DIELECTRIC AND PYROELECTRIC SUSCEPTIBILITIES
OF EPITAXIAL FERROELECTRIC THIN FILMS

BY

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DISSERTATION

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Abstract

The dielectric and pyroelectric properties of ferroelectrics have been utilized extensively in a variety of applications such as memories, transducers, and sensors. Traditionally, such applications have utilized bulk or single crystal versions of ferroelectrics but modern electronic devices increasingly require micro-fabricated architectures on thin-films. Despite spectacular advances in our ability to synthesize high-quality thin films, much remains to be understood regarding the evolution of their dielectric and pyroelectric properties. In the present work, we investigate the dielectric and pyroelectric susceptibilities of ferroelectric thin films with PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) as a model system using a combination of phenomenological Ginzburg-Landau-Devonshire (GLD) modeling, epitaxial thin-film growth, and ex situ characterization techniques such as x-ray diffraction, piezoresponse force microscopy, and electrical measurements. We show that large dielectric and pyroelectric susceptibilities can be obtained in tensile strained PZT thin films due to the displacement of 90° domain walls and thermal expansion mismatch with the substrate. The primary advances made herein that enable this are the development of a polydomain GLD model to predict ferroelectric susceptibilities, the development of a hard-mask technique for the fabrication epitaxial capacitor structures, and the implementation of a phase-sensitive technique for the accurate measurement of pyroelectric properties. We then proceed to study the effect of composition and strain gradients on the ferroelectric properties of PZT. A combined theoretical and experimental study indicates that the graded heterostructures possess exotic structural and ferroelectric properties that are largely determined by the structure of the initial growth layer. We show that obtain large residual strains and novel ferroelectric properties (such as large built-in electric fields and low dielectric susceptibility) can be obtained in graded structures that are not found in the single layer variants. Finally, we present preliminary results of pyroelectric energy conversion in a micro-fabricated device utilizing the concepts developed in this work. Analysis of reversible pyroelectric cycles indicate that large temperature ramp rates and power densities can be obtained for thermal to electrical energy conversion in thin films as compared to prior experiments on bulk ferroelectric ceramics.
To Amma, Appa, and Jeyashree
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<table>
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>PZT</td>
<td>PbZr$_{1-x}$Ti$_x$O$_3$</td>
</tr>
<tr>
<td>MPB</td>
<td>Morphotropic phase boundary</td>
</tr>
<tr>
<td>MOCVD</td>
<td>Metal organic chemical vapor deposition</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed-laser deposition</td>
</tr>
<tr>
<td>MBE</td>
<td>Molecular beam epitaxy</td>
</tr>
<tr>
<td>BST</td>
<td>Ba$_{1-x}$Sr$_x$TiO$_3$</td>
</tr>
<tr>
<td>RHEED</td>
<td>Reflection high energy electron diffraction</td>
</tr>
<tr>
<td>PUND</td>
<td>Plus up negative down</td>
</tr>
<tr>
<td>GLD</td>
<td>Ginzburg-Landau-Devonshire</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>PFM</td>
<td>Piezoresponse force microscopy</td>
</tr>
<tr>
<td>RSM</td>
<td>Reciprocal space map</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>AAO</td>
<td>Anodic aluminum oxide</td>
</tr>
<tr>
<td>LFP</td>
<td>Low frequency technique</td>
</tr>
<tr>
<td>LIM</td>
<td>Laser intensity modulation</td>
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</table>
List of Symbols

