 = P_3 = 0)$, $(P_2 > 0, P_1 = P_3 = 0)$, $(P_1 < 0, P_2 = P_3 = 0)$, and $(P_2 < 0, P_1 = P_3 = 0)$, respectively. In the 3-D simulations, a domain structure may have all its six possible tetragonal variants, i.e., in addition to those present in 2-D, $a_3$ positive and $a_3$ negative with polarization components $(P_1 = P_2 = 0, P_3 > 0)$ and $P_1 = P_2 = 0, P_3 < 0$ are included. As shown in Fig. 3.1 the predicted coercive field of 131.7 kVcm$^{-1}$ in 3-D is less than that (170.54 kVcm$^{-1}$) obtained in 2-D. The decrease in the predicted coercive field in 3-D as compared to 2-D can be attributed to the additional two tetragonal variants. For comparison, the hysteresis loop obtained from the thermodynamic calculation under a single tetragonal domain assumption is shown by the green solid line in the same figure. It is seen that the coercive field from the thermodynamic calculation is about three and half times large as that obtained from the 3-D phase field simulation. Based on the hysteresis loops for PZT ($x = 0.80$) single crystals obtained from the thermodynamic calculation, 2-D and 3-D phase field simulations, we make a hypothesis that the coercive field of a ferroelectric is closely related to the number of ferroelectric domain variants. The predicted coercive field decreases as the number of variants increases for the same system.

To test this hypothesis, additional 3-D phase field simulations of PZT single crystals was performed near the morphotropic phase boundary. In this case, it is possible to have all six tetragonal variants as well as eight rhombohedral variants for a total of fourteen variants in the domain structure. The red solid line in Fig. 3.1 is the corresponding hysteresis loop. Quite remarkably, the coercive field is dramatically
Fig. 3.2. Domain structure during domain switching of a PZT (x=0.80) single crystal corresponding to point A in Fig. 3.1 obtained from the 2-D phase field simulation. The polarization directions of the ferroelectric variants are indicated. Areas marked by circles show that the $a_1$ negative domains nucleate at the twin boundaries.
Fig 3.3. Domain structure corresponding to point B in Fig. 3.1 for a PZT single crystal with composition of $x=0.575$ from the 3-D simulation. The blue colors represent rhombohedral phase while rest of the colors represent tetragonal variants. Areas marked by the circles show the nucleation locations of tetragonal $a_1$ negative variant during switching.
reduced, approximately 20.05 kVcm\(^{-1}\), which is about one seventh of that for the tetragonal ferroelectric state of PZT at x=0.80 predicted by the 3-D simulation.

To understand the role of the number of domain variants in reducing the coercive field, I examined the domain structure evolution during switching. Fig. 3.2 is a 2-D domain structure corresponding to the point A in Fig. 3.1. Each color represents a tetragonal variant and the direction of the polarization is indicated for each variant. It is shown that \(a_1\) negative domains nucleate at the twin boundaries, i.e. 90\(^\circ\) domain walls (marked by the circles). Fig. 3.3 is a domain structure from a 3-D simulation of PZT at the MPB composition (x = 0.575), corresponding to point B in Fig. 3.1. The domain structure contains a phase mixture. Rhombohedral ferroelectric variants are represented by different blue shades, while other colors denote the tetragonal variants. It is demonstrated that \(a_1\) negative domains nucleate either at the domain boundaries between tetragonal and rhombohedral variants or at the boundaries between different tetragonal variants (marked by circles) during switching. Comparing the 2-D and 3-D domain structures, the significantly reduced coercive field at the MPB composition can be mostly attributed to the increase in the number of ferroelectric variants as compared to the tetragonal composition.

The experimentally measured coercive fields for tetragonal compositions and for compositions near the MPB are 22-40 kVcm\(^{-1}\)\(^{18-20}\) and 9-20 kVcm\(^{-1}\)\(^{7}\), respectively. The predicted coercive fields for single crystals obtained from our 3-D phase field simulations for compositions of x=0.80 and x=0.575 are about 3-6 times and 1-2 times the experimental measurements while the predicted coercive field assuming a single tetragonal domain is 11-20 times the experimental measurements. It should be pointed out that the experimentally measured hysteresis loops for PZT are
for polycrystalline samples. Therefore, the additional difference in the simulated coercive fields and experimental measurements is possibly due to the presence of defects such as grain boundaries and dislocations present in polycrystalline ceramics. The role of these extrinsic defects becomes increasingly important as the number of ferroelectric variants decreases. Theoretical models are now available\textsuperscript{10,11} for introducing defects like dislocations as well as grain structures (as presented in previous chapter), and it has been shown that they will likely further reduce the predicted coercive field.

3.5 Summary

To summarize, the presence of multivariants/multidomains accounts for the dramatically different values of coercive fields of bulk ferroelectric crystals predicted from prior phenomenological thermodynamic theory. It is shown that the nucleation of domains during polarization switching occurs at the domain walls among various ferroelectric domains in a single crystal.
References


Chapter 4

A Phase Diagram for Epitaxial PbZr\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{3} (PZT) Thin Films at the Bulk Morphotopic Boundary Composition

In this chapter phase-field simulations were performed to construct a phase diagram of temperature versus strain was constructed for a (001)-oriented PbZr\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{3} (PZT) epitaxial thin film near the bulk morphotropic boundary composition (\(x = 0.47\)) on an (001)-oriented cubic substrate. The predicted phase stability obtained from phase field simulations is compared with the phase stability obtained from thermodynamic calculations assuming a single-domain state.

4.1 Literature Review

Epitaxial PbZr\textsubscript{1-x}Ti\textsubscript{x}O\textsubscript{3} (PZT) thin films find wide applications in microwave acoustic devices, dynamic random access memories (DRAMs), and ferroelectric random access memories (FeRAMs).\textsuperscript{12,13} Recently considerable attention has been paid to the preparation of epitaxial PZT thin films on a wide variety of substrates such as LaAlO\textsubscript{3}, MgO, STO,\textsuperscript{13} La\textsubscript{0.5}Sr\textsubscript{0.5}CoO\textsubscript{3} layer on LaAlO\textsubscript{3}\textsuperscript{14} and STO using a SrRuO\textsubscript{3} buffer layer.\textsuperscript{15} In particular, epitaxially oriented PZT thin films\textsuperscript{13,16,17} have been grown for compositions near the morphotropic phase boundary (MPB) as high dielectric and electromechanical properties are obtained for bulk polycrystalline ceramics near the MPB. There is growing evidence, both experimentally\textsuperscript{15,18} and theoretically\textsuperscript{19-21} that phase stability in PZT thin films can be significantly different from the corresponding
bulk because of the presence of strains imposed by a substrate. For example, using a temperature-composition phase diagram for PZT film under a few representative strains Li et al., 21 showed that the phase diagram in thin film is dramatically different than the corresponding stress-free bulk phase diagram.