\( P_s \)  Spontaneous polarization
\( T_c \)  Curie temperature
\( E_c \)  Coercive field
\( P_r \)  Remnant polarization
\( \epsilon_0 \)  Vacuum permittivity
\( \epsilon_{ij} \)  Dielectric susceptibility
\( d_{ijk} \)  Piezoelectric coefficient
\( \pi_i \)  Pyroelectric coefficient
\( i_p \)  Pyroelectric current
\( E_i \)  Electric field
\( \alpha_{ijk} \)  Stiffness coefficient
\( T \)  Temperature
\( s_{ij} \)  Elastic compliance
\( \sigma_i \)  Stress
\( S_i \)  Strain
\( Q_{ij} \)  Electrostrictive coefficient
\( P_i \)  Polarization
\( G \)  Gibbs free energy
\( \tilde{G} \)  Helmholtz free energy
\( \phi_a \)  Fraction of in-plane domains
\( \phi_c \)  Fraction of out-of-plane domains
\( x \)  Titanium content of PZT
\( \alpha_f \)  Thermal expansion coefficient of substrate
\( \alpha_f \)  Thermal expansion coefficient of film
$C$ Capacitance
$a$ In-plane lattice constant
$c$ Out-of-plane lattice constant
$\lambda$ Laser wavelength
$D$ Average domain size
$\omega$ Frequency
$A$ Capacitor Area
$t$ Film thickness
$\epsilon_{ex}$ Extrinsic contribution to dielectric permittivity
$k$ Domain wall stiffness
$l$ Amplitude of domain wall vibration
$i_s$ Thermally stimulated current
$T_0$ Amplitude of sinusoidal temperature oscillation
$T_b$ Background temperature
$\theta$ Phase difference between pyroelectric current and temperature oscillation
$\mu_{ij}$ Flexoelectric coefficient
$g_{ij}$ Gradient energy coefficient
$Y$ Biaxial modulus
$G$ Shear modulus
$\rho$ Dislocation density
$b$ Modulus of the Burgers vector
$U$ Strain energy
$T_g$ Growth temperature
$C_{ij}$ Elastic stiffness
$n_3$ Magnitude of the substrate normal vector
$E_d$ Depolarization field
$G_{\mu}$ Flexoelectric energy
$W_{tot}$ Total work done
$\eta$ Energy conversion efficiency
$Q_{in}$ Total heat input
$T_L$ Low temperature
$T_H$ High temperature
$E_L$ Low electric field
$E_H$ High electric field
Chapter 1

Ferroelectricity: Materials, Properties, and Phenomenology

In this Chapter, we provide a brief introduction to the physics of ferroelectricity including a review of their equilibrium properties and then move to the specific case of ferroelectric thin films. We then discuss various aspects specific to thin films in greater detail such as the growth of ferroelectric films, domain formation, characterization of their ferroelectric properties, and phenomenological modeling of ferroelectricity. Throughout, we will motivate the central focus of the rest of the thesis - the optimization of dielectric and pyroelectric susceptibilities in ferroelectric thin films and touch upon various aspects of ferroelectricity relevant to address this central question. The Chapter concludes with a summary of the organization of the rest of the thesis.
1.1 Introduction to Ferroelectrics

A material is considered to be ferroelectric when it has two or more stable states with a spontaneous electric polarization (or a dipole moment per unit volume) in the absence of an applied electric field and can be switched from one of these states to any other by the application of an electric field [2–4]. These different states possess identical crystal structures and differ only in the direction of the polarization at zero external field. Of the 32 total crystal classes, 20 crystal classes exhibit a change in polarization when subjected to stresses (i.e. piezoelectricity). Among the 20 piezoelectric crystal classes, exactly 10 possess a unique polar axis and a spontaneous polarization [2,5]. The spontaneous polarization is often temperature dependent and the existence of such a polar axis in a crystal can be detected by measuring the charges released from its surface in response to a change in temperature. This is called the pyroelectric effect and the 10 polar crystal classes are often called the pyroelectric classes. Among the pyroelectric crystals only those whose polarization can be switched by an electric field constitute ferroelectrics. Therefore, ferroelectrics form a subgroup of the pyroelectric class and the definition of ferroelectricity is an engineering rather than a crystallographic one. Thus, whether or not a pyroelectric crystal is ferroelectric depends on the ability to switch its polarization with an applied field and may often depend on experimental limitations such as crystal perfection, electrical conductivity, temperature, etc.

The high symmetry paraelectric phase from which the ferroelectric phase can be understood via small structural distortions is called the prototype phase. For most ferroelectric materials, the prototype phase is cubic and occurs at a high temperature. As the temperature of the cubic phase is reduced, it undergoes a structural phase transition which breaks the centrosymmetry of the cubic phase and forms the low-symmetry ferroelectric phase. This transition is accompanied by a spontaneous strain and a spontaneous polarization ($P_s$) due to the structural distortion. The temperature corresponding to this phase transition is called the Curie temperature ($T_c$) and $P_s$ usually increases with decreasing temperature below $T_c$.

As the crystal is cooled through $T_c$, the emergence of a spontaneous polarization results in a large electrostatic energy from stray electric fields due to the uncompensated bound charges if the ferroelectric is homogeneously polarized. This electrostatic energy is called the depolarization energy (similar to demagnetization energy for magnetic materials) and tends to destabilize the spontaneous polarization [2,6,7]. The electrostatic energy is, however, usually reduced by the formation of different structural variants (or domains) of the low-symmetry phase that coexist below $T_c$. As a result, two domains with polarization pointing in opposite directions are formed to accommodate the lack of compensation. These domains are separated by 180° domain walls across which the polarization rotates from one domain to the other [7,8].
electrostatic energy, domains can also be formed below $T_c$ by elastic constraints where different structural variants are formed to minimize the elastic energy of the ferroelectric phase and this is particularly relevant in mechanically constrained crystals or thin film ferroelectrics [7, 8]. Elastic and electrical constraints can thus be used to tune the morphology of the ferroelectric phase and this has a profound effect on the ferroelectric properties.

Since the ferroelectric polarization can be switched with an electric field, the response of a ferroelectric is characterized by a hysteresis loop as a function of the applied field. The electric field at which the polarization switches its direction is called the coercive field ($E_c$) and the polarization at zero external field is known as the remnant polarization ($P_r$) [Fig. 1.1]. Such a history dependent behavior of the polarization forms the basis of ferroelectric memory (or FeRAM) where bits of information can be stored as the polarization direction in a ferroelectric capacitor [7,9]. For such a memory device, materials with large values of $P_r$ and a small $E_c$ are required so as to enable easy read/write operations while minimizing the power consumption. Apart from the switching of polarization and the highly non-linear hysteretic response at large electric fields, the strong thermo-electro-mechanical coupling in these materials results in large linear (or small-signal) susceptibilities to electric fields, stresses, and temperature. These are usually characterized by the dielectric, piezoelectric,
Figure 1.2: The composition-temperature phase diagram of the PZT system showing the various ferroelectric phases and their Curie temperatures (adapted from Ref. [1]).

and pyroelectric coefficients respectively as [2,4,9]

\[ \epsilon_{ij} = \frac{\partial P_i}{\partial E_j}, \quad d_{ijk} = \frac{\partial x_{ij}}{\partial E_k}, \quad \pi_i = \frac{\partial P_i}{\partial T} \]  

(1.1)

These susceptibilities are maximized near the structural or polar instabilities (such as near \( T_c \)) and form the basis of a variety of applications including dielectric capacitors, piezoelectric transducers, and temperature sensing elements [2, 7]. For a large number of practical applications of ferroelectrics, therefore, we desire materials with a large polarization and high susceptibilities near the temperature of operation.

Among the most commonly used ferroelectric materials are members of the lead zirconium titanate (i.e., PbZr\(_{1-x}\)Ti\(_x\)O\(_3\) (PZT)) family of ferroelectrics [7,10]. The high temperature prototype phase in PZT is the cubic perovskite phase and at lower temperatures, they adopt many distorted versions of the parent phase depending on the composition and the temperature [Fig. 1.2] [10,11]. For \( x > 0.06 \), the low temperature phase is ferroelectric and across this range of composition (0.06 < \( x < 1.0 \)), the off-centering of the central Ti or Zr ion in the unit cell below \( T_c \) is the source of ferroelectricity. Depending on the direction of the structural distortion that occurs, different ferroelectric structures result. Ti-rich compositions form a tetragonal ferroelectric (with the polarization along the pseudo-cubic [001] direction) and Zr-rich compositions
condense into a rhombohedral ferroelectric (with the polarization along the pseudo-cubic [111] direction). Throughout, the PZT system has a ferroelectric transition temperature exceeding 200°C and this enables convenient device operation near room temperature. The rhombohedral and tetragonal phases are separated by an almost temperature independent morphotropic phase boundary (MPB) at $x = 0.48$. The presence of such a structural competition near the MPB results in large ferroelectric susceptibilities at this composition and in combination with the robust ferroelectric properties near room temperature, this has made MPB PZT one of the most widely used ferroelectric materials. For applications which require large polarization, however, Ti-rich compositions are usually preferred due to their larger $P_s$ and square hysteresis.

### 1.2 Ferroelectric Thin Films

A large number of applications have traditionally relied on bulk, sintered ceramic materials with lateral dimensions in the range of 0.1 - 10 mm. These are typically polycrystalline ferroelectrics with a grain size in the range of 1 - 10 $\mu$m. Even though such bulk ferroelectrics have been the workhorse of piezoelectric transducers and sensors for decades, they pose significant challenges for advanced applications. The presence of a polycrystalline microstructure requires frequent electrical poling operations to orient the domains, the grain boundaries within the ceramics adversely affect the ferroelectric properties, the large dimensions necessitate enormous external voltages ($> 1$ kV) for switching, and due to their bulky nature they are impossible to integrate into micro-fabricated architectures and modern oxide nanoelectronic devices. Thin-film ferroelectrics overcome these limitations and provide a convenient platform for advanced applications. Epitaxial single crystalline ferroelectrics on lattice matched substrates provide exceptional ferroelectric properties and enable easy integration into micro-fabricated devices. Furthermore, in thin-films the domain morphologies and ferroelectric properties can also be engineered via epitaxial strain, film thickness, electrodes, artificial superlattice structures, etc., apart from composition of the film to provide an enormous phase space for materials design [12,13].