The objective of this chapter is to construct a temperature-strain phase diagram, i.e. the types of stable phases and domain structures as a function of strain and temperature, for epitaxial PZT thin films with a particular composition near the bulk morphotropic boundary (x = 0.47). The emphasis will be on both the qualitative and quantitative differences between the temperature-strain diagram obtained in this work using the phase-field approach and that predicted by thermodynamic calculations20 which assume a single-domain state for all the ferroelectric phases. Particularly, the present phase-field simulations demonstrate that mixtures of ferroelectric phases can exist under certain strains and temperatures and that the formation of domain structures can change the relative stability of different ferroelectric phases, e.g. the relative stability of an orthorhombic phase and the tetragonal a-domain under a large tensile strain.

4.2 Phase-field model

In the phase-field approach the spontaneous polarization \( \mathbf{P} = (P_1, P_2, P_3) \) is chosen as the order parameter. Its evolution with time can be described by the Ginzburg-Landau equations:

\[
\frac{\partial P_i(x, t)}{\partial t} = -L \frac{\delta F}{\delta P_i(x, t)}, \quad i = 1, 2, 3, \tag{4.1}
\]
where $L$ is a kinetic coefficient which is related to the domain mobility, and $F$ is the total free energy of the system. $\mathbf{x} = (x_1, x_2, x_3)$ denotes the spatial position and $t$ is time. The total free energy is given by

$$F = F_{\text{bulk}} + F_{\text{elas}} + F_{\text{grad}} = \int_V \left( f_{\text{bulk}} + f_{\text{elas}} + f_{\text{grad}} \right) dV,$$  

where $f_{\text{bulk}}$, $f_{\text{elas}}$ and $f_{\text{grad}}$ are the bulk, elastic and gradient energy densities, respectively, while $V$ is the volume of the film. Inclusion of the gradient energy automatically takes into account the domain wall energy contribution. The dipole-dipole interaction is ignored and fully charge compensated surfaces and domain walls are assumed.

For describing a ferroelectric phase transition, the bulk free energy density is expanded using a polynomial of polarization components. In phase-field simulation the six-order polynomial is employed,

$$f_{\text{bulk}} = \alpha_1 (P_1^2 + P_2^2 + P_3^2) + \alpha_{11} (P_1^4 + P_2^4 + P_3^4) + \alpha_{12} (P_1^2 P_2^2 + P_2^2 P_3^2 + P_3^2 P_1^2) + \alpha_{111} (P_1^6 + P_2^6 + P_3^6) + \alpha_{112} [P_1^2 (P_2^4 + P_3^4) + P_2^2 (P_3^4 + P_1^4) + P_3^2 (P_1^4 + P_2^4)] + \alpha_{123} P_1^2 P_2^2 P_3^2,$$  

where $\alpha_1$, $\alpha_{11}$, $\alpha_{12}$, $\alpha_{111}$, $\alpha_{112}$ and $\alpha_{123}$ are the dielectric stiffness and higher order stiffness constants under stress-free condition, and take the values of

$$\alpha_1 = 1.58(T - 384.3) \times 10^5 \text{ C}^{-2}\text{m}^2\text{N}, \quad \alpha_{11} = 6.68 \times 10^7 \text{ C}^{-4}\text{m}^6\text{N}, \quad \alpha_{12} = 1.94 \times 10^8 \text{ C}^{-4}\text{m}^6\text{N}, \quad \alpha_{111} = 1.66 \times 10^9 \text{ C}^{-6}\text{m}^{10}\text{N}, \quad \alpha_{112} = 7.58 \times 10^8 \text{ C}^{-6}\text{m}^{10}\text{N}, \quad \alpha_{123} = -3.57 \times 10^9 \text{ C}^{-6}\text{m}^{10}\text{N}.$$

Isotropic domain-wall energy is assumed and the following gradient energy expression is employed,

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

where, $P_{i,j} = \partial P_i / \partial x_j$ and $G_{11}$ is the gradient energy coefficient.
The elastic energy density at a given strain state is given by

\[ f_{\text{elas}} = \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{kl} \]

\[ = \frac{1}{2} c_{ijkl} \left( \varepsilon_{ij} - Q_{ijkl} P_{m} P_{n} \right) \left( \varepsilon_{kl} - Q_{klmn} P_{m} P_{n} \right) \]

\[ = \frac{1}{2} c_{ijkl} Q_{ijkl} Q_{ijkl} P_{m} P_{n} P_{s} P_{t} - c_{ijkl} \varepsilon_{ij} Q_{ijkl} P_{m} P_{n} + \frac{1}{2} c_{ijkl} \varepsilon_{ij} \varepsilon_{ij}, \]  

(4.5)

where \( \varepsilon_{ij} \) and \( \varepsilon_{ij} \) denote the elastic strains and total strains measured with respect to the paraelectric cubic phase, and \( c_{ijkl} \) and \( Q_{ijkl} \) are the corresponding elastic stiffnesses and electrostrictive coefficients. It is evident from Eq. (4.5) that presence of strains modifies the second-order and the fourth order terms of the bulk free energy polynomial compared to the stress free state in Eq. (4.3), and hence the presence of strain affects the ferroelectric transition temperature and the stability of the individual phases. The details of the calculation of the total strain \( \varepsilon_{ij} \) in a (001)-oriented film under a biaxial strain, \( \bar{\varepsilon}_{11} = \bar{\varepsilon}_{22} = \varepsilon_{0} \) and \( \bar{\varepsilon}_{12} = 0 \) is obtained from literature\(^9,24\), where the overbar means the volume average. The biaxial strain can be due to a thermal mismatch between a film and substrate if the film-substrate interface is incoherent or due to a lattice mismatch if the interface is coherent. Assuming an (001)-oriented film is coherent with an (001)-oriented cubic substrate; the biaxial strain is \( \varepsilon_{0} = (a_{s} - a_{f}) / a_{s} \), where \( a_{s} \) and \( a_{f} \) are the lattice parameters of the thin film in the cubic paraelectric state and the substrate.

### 4.3 Numerical Simulations

In computer simulations, Eq. (4.1) is numerically solved by the semi-implicit Fourier-spectral method.\(^{25}\) A simulation cell of \( 128\Delta x \times 128\Delta x \times 36\Delta x \) with a uniform grid space \( \Delta x / l_0 = 1.0 \) is employed, where \( l_0 = \sqrt{G_{110} / \alpha_0} \) and \( \alpha_0 = |\alpha|_{T=25^\circ C} \). \( G_{110} \) is
a constant for normalizing $G_{11}$ during simulation and relates to the grid spacing in real space ($l_0$). Periodic boundary conditions are applied along both the $x_1$ and $x_2$ directions. I choose the gradient energy coefficient such that $G_{11}/G_{110} = 0.4$. The corresponding width of domain wall is about $1.3\Delta x$, and the domain wall energy density at $T = 25^\circ C$ is evaluated to be about $0.60 \alpha_0 l_0 P_0^2$ for $90^\circ$ domain walls. $P_0 = 1$ Cm$^{-2}$ is the polarization value used for the normalization during simulation. I choose $l_0 = 1$ nm such that the domain wall width is about $13\AA$, and then the corresponding domain wall energy density is 0.045 Jm$^{-2}$, which is close to experimental measurements.$^{26}$

The film thickness is taken as $h_f = 20\Delta x$ and the heterogeneous elastic deformation in the substrate is limited to a distance of $h_s = 12\Delta x$ from the film/substrate interface. The elastic constants of the film and substrate are assumed to be same and have cubic anisotropy: $c_{11} = 1.746 \times 10^{11}$, $c_{12} = 7.937 \times 10^{10}$, $c_{44} = 1.111 \times 10^{11}$ (Nm$^{-2}$) or $s_{11} = 8.0 \times 10^{-12}$, $s_{12} = -2.5 \times 10^{-12}$, $s_{44} = 9.0 \times 10^{-12}$ (Nm$^{-1}$). The nonzero electrostrictive coefficients take the values of $Q_{11} = 0.0908$, $Q_{12} = -0.0416$, $Q_{44} = 0.0387$ (C$^{-2}$m$^{4}$).$^{22}$ $c_{ij}$, $s_{ij}$ and $Q_{ij}$ are the corresponding elastic stiffness, compliance and electrostrictive coefficients in Voigt’s notation.

4.4 Results and Discussion

A phase stability map of a PbZr$_{0.53}$Ti$_{0.47}$O$_3$ film as a function of both temperature and strain was constructed. The types of stable phases are analyzed from the polarization distribution at the end of a simulation that was started from an initial
paraelectric state with small random perturbations. The results are summarized in Fig. 4.1. The open squares represent tetragonal $c$-domains with polarization of $P_1 = P_2 = 0, P_3 \neq 0$. The squares with crosses inside represent the tetragonal $a$-domains with polarization $P_1 \neq 0, P_2 = P_3 = 0$ ($a_1$-domain) and $P_2 \neq 0, P_1 = P_3 = 0$ ($a_2$-domain). It was found that the $a_1$-domain and $a_2$-domain always coexist, which releases the biaxial tensile strain. In addition, a mixture of distorted rhombohedral phase, orthorhombic phase, and tetragonal phase is stabilized near the zero strain while a mixture of the orthorhombic phase ($|P_1| = |P_2| > 0, P_3 = 0$) and the tetragonal $a$-domains exists under a large tensile strain at high temperature. In Fig. 4.1 the filled circles represent the transition temperature from paraelectric to the mixture of ferroelectric orthorhombic and tetragonal phases. The mixture regions are non-shaded in the figure while the shaded regions represent uniform phases. The two solid lines in the figure represent the transition temperatures from the paraelectric phase into a single tetragonal $c$-domain or into a single orthorhombic domain predicted from a thermodynamic analysis. They are given by

$$\alpha_1 - \frac{2e_0 Q_{12}}{s_{11} + s_{12}} = 0 \text{ if } e_0 \leq 0 \text{ and } \alpha_1 - \frac{e_0 (Q_{11} + Q_{12})}{s_{11} + s_{12}} = 0, \text{ if } e_0 \geq 0.$$  (4.6)

Both the orthorhombic and the tetragonal $a$-domains have the same transition temperatures. It is obvious that the transition temperature increases with increasing strain irrespective of its nature, i.e., tensile or compressive as it has been shown previously.
Fig. 4.1. Phase stability map of temperature versus strain for PbZr_{0.53}Ti_{0.47}O_3 epitaxial film obtained from the phase-field simulation. Squares used to demarcate the stability region of tetragonal (both $a$- and $c$-phases) while the filled circles represent the ferroelectric transition temperature to a mixture of tetragonal $a_1/a_2$ and orthorhombic phase with in-plane polarization. The solid and dashed lines delineate the transition temperatures obtained with two sets of elastic compliance constants.
The phase-field simulations show that tetragonal phase is stabilized under large strains regardless whether they are tensile or compressive. This is consistent with experimental studies. It was found that under a compressive strain, the tetragonal $c$-domain was stabilized in (001) oriented PbZr$_{0.52}$Ti$_{0.48}$O$_3$ epitaxial thin films grown on (100) STO substrate$^{16}$ while under a tensile strain predominantly tetragonal $a$-domains were obtained in a PZT thin film with compositions near the MPB grown on LSCO/CeO$_2$/YSZ/(001)Si$^{29}$ and MgO.$^{30}$

As a comparison, a phase stability diagram of temperature versus strain is also calculated using thermodynamics assuming a single-domain state for all possible ferroelectric phases. The corresponding results are plotted in Fig. 4.2, which is essentially the same as that obtained with $x = 0.5$ previously by Pertsev et al.$^{20}$ Four phases are found to be stable namely cubic ($P_1 = P_2 = P_3 = 0$), tetragonal $c$-domain ($P_1 = P_2 = 0, \ P_3 \neq 0$), orthorhombic ($|P_1| = |P_2| > 0, \ P_3 = 0$) and distorted rhombohedral phase ($|P_1| = |P_3| > 0, \ |P_3| > 0$). A comparison of the phase diagrams obtained by the thermodynamic calculation and the phase-field simulation reveals fundamental differences. For example, under low strains, the thermodynamic
Fig. 4.2. Phase stability map of temperature versus strain for PbZr$_{0.53}$Ti$_{0.47}$O$_3$ epitaxial film obtained from thermodynamic calculation.
Fig. 4.3. Domain structures of the PZT(x=0.47) thin film (a) $T=25^\circ C$ & $e_o = -0.005$ showing a mixture of different variants of tetragonal, distorted rhombohedral and orthorhombic phases. R1, R2, R3, R4 represent variants of the rhombohedral phase with polarization directions along $[11\bar{1}1]$, $[1\bar{1}1\bar{1}]$, $[\bar{1}1\bar{1}\bar{1}]$, respectively, while O3a, O3b and T3 represent variants of the orthorhombic and tetragonal c-phase with polarization directions along $[10\bar{1}]$, $[011]$, $[001]$, respectively; (b) at $T=25^\circ C$ and $e_o = 0.008$ showing a twin domains of tetragonal $a_1/a_2$. T1+, T1-, T2+, and T2- show the variants of the tetragonal phase with polarization directions along $[100]$, $[\bar{1}00]$, $[010]$ and $[0\bar{1}0]$ respectively.
calculation predicted a distorted rhombohedral phase whereas the phase-field simulation produced a mixture of distorted rhombohedral, orthorhombic and tetragonal phases. It should be noted that a zero-strain implies an in-plane clamped boundary condition for the film. Furthermore, under a high tensile strain the thermodynamic calculation showed an orthorhombic phase as the stable phase while the phase-field simulation demonstrated that the tetragonal \( a \)-domain is the most stable phase with \( a_1/a_2 \) twin structures, in agreement with experiments.\(^{29,30}\) Fig. 4.3 shows examples of domain structures in the PZT thin film at two different strains. Fig. 4.3a is a mixture of tetragonal, orthorhombic and distorted rhombohedral phases obtained under a compressive strain of \( e_0=-0.5\% \) at 25\(^\circ\)C, where different variants of individual phases along with the polarization directions are shown. The domain walls among the different variants of the rhombohedral phase are found to be along the \{100\} or \{110\} planes, which are consistent with prior crystallographic analyses by Streiffer et. al.\(^{31}\) Fig. 4.3b displays the domain structure of the tetragonal ferroelectric phase under a high tensile strain \( e_0=0.8\% \) at room temperature. The figure shows the coexistence of the four domain variants of the tetragonal phase and the domain walls lie along the \{110\} planes.