#### 1.2.1 Growth of Ferroelectric Thin Films

A variety of techniques have been developed to synthesize epitaxial ferroelectric thin films including sputtering, metal-organic chemical vapor deposition (MOCVD), pulsed-laser deposition (PLD), and molecular beam epitaxy (MBE). RF magnetron sputtering from alloy targets in an Ar + O$_2$ gas mixture been used to deposit ferroelectrics such as PZT and Ba$_{1-x}$Sr$_x$TiO$_3$ (BST) [7, 9, 14]. High temperature sputtering of complex oxide materials, however, is challenging due to problems associated with stoichiometry control (due
to different sputtering rates of the atoms), re-sputtering, and low growth rate. MOCVD has been developed more successfully with liquid precursors and high-quality epitaxial thin films of PZT and BiFeO$_3$ have been demonstrated [15, 16]. MOCVD is particularly suitable for large area deposition but the growth systems are complex and require careful tuning of the precursor chemistries, flow rates, partial pressures, and growth temperature to obtain stoichiometric thin films. This often results in very narrow growth windows for high-quality films via MOCVD and intensive precursor development for every material desired. Due to the problems associated with sputtering and MOCVD, they have largely been replaced by PLD [17–19] and MBE [20,21] for advanced research and development. In PLD, a pulsed laser source is used to create a plasma plume from a target of the desired film composition and the plume is directed towards a hot substrate on which the material is deposited. The high energy density of the laser ensures complete vaporization of the target and enables stoichiometric transfer of material from target to film. This makes PLD relatively easy to operate and provides for a high throughput. Consequently, a number of materials can typically be grown in a single PLD chamber allowing for seamless integration of ferroelectric thin films with dielectrics, metals, superconductors, and more. The low growth rate per laser pulse also allows unit-cell control of film thickness via reflection high energy electron diffraction (RHEED) enabling the growth of ultra-thin films. The deposition is confined to a small area due to the size of the target plume and this makes it difficult to scale PLD for industrial applications. MBE of ferroelectric materials from elemental metallic sources in an oxidizing atmosphere has also been developed successfully in the past decade for ferroelectrics and it has produced thin films with low defect densities of many complex oxide materials. MBE enables very high-quality thin
films and an exceptional control of stoichiometry and thickness but suffers from low throughput and high operation costs. In recent times, MBE is gaining increased attention within the ferroelectrics community for research applications due to the high quality of the films which enables the study of the intrinsic ferroelectric properties of thin film materials. In this thesis, ferroelectric thin films of PZT grown by PLD were utilized for a detailed study of their dielectric and pyroelectric properties. Details of the growth including the optimized growth conditions for the various materials utilized in this thesis are provided in Chapter 2 and in Appendix A.

The epitaxial growth of thin films via PLD and MBE has been developed vastly in the last decade and these techniques are now routinely capable of producing high-quality stoichiometric ferroelectric thin films with unit-cell level control of thickness on single crystalline substrates [12,18]. Simultaneously, complex oxide metals and substrates have also been developed to provide for fully epitaxial ferroelectric capacitor structures with oxide metal electrodes and epitaxial strain in the range of 2% for a variety of ferroelectric materials such as PZT and BST [Fig. 1.3] [12]. This has produced an array of spectacular results in the past decade such as strain induced enhancement of $T_c$ in BaTiO$_3$ [22], strain induced ferroelectricity in SrTiO$_3$ [23], substrate vicinality and electrode control of domain morphologies [24], and even new strain-induced ferroelectric phases [25]. The growth of epitaxial thin films has also enabled integration of ferroelectrics into multi-functional architectures such as ferroelectric field effect devices [7], highly tunable ferroelectric-dielectric superlattices [12], and ferroelectric gating of superconductivity [26].