To test the sensitivity of the phase diagram with respect to the model parameters, I conducted a number of systematic studies. For example, I studied the effect of the gradient energy coefficients on the phase stability diagram using a range of gradient energy coefficients \( G_{11}/G_{110} = 0.2 - 0.6 \). For this range, the calculated domain wall width and domain wall energy for 90\(^\circ\) domains in PT lies within the theoretically and experimentally observed domain wall width and domain wall energy\(^{26,32}\) of 5-21\(\AA\) and 0.035-0.050 J/m\(^2\), respectively. It was found that the
gradient energy coefficient affects only the stability range of the mixture of the orthorhombic and tetragonal $a$-phase, i.e., with the decrease in gradient energy coefficients the stability region of the mixture of orthorhombic and tetragonal $a$-domains shrinks.

The effect of elastic stiffness on the phase diagram was also investigated. The elastic constants used in the simulation are those for PbTiO$_3$ at its cubic state as the elastic constant data for the single crystal cubic PbZr$_{0.53}$Ti$_{0.47}$O$_3$ is currently not available. But the elastic compliance data for PbZr$_{0.52}$Ti$_{0.48}$O$_3$ ceramic sample$^{33}$ shows that $s_{11}$ is significantly different from the corresponding PbTiO$_3$. Pertsev et al.$^{20}$ used the room temperature PZT ceramics data to obtain the elastic compliance data for the cubic state. In order to study the variation of elastic compliance data on the phase stability I used the elastic compliance data corresponding to $x = 0.5$ in Ref. 10: $s_{11} = 10.5 \times 10^{-12}$, $s_{12} = -3.7 \times 10^{-12}$, $s_{44} = 28.7 \times 10^{-12}$ (N$^{-1}$m$^2$). It was found that difference in elastic constant changes the stability region of the individual phase significantly. Firstly, at large strains, the transition temperature was lowered by $\sim100^\circ C$. The dashed lines in Fig.4.1 showed the corresponding transition temperatures by using the second set of elastic compliance data. These changes are clearly shown by Eq. (4.6). Moreover, the stability region of the phase mixture at low strains is reduced and is replaced by the tetragonal phase.

4.5 Summary

A phase diagram of temperature versus strain was constructed for a (001)-oriented PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) epitaxial single crystal thin film near the bulk
morphotropic boundary composition \((x = 0.47)\) on an (001)-oriented cubic substrate. Under a large tensile strain a tetragonal \(a_1/a_2\)-domain structure is found to be stable except close to the transition temperatures where a mixture of orthorhombic and tetragonal phases co-exist, whereas thermodynamic calculations assuming a single domain state predicted a single orthorhombic phase. Furthermore, unlike thermodynamic calculations, which predicted a single distorted rhombohedral state under low values of strains, my phase-field simulations showed a mixture of ferroelectric phases as a stable state. The stability of the individual ferroelectric state varies considerably with the elastic constants used in simulation. The gradient energy coefficients affect the size of stability regions of the mixture states but do not qualitatively change the phase diagram.
References


Chapter 5

Effect of Substrate Strain on Coercive Field in Epitaxial Barium Titanate Thin Films

Strain is generally known to increase the coercive field of a ferroelectric thin film as compared to a stress-free single crystal or a strain-relaxed film. In this chapter the coercive fields and remanent polarization of (001)-oriented epitaxial barium titanate thin films at 0°C were studied using the phase-field approach. Domain structure under a particular substrate constraint is used to explain the observed variation of coercive fields and remanent polarization with substrate strain.

5.1 Literature Review

Ferroelectric materials form spontaneous polarization when it is cooled below a critical temperature also known as the Curie temperature. The polarization direction can be switched by externally applying a critical electric field. The behavior of the ferroelectric under an applied electric field is characterized by two important physical properties namely remanent polarization (polarization with applied electric field reduced to zero) and coercive field (electric field required to reduce the net polarization to zero). From a scientific standpoint, the magnitude of these physical properties provide valuable information regarding polarization switching dynamics and physics of ferroelectricity in general. In the form of thin films, while many factors are expected to determine the magnitude of these physical properties, epitaxial strain arising primarily due to the difference in lattice parameter and thermal
expansion coefficient between the thin film and the substrate has been recognized as being of particular importance for ferroelectric materials.\textsuperscript{35} Despite numerous studies, the exact nature on the effect of substrate strain on coercive field and remanent polarization is poorly understood. Generally, it has been observed both experimentally and theoretically that both coercive field\textsuperscript{36,37} and remanent polarization\textsuperscript{38} increases drastically with the increase in substrate strain. For example, Pertsev \textit{et. al.} reported that coercive field in fully coherent PbZr\textsubscript{0.52}Ti\textsubscript{0.48}O\textsubscript{3} (PZT) thin films on SrTiO\textsubscript{3} substrate under a biaxial strain of 2\% can be about an order of magnitude higher compared to a thin film under zero substrate strain.\textsuperscript{39} However, there are some reports showing these properties does not change monotonically with substrate strain.\textsuperscript{34,40} Nonetheless, it is clear that understanding the effect of substrate strain on coercive field as well as remanent polarization although controversial, is critical for application of ferroelectric thin films.

Experimentally, it is often difficult to separate the intrinsic effect of substrate strain on ferroelectric properties from other factors like defects and passive layers. In particular, passive layers are known to have significant effect on the measured coercive field\textsuperscript{41} and remanent polarization.\textsuperscript{42} In this chapter, I employ phase-field approach to study the effect of biaxial substrate strains on coercive fields and remanent polarization in ferroelectric thin films in an attempt to demonstrate that the coercive field and remanent polarization can be tuned by strain. I use (001)-oriented epitaxial barium titanate (BaTiO\textsubscript{3}) thin films as a model system.
5.2 Phase-field model

In the phase-field approach, a ferroelectric domain structure is described by the spatial distribution of polarization $\mathbf{P} = (P_1, P_2, P_3)$. Its temporal evolution is assumed to follow the time-dependent Ginzburg-Landau (TDGL) equations

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

where $L$ is a kinetic coefficient related to the domain wall mobility. $F$ is the total free energy of the system, which 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.,

$$F = F_{\text{bulk}} + F_{\text{wall}} + F_{\text{elas}} + F_{\text{elec}}.$$  \hspace{1cm} (5.2)

The mathematical expressions for the ferroelectric bulk free energy, ferroelectric domain wall energy, and elastic energy (similar to the expressions given in previous chapter) are obtained from Ref.17.

The electrostatic energy of a domain structure is calculated as:

$$f_{\text{elec}} = -\frac{1}{2} E_i \left( \varepsilon_0 \kappa_j E_j + P_i \right)$$

where $E_i$ is the electric field component. The electrical displacement $D_i$ is defined as $D_i = \varepsilon_0 \kappa_j E_j + P_i$, where $\kappa_j$ is the relative permittivity of film. If we assume there is no charge inside the film then the electrostatic equilibrium equations of the film can be written as $D_{i,i} = 0$. The electrostatic equilibrium equation is solved under a constant electrical potential boundary condition. The boundary conditions are written as

$$\phi \big|_{x=0} = \phi_1, \phi \big|_{x=h_f} = \phi_2,$$

where $\phi$ is the electrical potential.
where $\phi$ is the electric potential and $\phi_1, \phi_2$ are the values of electric potential at the top and bottom surfaces of the film. $\phi$ is related to electric field ($E_i$) through $E_i = -\phi_i$. Hence, by assuming $\kappa_{ij} = 0$ for $i \neq j$ and rearranging the terms in equilibrium equation, we obtain

$$
(\kappa_{11}\phi_{11} + \kappa_{22}\phi_{22} + \kappa_{33}\phi_{33}) = \frac{1}{\varepsilon_0} (P_{i,1} + P_{2,2} + P_{3,3}).
$$

(5.5)

In order to solve Eq. (5.5), the electric potential is broken into two components such that:

$$
\phi = \phi^A + \phi^B,
$$

(5.6)

$$
(\kappa_{11}\phi^A_{11} + \kappa_{22}\phi^A_{22} + \kappa_{33}\phi^A_{33}) = \frac{1}{\varepsilon_0} (P_{i,1} + P_{2,2} + P_{3,3}),
$$

(5.7)

$$
(\kappa_{11}\phi^B_{11} + \kappa_{22}\phi^B_{22} + \kappa_{33}\phi^B_{33}) = 0
$$

(5.8)

First Eq. (5.7) is solved in 3D space employing the 3D Fourier transform, i.e.

$$
\phi^A(x) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \phi^A(\zeta)e^{ix\zeta}d^3\zeta
$$

(5.9)

$$
\phi(\zeta) = -\frac{1}{\varepsilon_0} \frac{I(\zeta_1 P_1(\zeta) + \zeta_2 P_2(\zeta) + \zeta_3 P_3(\zeta))}{(\kappa_{11}\zeta_1^2 + \kappa_{22}\zeta_2^2 + \kappa_{33}\zeta_3^2)}
$$

(5.10)

$$
P_1(\zeta) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} P_1(x)e^{-ix\zeta}d^3x
$$

(5.11)

where $I = \sqrt{-1}$. $\phi^B$, is obtained for an infinite plate thickness $h_f$, such that it satisfies Eq. (5.8) together with the boundary conditions,

$$
-\kappa_{33}(\phi^A_3 + \phi^B_3)_{x_3 = 0, h_f} = 0,
$$

(5.12)

or $(\phi^A + \phi^B)_{x_3 = 0} = \phi_1$, $(\phi^A + \phi^B)_{x_3 = h_f} = \phi_2$.

(5.13)
Eq. (5.8) is solved by applying a 2D Fourier transforms on the Eq.(5.8) and Eq. (5.14).

\[
\kappa_{33} \frac{d^2 \hat{\phi}^B}{dx_3^2} - (\kappa_{11} \zeta_1^2 + \kappa_{22} \zeta_2^2) \hat{\phi}^B = 0, 
\]

(5.14)

where

\[
\hat{\phi}^B(\zeta_1, \zeta_2, x_3) = \frac{1}{(2\pi)^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \hat{\phi}^B(x_1^G, x_2^G, x_3^G) e^{-i(k_1^G \zeta_1 + k_2^G \zeta_2)} dx_1^G dx_2^G.
\]

(5.15)

The solution to Eq. (5.14) is of the form

\[
\hat{\phi}^B(\zeta_1, \zeta_2, x_3^G) = C_1(\zeta_1, \zeta_2) e^{i G(\kappa_{11} \zeta_1^2 + \kappa_{22} \zeta_2^2)/\kappa_{33}} + C_2(\zeta_1, \zeta_2) e^{-i G(\kappa_{11} \zeta_1^2 + \kappa_{22} \zeta_2^2)/\kappa_{33}}.
\]

(5.16)

The coefficients \(C_1\) and \(C_2\) are obtained from the boundary conditions. \(\phi^B\) is obtained by employing a 2D inverse Fourier transform on Eq. (5.16), i.e.,

\[
\phi^B(x_1^G, x_2^G, x_3^G) = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \hat{\phi}^B(\zeta_1, \zeta_2, x_3^G) e^{i G(\kappa_{11} \zeta_1^2 + \kappa_{22} \zeta_2^2)} d\zeta_1^G d\zeta_2^G.
\]

(5.17)

Once \(\phi^B\) is obtained, the electric potential, the electric field as well as the electrostatic energy can be calculated easily.\(^{438}\)

### 5.3 Numerical Simulations

In the simulations, the simulation cell is discretized as \(128\Delta x \times 128\Delta x \times 36\Delta x\), with periodic boundary conditions along \(x_1\) and \(x_2\) axes in the film plane where \(\Delta x\) is the simulation grid spacing. The thickness of the film is taken as \(h = 20\Delta x\). The bulk free energy coefficients, the elastic and the electrostrictive coefficients are given in Ref. 17 and references therein. \(\kappa_{11} = \kappa_{22} = \kappa_{33} = 500\) was used for electrostatic energy calculations. The average strains induced by the substrate are assumed to be \(\overline{\varepsilon_{11}} = \overline{\varepsilon_{22}} = \varepsilon_0\). The domain wall energy was assumed to be isotropic in phase-field simulations. A domain structure was first generated by performing the simulations
under short-circuit electrostatic boundary conditions \( (\phi_1 = \phi_2 = 0) \), starting from an initial paraelectric state with small random perturbations. In order to compute the hysteresis loop the potential \( \phi_2 \) is changed gradually in my simulations with an interval of \( 5 \times 10^{-5} \) V, and the domain structure from a previous step was used as the input at each increment of the potential.