1.2.2 Domain Formation in Ferroelectric Thin Films

As mentioned previously, the domain morphologies in ferroelectric thin films can be controlled using elastic and electrostatic constraints. Depending on the structure of the ferroelectric phase, various domain variants are possible. In the case of tetragonal ferroelectrics such as the Ti-rich member of the PZT family PbZr$_{0.2}$Ti$_{0.8}$O$_3$ with lattice constants $a = b = 3.94$ Å and $c = 4.12$ Å [27, 28], three domain variants are possible for growth on (001)-oriented substrates with the tetragonal axis along each of the [100], [010], and [001] substrate directions. These correspond to six polarization variants since each structural domain corresponds to two degenerate polarization directions. Depending on the elastic and electrostatic boundary conditions, a coexistence of these six polarization variants is formed which minimizes the total energy (elastic and electrostatic) of the system. Since $c$ axis oriented tetragonal thin films are typically desired with a large out-of-plane polarization, we will restrict ourselves to the domain formation on substrates with lattice parameters close (within 1%) to the in-plane lattice parameter of the ferroelectric. In this case, if the ferroelectric thin film is grown on insulating substrates with no metallic electrodes, the depolarization
fields are dominant and $180^\circ$ domain structures are formed with $c^+$ and $c^-$ domain variants [Fig. 1.4 a]. For most practical applications, ferroelectric capacitor structures with metallic electrodes are used. As a result, the depolarization energy is negligible and $180^\circ$ domain structures are not common. Elastic constraints can, however, be a very powerful route to control the domain structures in thin films. In response to a substrate induced epitaxial strain a $90^\circ$ domain structure can be formed where the out-of-plane oriented ($c$) and in-plane oriented ($a$) domain variants coexist. These two domain types are separated by $90^\circ$ domain walls oriented at $45^\circ$ to the substrate (to main charge neutrality) [Fig. 1.4 b]. Depending on the compatibility of the substrate to the lattice constants of the film, epitaxial thin films of $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ have a coexistence of these two domain variants to reduce the total energy. Domain formation is energetically unfavourable for ultrathin or extremely thick films since domain wall energy prevents the former while dislocation formation (and strain relaxation) precludes the latter. In a wide range of intermediate thickness relevant for practical applications (10 - 1000 nm), however, the domain structures of ferroelectric thin films can be successfully engineered with elastic and electrostatic driving forces.

These domain structures have a profound effect of the ferroelectric polarization and the susceptibilities. The fraction of $c$ domains determines the usable (or switchable) spontaneous polarization. For ferroelectric susceptibilities the situation is more complex. In response to applied electric fields and temperature changes, both the magnitude of polarization within and the fraction of the $c$ domains change. The latter occurs due to the movement of domain walls in response to the applied stimulus. This results in both bulk (due to the change in polarization) and domain wall (due to the change in domain fractions) contributions on ferroelectric susceptibilities. Such a domain wall effect on dielectric susceptibility has been known for decades and experimental work has indicated large domain wall contributions to dielectric and piezoelectric properties [29, 30]. The exact magnitude of the effect and the importance of $90^\circ$ domain walls, however, is unknown due to the difficulty in isolating the domain wall response in ceramic materials. Pyroelectric susceptibilities of thin films have, on the other hand, seen very little theoretical or experimental work and much remains to be clarified in this regard. As a consequence, the optimization of pyroelectric susceptibilities,
in spite of its enormous practical significance, is vastly understudied and will be the primary focus of this thesis.

1.3 Characterization of Ferroelectric Properties

1.3.1 Spontaneous Polarization and Switching Characteristics

The spontaneous polarization and the coercive fields of a ferroelectric thin film are characterized using a frequency dependent hysteresis loop measurement (i.e. polarization as a function of the applied electric field). For such a measurement, two measurement sub-systems are typically required - a waveform generator capable of AC electric fields and a charge measurement circuit. The charge measurement circuit is used to monitor the charge on the ferroelectric capacitor as a function of the applied voltage and the polarization can be obtained by dividing the charge by the area of the capacitor. Since only the flow of charges is measured, the absolute value of polarization is not obtained in such a measurement and the loops are centered in the polarization axis assuming that the switchable polarization is identical in either direction. Traditionally, a Sawyer-Tower circuit is used to perform this measurement where the voltage across a reference capacitor placed in series with the ferroelectric capacitor is monitored to measure the charge on the ferroelectric as a function of the voltage. Sawyer-Tower circuits are plagued by problems associated with parasitic capacitance and back-voltages. As a result, Sawyer-Tower circuits have been largely replaced by virtual ground measurement techniques which are more immune to the aforementioned problems.

The polarization switching characteristics and long-term reliability of the ferroelectric capacitors are probed via pulsed testing through PUND (for Positive Up Negative Down) measurements. In such a measurement, a five pulse train is used. Here, the first pulse switches the polarization to a known state. The second pulse, in the opposite direction, measures the total switchable polarization in that direction. A third pulse, in the same direction as the second, measures the non-remnant fraction of the polarization. The fourth and fifth pulses are opposite in direction to the previous two and measure the switchable and non-remnant polarization in the other direction. The PUND measurements can thus be used to obtain the total switchable and remnant polarization in the ferroelectric capacitor and form the basis of reliability testing and fatigue measurements for memory and other long-term switching applications.