### 5.4 Results and Discussion

To study the effect of substrate strain on switching behavior, I choose a range of in-plane strains from \( e_0 = 0.1\% \) to \( e_0 = -0.3\% \) while the temperature is maintained at \( T = 0 \) °C. It has been reported by Li and Chen that within this range of the strain different ferroelectric phases and their mixtures are observed. Further, each phase can have multiple ferroelectric variants. For example, under a compressive strain between \( e_0 = 0.0\% \) and \( e_0 = -0.16\% \) a ferroelectric phase denoted as M\(_1\) with polarization \((|P_1| > 0, P_2 = 0, |P_3| > 0)\) or \((P_1 = 0, |P_2| > 0, |P_3| > 0)\) is stabilized while for a larger compressive strain tetragonal phase with polarization \((P_1 = 0, P_2 = 0, |P_3| > 0)\) is stable. For a tensile substrate strain between \( e_0 = 0.0\% \) and \( e_0 = 0.1\% \) a mixture of M\(_1\) and O\(_2\) phases is observed, where O\(_2\) is a ferroelectric phase with polarization \((|P_1| > 0, |P_2| > 0, |P_3| = 0)\). Using phase field approach it was demonstrated in chapter 3 that coercive field in bulk lead zirconate titanate single crystals is closely related to the number of ferroelectric variants present in the system. As the number of ferroelectric variants that are stabilized within the chosen range of substrate strain varies it is expected that coercive field will change significantly with substrate strain.
Fig. 5.1 Hysteresis loops for epitaxial BTO thin films at temperature (T)=0°C with four representative in-plane strain ($e_0$) = 0.1%, -0.13%, -0.165%, and -0.3%;
Figure 5.1 presents the hysteresis loops for four representative strains within the range, namely, \( e_0 = 0.1\%, -0.13\%, -0.165\%, -0.3\% \). It is seen that the remanent polarization increases monotonically as the substrate strain changes from tensile to compressive, and the highest remanent polarization is obtained at strain \( e_0 = -0.3\% \). This can be explained from the phase stability within the chosen range of strain (Ref. 17). As the strain changes from tensile to compressive, phases with larger out of plane polarization component \( P_3 \) are stabilized. It is interesting to observe that unlike the remanent polarization, the coercive field does not change monotonically as the strain is varied from tensile to compressive. Although the coercive field is the minimum at the tensile substrate strain of \( e_0 = 0.1\% \), the coercive field at the compressive substrate strain of \( e_0 = -0.13\% \) is about 1.4 times higher than that at \( e_0 = -0.165\% \). The highest coercive field is observed for strain \( e_0 = -0.3\% \). To understand the change of the coercive field with the substrate strain, I analyzed the domain structures in Fig. 5.2(i-iv). They are obtained at the corresponding substrate strains under the short circuit boundary condition. In the figures, each of the color represents a ferroelectric variant. The color green and blue represent orthorhombic (O2) and tetragonal (T) phase while rest of the colors indicates ferroelectric variants of \( \text{M}_1 \) phase. It is seen that the domain structures with \( e_0 = -0.3\% \) and \( e_0 = -0.13\% \) comprised of single phases of T and \( \text{M}_1 \) respectively while the domain structures for \( e_0 = -0.165\% \) and \( e_0 = 0.1\% \) are phase mixtures. It demonstrates once again that the coercive field can change significantly around phase boundaries.

To further analyze the effect of substrate strain on coercive field I computed the hysteresis loops for epitaxial BTO thin films by changing the substrate strain.
Fig. 5.2. Simulated domain structures of epitaxial BTO thin films under short-circuit electrostatic boundary conditions for different substrate strains. The domain structures are obtained from an initial paraelectric state with small random perturbations and used as the starting domain structure to construct the hysteresis loop. The polarization components of individual phases are indicated. The green and the blue color represent orthorhombic (O2) and tetragonal (T) phases respectively, while rest of the colors indicate M1 ferroelectric phase.
within the range $e_0 = 0.1\%$ to $e_0 = -0.3\%$ in a step of 0.025\% and plotted the coercive field as well as the remanent polarization as a function of in-plane substrate strain (Figure 5.3). In the figure the shaded area represents the stability regions of a single ferroelectric phase, and the non-shaded region shows a phase mixture. Error bars represent the range of the predicted coercive fields obtained from phase-field simulation starting with different sets of random numbers. The figure shows within ($e_0 = -0.3\%$ to $e_0 = -0.225\%$) the coercive field decreases linearly with substrate strain. Decrease in compressive strain reduces domain wall clamping by the substrate, resulting in an increase in domain wall mobility, thus a smaller electric field is required for polarization switching. As the compressive strain is reduced further ($e_0 = -0.225\%$ to $e_0 = -0.16\%$) the coercive field decreases significantly. Decrease in coercive field with substrate strain in this range can be attributed to two factors. First a decrease in compressive strain increases domain wall mobility, resulting in a decrease in predicted coercive field (schematically shown by the dotted line AB). Second within this region a phase mixture (T+M$_1$) is stabilized. Domain boundaries between these two phases provide additional sites for new domain nucleation during polarization switching. Similar to the area bounded by the tetragonal phase, coercive field decreases linearly with compressive substrate strain within the phase stability region bounded by the M$_1$ phase ($e_0 = -0.16\%$ to $e_0 = -0.0\%$). Within the tensile strain regime ($e_0 = -0.0\%$ to $e_0 = 0.1\%$) a phase mixture (M$_1$+O$_2$) is stabilized which causes a further decrease in coercive field with the increase of tensile strain. Unlike the coercive field the remanent polarization decreases continuously within the
Fig. 5.3 Plot for simulated coercive field and remanent polarization in an epitaxial BTO thin film as a function of biaxial in-plane substrate strain at temperature (T) =0°C. The shaded areas indicate regions bounded by single ferroelectric phase while the non-shaded area represent regions where a phase mixture is stabilized under short-circuit electrostatic boundary conditions. The polarization components of individual phases are indicated.
chosen range of substrate strains. However, as the compressive substrate strain is decreased from $e_0 = -0.16\%$ a jump in the value of remanent polarization is observed. This is because for strain below $e_0 = -0.16\%$, phases with in-plane polarization components are stabilized.

5.5 Summary

To summarize, the effect of substrate strain on the coercive field in epitaxial thin films is studied. It was found that coercive field is strongly dependent on the substrate strain especially if the strain can cause ferroelectric to ferroelectric or inter-ferroelectric transitions. For such inter-ferroelectric transitions in $\text{BaTiO}_3$ thin films under biaxial substrate strain close to zero and temperature around 0 ºC it was observed that the coercive field can change more than hundred percent just by changing the substrate strain by 0.05% without a significant drop in remanent polarization. Thus, choosing appropriate substrate strain, it is possible to control both polarization and coercive field in ferroelectric thin films.
References


Chapter 6

Effect of Ferroelastic Twin Walls on Local Polarization Switching

In this chapter the local polarization switching in epitaxial ferroelectric thin films in the presence of ferroelastic domain walls is studied using phase-field approach. The spatial distribution of the nucleation bias across a twin wall was analyzed. This analysis was further extended to a realistic domain structure with multiple twin boundaries.

6.1 Literature Review

During the last decade, epitaxial ferroelectric thin films have drawn considerable research attention for their potential applications in nonvolatile memories\textsuperscript{47} and data storage.\textsuperscript{48} Progress in these applications necessitates the understanding of polarization switching mechanisms on the nanoscale level of individual capacitor (FeRAM) or tip-junction region (data storage), and the role of structural and morphological defects on domain nucleation and wall motion. Following the pioneering work of Landauer\textsuperscript{2} it is recognized that ferroelectric domain nucleation in uniform fields is controlled by a number of discrete switching centers, which allows nucleation under a low electric field.\textsuperscript{1,4} The role of particular center type in macroscopic switching dynamics is determined by both the center concentration and nucleation activity, i.e. local field required to induce nucleation.
In recent years Piezoresponse Force Microscopy (PFM) has emerged as a powerful technique to study the local switching behavior in ferroelectric materials. In PFM, the inhomogeneous electric field is strongly localized below the tip, resulting in nucleation of a single domain at the tip-surface junction.\textsuperscript{49} Thus PFM offers the possibility of correlating the local switching behavior with the microstructure. The progress in PFM over these years has also stimulated simultaneous development of theoretical models to relate the experimentally observed switching behavior.\textsuperscript{50,51} Prior theoretical models typically assume the shape of the nucleated domain as \textit{a priori}, and the thermodynamics of domain switching in PFM was analyzed in a perfect crystal.\textsuperscript{2,50} Recently, Rodriguez \textit{et al.} have shown that using a combination of the Switching Spectroscopy Piezoresponse Force Microscopy (SS-PFM) and phase field modeling it is possible to map local nucleation biases on the \textasciitilde 10 nanometer level.\textsuperscript{52} It was shown that the bias for 180° domain nucleation is lower at the junction of two 90° twin domains compared to the matrix. 90° domain twins (\textit{a}-domains) are known to present in the tetragonal ferroelectric films in the broad range of misfit strains.\textsuperscript{37,53} In this chapter, a 3D phase-field model is developed to correlate the switching behavior with the number of twin defects below the tip. As a first example, an in-depth analysis of switching behavior with a single defect is presented. Later, the switching behavior of a realistic domain structure with multiple defects is studied.

### 6.2 Phase-field model

In phase-field approach, a ferroelectric domain structure is described by the spatial distribution of polarization $\mathbf{P}(P_1, P_2, P_3)$. The temporal evolution of the polarization vector is described by time-dependent Ginzburg-Landau (TDGL) equation as described in chapter 4. The mathematical expressions for the total free
energy of the system is exactly the same as given in chapter 4 and chapter 5, so they are not listed here for the sake of brevity.

In the absence of space charge, the electrostatic distribution on the film can be obtained from the condition $D_{i,j} = 0$, where $D_{i,j} = \partial D_i / \partial x_j$, and the summation convention for the repeated indices is employed. The electrostatic equilibrium equation is solved using a specified boundary condition,

$$
\phi_{\text{substrate-film interface}} = 0, \phi_{\text{filmsurface}} = \phi_i(x, y)
$$

(6.1)

To model the writing process using the PFM, the tip-induced potential distribution is approximated by a two-dimensional Lorentz like function,

$$
\phi_i(x, y) = \phi_0 \left[ \frac{\gamma^2}{(x-x_0)^2 + (y-y_0)^2 + \gamma^2} \right],
$$

(6.2)

where $(x_0, y_0)$ is the location of the tip (the peak of distribution) and $\gamma$ stands for the length scale from the tip over which the applied electric potential reduces to half of its peak value. Fig. 6.1(a) shows a typical distribution of the applied potential on the top surface of the thin film.

### 6.3 Numerical Simulations

The simulation cell was $256\Delta x \times 256\Delta x \times 36\Delta x$, with periodic boundary conditions along $x_1$ and $x_2$ axes along the film plane where $\Delta x$ is the simulation grid spacing. The thickness of the film is taken as $h = 20\Delta x$. The materials parameters are chosen for the epitaxial PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin film. The bulk free energy coefficients, the elastic and the electrostrictive coefficients are given in Ref. 14. The tip parameter in PFM is chosen as $\gamma = 30$ nm. The average strains induced by the substrate are taken as $\varepsilon_{11} = \varepsilon_{22} = -0.003$. We assumed the domain wall energy to be isotropic. In order to find the critical nucleation potential, we gradually increase the
Fig. 6.1(a) Distribution of the applied potential on the top surface of the thin film for $\phi_0 = 1V$ and $(x_0, y_0) = (64, 64)$; (b) Domain structure of epitaxial PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin film with a preexisting $a_2$-positive domain within a matrix of $c$-negative domain under short-circuit boundary condition. The dots show the location of the PFM tip during measurement of nucleation potential along the profile A-M-N-B.
potential $\phi_0$ in a step of 0.025V, and the domain structure from a previous simulation was used as the input at each increment of the potential. At a critical applied electric potential a new tetragonal domain with polarization along [001] was found to nucleate below or near the tip and the corresponding electric potential was identified as the nucleation potential.

### 6.4 Results and Discussion

To examine the role of a single ferroelastic twin boundary, I consider the switching of a film containing an $a_2$-positive domain within a matrix of $c$-negative (Figure 6.1(b)). The nucleation bias was calculated across the profile A-M-N-B, where each dot shows the location of the PFM tip. Figure 6.2(a) plots the variation of the nucleation voltage along the selected profile. Each square symbol indicates the nucleation potential corresponding to a dot in Figure 6.1(b). It is clear from the figure that the potential required to nucleate an 180º domain is lower near the twin defect (~1.6V) as compared to ~2.6 V away from the twin defect within the matrix. The variation of the nucleation voltage around the twin defects reveals that the two interfaces are not equivalent. The potential required to nucleate the 180º domain is significantly lower on the left interface compared to the right interface. Furthermore, the nucleation voltage increases sharply away from the left interface within the matrix compared to the right interface.