1.3.2 Ferroelectric Susceptibilities

The susceptibility of ferroelectrics to electric fields, stresses, and temperature are also commonly characterized for practical applications. As mentioned previously, these susceptibilities are known as dielectric,
piezoelectric, and pyroelectric coefficients, respectively. In this thesis, we will focus primarily on electric field and temperature dependent susceptibilities.

The dielectric susceptibility of a ferroelectric is defined as $\epsilon_{ij} = \frac{\partial P_i}{\partial E_j}$. For a thin film with an applied electric field along the out-of-plane substrate direction (i.e. along the $c$ axis), the component $\epsilon_{33}$ is usually measured. This can be obtained by measuring the capacitance ($C$) of a ferroelectric capacitor structure with an area $A$ and thickness $t$ where $C = \epsilon_0 \epsilon_{33} A / t$ with an applied AC electric field and utilizing it to derive the dielectric susceptibility. For the case of thin films, particular attention has to be paid to the nature of electrodes, the magnitude of the applied electric field, and the parasitic capacitances during measurement. For thin-film ferroelectrics, it has been shown in numerous prior studies that the nature of the electrode plays a crucial role in the measurement of ferroelectric susceptibilities. The presence of elemental metal electrodes results in the formation of a dead-layer and space charge accumulation at the interface with the ferroelectric due to the poor chemical and structural compatibility [31–36]. This results in an inactive interface layer and thus erroneous measurements of dielectric properties using the formula above. This problem can be alleviated by using epitaxial oxide electrodes such as SrRuO$_3$, LaSr$_{0.5}$Co$_{0.5}$O$_{3}$, and La$_{0.7}$Sr$_{0.3}$MnO$_3$. In the work presented here, epitaxial electrodes of SrRuO$_3$ have been used for the all the ferroelectric capacitors. At the same time, the magnitude of the applied electric field is also an important measurement consideration. Typically, the dielectric susceptibility of a ferroelectric refers to the reversible or the small-signal response of the material and is independent of the magnitude of the applied electric field. At large electric fields, the response of the ferroelectric is no longer linear (due to domain wall motion and switching effects). In order to measure the true linear response of the material, electric field amplitude dependent studies (called Rayleigh analysis) is usually performed to confirm that the linear behavior is indeed valid at the applied electric fields [37, 38]. Accurate measurements also require careful calibration of the parasitic capacitances in the measurement circuit due to fixtures, cabling, etc. because the measured capacitances can often be small (< 1 nF) and comparable to the parasitics.

The pyroelectric susceptibility of a ferroelectric is defined as $\pi_i = \frac{\partial P_i}{\partial T}$. For a ferroelectric, this is usually measured by applying a known temperature change and measuring the change in polarization that results. The polarization change is measured by monitoring the current that flows between the short-circuited electrodes (i.e., the pyroelectric current) to compensate for the polarization. Since the current in the external circuit is related to the out-of-plane polarization, the component $\pi_3$ is usually measured and is the most practically relevant component. In terms of the pyroelectric current ($i_p$), the definition of $\pi_i$ can be rewritten as $i_p = \pi_i A \frac{dT}{dt}$ and this forms the basis of pyroelectric susceptibility measurements. Many techniques have been developed to apply this measurement principle. These include pulsed-laser based heat sources, constant
rate temperature ramp in ovens, and phase-sensitive techniques using sinusoidal temperature oscillations [39–41]. Among the various techniques, the phase-sensitive measurements are the most preferred for accurate quantitative measurements in thin films. This is because of the difficulty in measuring the temperature rise of the sample and the contribution of non-pyroelectric thermally stimulated currents in the other two techniques [41, 42]. In this thesis, we have implemented a phase-sensitive measurement for characterizing the pyroelectric susceptibility of ferroelectric thin films. Detailed description of the measurement system utilized in this study will be presented in Chapter 4.

1.4 Phenomenological Modeling of Ferroelectricity

The properties of a ferroelectric thin film such as the spontaneous polarization and the ferroelectric susceptibilities as well as their dependence on temperature, electric fields, and epitaxial strain can be described by mean field thermodynamic models such as the Ginzburg-Landau-Devonshire (GLD) theory of ferroelectricity [2–4]. By expanding the free energy of a ferroelectric in terms of a power series of the polarization order parameter and including the coupling of the polarization to stresses and electric fields, the equilibrium properties can be obtained by minimization of the free energy. Such an approach has been used very successfully to describe the properties of a variety of ferroelectric materials such as PZT, BST, and BiFeO$_3$ in both single crystal and thin film form [11, 12]. Recently, GLD models have also been adapted to describe the domain formation and thickness effects in a variety of ferroelectric thin films and have been instrumental in guiding experimental efforts towards a more systematic and thorough understanding of ferroelectricity [22, 23]. Quite often, a number of different factors govern the properties of thin films including strain, thickness, domain structure, etc, and GLD models provide a fertile starting point towards understanding and optimizing the various contributions to the property of interest. In this thesis, we will use GLD models extensively to help understand and optimize the ferroelectric susceptibilities. This approach, however, suffers from intrinsic deficiencies of such mean field thermodynamic models. They provide a purely macroscopic picture and do not describe the microscopic atomic displacements that accompany the ferroelectric response. At the same time, they are useful only to understand the equilibrium thermodynamic properties of the ferroelectric and are not suitable for non-equilibrium phenomena such as ferroelectric switching and leakage. In any case, they provide an excellent starting point to phenomenologically model the equilibrium ferroelectric properties and will be used extensively in Chapter 2 to understand the effect of epitaxial strain, composition, and temperature on ferroelectric susceptibilities.

For the simplest case of a homogeneously polarized ferroelectric with polarization along the $z$-direction,
with zero external stresses and an electric field $E$, the Gibbs free energy density ($G$) with respect to the paraelectric phase can be written as a power series in the polarization as \[3,4\]

$$ G = \alpha_1 P^2 + \alpha_{11} P^4 + \alpha_{111} P^6 - E P $$

(1.2)

where the first three terms correspond to the energy of the bulk ferroelectric phase (or bulk energy) and the last term corresponds to the coupling of the polarization to the electric field. Here, only the even powers of $P$ occur in the bulk energy because of $+P \leftrightarrow -P$ symmetry. The spontaneous polarization can be obtained by minimizing the free energy as the solution of

$$ 2\alpha_1 P + 4\alpha_{11} P^3 + 6\alpha_{111} P^5 = E $$

(1.3)

and the dielectric susceptibility ($\epsilon$) can thus be obtained as

$$ \epsilon \left( 2\alpha_1 + 12\alpha_{11} P^2 + 30\alpha_{111} P^4 \right) = 1 $$

(1.4)

Since the dielectric stiffness diverges at the Curie temperature ($T_c$), the coefficient $\alpha_1$ is usually assumed to have a temperature dependence of the form $\alpha_1 = \alpha_0 (T - T_c)$ where $\alpha_0$ is independent of temperature. The other coefficients are considered constant in the simplest approximation and their sign describes the transition to ferroelectricity. First order transitions are described by free energies with $\alpha_{11} < 0$ and $\alpha_{111} > 0$ and second order transitions have $\alpha_{11} > 0$ and $\alpha_{111} > 0$. Similarly, minimization of the above equation with respect to temperature gives the pyroelectric coefficient ($\pi$) as

$$ \pi \left( 2\alpha_1 + 12\alpha_{11} P^2 + 30\alpha_{111} P^4 \right) + 2\alpha_0 P = 0 $$

(1.5)

Thus, the equilibrium thermodynamic properties such as spontaneous polarization, dielectric constants, and pyroelectric coefficients can be obtained from the free energy describing the ferroelectric phase.

In the presence of finite external stresses, one needs to include two additional terms to the energy - the bulk elastic energy ($G_{\sigma}$) and also electrostrictive coupling energy ($G_{P\sigma}$). These can be written as \[2–4\]

$$ G_{\sigma} = \frac{1}{2} s_{11} \left( \sigma_1^2 + \sigma_2^2 + \sigma_3^2 \right) + s_{12} (\sigma_1 \sigma_2 + \sigma_2 \sigma_3 + \sigma_3 \sigma_1) + \frac{1}{2} s_{44} \left( \sigma_4^2 + \sigma_5^2 + \sigma_6^2 \right) $$

(1.6)

$$ G_{P\sigma} = -Q_{11} \sigma_3 P^2 - Q_{12} (\sigma_1 + \sigma_2) P^2 $$

(1.7)
where \( \sigma \) are the components of the stress tensor (in Voigt notation) and \( Q_{ij} \) are the electrostrictive coefficients. The energy can be modified trivially to include polarization components along all three coordinate axis and extended to calculate the thermodynamic properties of monodomain ferroelectrics with polarization components along all three spatial directions.