To analyze the origins of the asymmetric variation of the nucleation voltage near the two interfaces we map the built-in electrostatic energy density on the surface of the thin film [Figure 6.2(b)]. The observed asymmetric distribution of the
Fig. 6.2(a) Spatial distribution of the nucleation potential along the selected profile. Each square symbol indicates the nucleation potential corresponding to a dot in Fig. 6.1(b); (b) Distribution of the electrostatic energy density (MJ/m$^3$) along the selected profile without any applied potential. Distributions of the electrostatic energy around the two interfaces of the twin domain are marked by oval shapes.
electrostatic energy density can be explained by the interplay between the charge
distribution induced by the compressive strain across the domain and depolarization
field effect. During switching, the additional energy provides the driving force for
180° domain nucleation, explaining the observed difference of nucleation voltage near
the two interfaces. It should be pointed out that phase-field simulations show that the
voltage required to nucleate 180° domain intrinsically within the matrix is less than 3V
for tip radius of ~30 nm. Thus, on the nearly-ideal surface, the large non-uniform
electric field under the PFM tip are sufficient to induce intrinsic polarization
switching even for moderately low tip biases.

To understand the spatial distribution of nucleation voltage in a more realistic
domain structure in a PZT epitaxial thin film I performed additional phase-field
simulations under the short-circuit boundary condition starting from an initial
paraelectric state with small random perturbations. The corresponding domain
structure is shown in Figure 6.3(a). Each of the colors represents a tetragonal variant.
The domain structure consists of $a_1$ and $a_2$ twin defects as well as multiple $a_1/a_2$
domain junctions. To understand the correlation between the spatial variation of
nucleation voltage and the domain structure I scanned across the profile P-Q-R-S-T-U-V using the probe, and the corresponding variation of the nucleation voltage is
presented in Figure 6.3(b). The numbers in the square bracket indicate the number of
defects at that particular location.
Fig. 6.3(a) Domain structure of epitaxial PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin film under short circuit electrostatic boundary condition. Each color represents a tetragonal variant, as indicated; (b) Spatial distribution of the nucleation potential along the profile P-Q-R-S-T-U-V. Each square symbol indicates the nucleation potential corresponding to a dot in Fig. 6.3(a). The numbers in the square bracket indicate the number of defects at that particular point. The figure shows the nucleation potential decreases as the number of defect increases.
It can be seen that the potential to nucleate $180^\circ$ domain changes continuously across the profile. Furthermore, the figure shows that the nucleation voltage is highest within the matrix (point R and U) followed by the area around a single twin defect (point S), and then by the area where $a_1$ and $a_2$ intersects (point Q). The lowest nucleation potential is observed near the triple junctions (point T). Thus, it is concluded that as the number of defects increases the potential required to nucleate an $180^\circ$ domain decreases.

It should be pointed out that although the predicted nucleation voltage depends on the value of $\gamma$ chosen during simulation the spatial distribution of the switching behavior remains unaltered. In addition, it also possible to introduce other types of defects like dislocations and grain boundaries in phase field approach, which could also affect the spatial distribution of switching behaviors in ferroelectric thin films.

### 6.5 Summary

To summarize, the role of twin defects in ferroelectric thin films on polarization switching under a non-uniform applied electric potential was studied. In the nearly ideal material, the $180^\circ$ domain can nucleate intrinsically within the matrix. The mechanism of the polarization switching within a single twin defect was analyzed, and observed variability of switching behavior was correlated with build-in electrostatic energy density. Finally, switching of a domain structure with multiple twin defects was studied. It was shown, that the electric potential required for $180^\circ$ domain switching decreases as the number of twin defects under the tip increases.
References


Chapter 7

Conclusions and Future Research

As mentioned in the first chapter, that the primary objective of this thesis is to develop a phase-field model to study the domain structure and domain switching mechanisms in ferroelectric bulk and thin films. In particular, to introduce various defects in the phase-field model, so that the domain switching mechanisms in realistic ferroelectric materials are clearly understood. Further, it was expected that the possibility of introducing defects in the phase-field model would explain the discrepancy between the values of coercive field predicted from thermodynamic approach and those measured experimentally.

7.1 Conclusions

1. A three dimensional phase-field model is developed to study the effect of grain boundaries on ferroelectric domain structure and switching. The model takes into account various energetic contributions present in realistic ferroelectrics. Using 2-D simulations, it is shown that 90° domain nucleates at the grain boundary and grows towards the grain interior during domain switching. It was observed that that polarization switching between neighboring grains is correlated.

2. It was demonstrated that during polarization switching domain nucleation occurs preferentially either at existing domain or grain boundaries.
3. Predicted coercive fields are now much closer to experimental measurements than prior theoretical predictions. Predicted coercive fields are 1-2 times of experimental measurements, which is unlike prior thermodynamic approach where the predicted coercive fields were at least one or two orders of magnitude higher than experimental measurements.

4. It was shown that choosing apposite substrate strain, it is possible to control the domain structure as well as physical properties like coercive field in ferroelectric thin films.

### 7.2 Future Work

The phase-field model developed in this thesis could be improved by adding additional features in to the model.

1. Although, as a first step, during the simulations experiments presented in this thesis, the effect of structural defects like dislocations and vacancies were ignored. But a comprehensive study of the domain switching mechanism should include the effects of these two types of defects. Numerical models are already available to introduce dislocations in to the phase-field model. Integrating the polycrystalline model and the dislocation model will certainly make the model more realistic.

2. The current version of the phase field model for ferroelectric ceramics does not take in to account the effect of grain boundary energy. In future, to make the model more effective, the contribution of the grain boundary energy should be taken in to account.
3. Although the phase-field model developed to study the polarization switching under a localized electric potential successfully predicts the nucleation voltage, but does not provide complete understanding of the switching mechanism. To make the model more useful, the existing phase-field model can be modified to study the hysteresis loop of the ferroelectric under a localized potential. This will provide adequate information of the individual stages of polarization switching under a localized electric potential.
Vita

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Samrat Choudhury received his Bachelors in Engineering (B.E) in 1998 and Masters in Engineering (M.E) in 2000 in Metallurgical Engineering from Regional Engineering College, Durgapur and Indian Institute of Science, Bangalore, India, respectively. He joined the Department of Materials Science and Engineering at the Pennsylvania State University as a Ph.D. student in Spring, 2002. Among other awards, Samrat is a recipient of the graduate excellence in materials science award (GEMS) from American ceramic society, MRS graduate student award and 2006 Annual Acta Materialia graduate student paper award. Listed below are some of the publications that Samrat has contributed during his Ph.D. program at Pennsylvania State University.

1. S.Choudhury, Y.L.Li, and L.Q.Chen “Correlation between number of ferroelectric variants and coercive field of PbZr_{1-x}Ti_{x}O_{3} (PZT) single crystals” Appl Phys. Lett., 91, 032902, 2007