For thin films, however, the appropriate free energy description is not the Gibbs free energy (\( G \)) but the Helmholtz free energy (\( \tilde{G} \)) which can be obtained from \( G \) via a Legendre transform as \( \tilde{G} = G + \sum_{i=1}^n \sigma_i u_i \) where \( u_i \) are the components of the strain tensor. These must be supplemented with the relevant mechanical boundary conditions (for the epitaxial strains from the substrate) and minimized to obtain the equilibrium properties of the thin film. Such a scheme can also be extended to ferroelectric thin films with complex polydomain structures such as the 90° domain structures described previously. This will be discussed in detail in Chapter 2 where we will utilize the GLD models to study the evolution of dielectric and pyroelectric properties of epitaxial thin film ferroelectrics with complex domain structures as a function of the composition, applied electric fields, temperature, and epitaxial strain.

### 1.5 Organization of the Dissertation

The remainder of this dissertation consists of eight main Chapters, two appendices, and a section for references.

In Chapter 2, we develop a phenomenological GLD model to investigate the dielectric and pyroelectric susceptibilities of polydomain thin films of PZT. We construct a temperature-strain phase diagram for polydomain PZT thin films and identify large dielectric and pyroelectric susceptibilities in Ti-rich thin films due to domain wall displacement and thermal expansion mismatch driven effects.

In Chapter 3, we present a detailed report on the growth of epitaxially strained \( \text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3 \) thin films via pulsed-laser deposition and an investigation of their crystal structures and ferroelectric domains. These films serve as model systems for an experimental investigation of the dielectric and pyroelectric susceptibilities.

In Chapter 4, we provide a brief overview of an MgO based hard-mask process to fabricate epitaxial top electrodes for the capacitor structures used in this work. After a detailed ferroelectric characterization of the \( \text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3 \) capacitors fabricated using this process, we then move on to the investigation of the ferroelectric susceptibilities of strained \( \text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3 \) thin films. We present measurements of the dielectric and pyroelectric coefficients in the strained thin films and compare the results to the predictions of the GLD model.
In Chapter 5, we experimentally investigate the structure and ferroelectric properties of compositionally graded PZT thin films using PbZr$_{0.2}$Ti$_{0.8}$O$_3$ and PbZr$_{0.8}$Ti$_{0.2}$O$_3$ as the end members. Detailed structural and ferroelectric characterization of the graded heterostructures reveal a number of useful functionalities such as high retained strains, novel ferroelectric domain structures, and large built-in electric fields in heterostructures with good film-substrate lattice compatibility.

In Chapter 6, we develop a phenomenological GLD theory including the effect of composition gradients, structural relaxation, and flexoelectric effects to accurately model the graded ferroelectric thin films. These models and comparison to the experiments in Chapter 5 reveal that the enhanced strain retention in graded heterostructures is due to a reduced tendency to form misfit dislocations and the built-in electric fields are due to the strong flexoelectric coupling within the graded thin films.

In Chapter 7, we present a preliminary experimental investigation of pyroelectric energy conversion using a microfabricated thin film platform with PZT thin films and lithographically patterned Pt-line heaters. These experiments indicate that large temperature cycling rates and high power densities in thin film pyroelectric energy harvesting devices as compared to prior experiments on bulk ferroelectric ceramics.

In Chapter 8, we summarize the major findings of the current work and provide suggestions for future work to build on the findings presented here.

Appendix A covers the details of PLD and gives a basic overview of thin film growth mechanisms with particular attention to the epitaxial growth of complex oxide thin films.

Appendix B provides details of the modified look ahead energy minimization scheme used in Chapter 6 for calculating the strain distribution within compositionally graded ferroelectric thin films.
In this Chapter, we develop a GLD theory of polydomain ferroelectric thin films to study their equilibrium thermodynamic properties such as spontaneous polarization, domain distributions, and ferroelectric susceptibilities as a function of applied electric fields and temperature. In particular, we consider the case of tetragonal ferroelectric thin films such as the Ti-rich PZT and explore the effects of electric fields, composition, and temperature on the ferroelectric susceptibilities. We show that that apart from the intrinsic susceptibility of the ferroelectric due to a change in the polarization in the bulk of the domains, there is an extrinsic contribution (or a domain wall contribution) to the dielectric and pyroelectric response due the electric field (for dielectric susceptibility) or temperature (for pyroelectric susceptibility) dependent movement of the domain walls in the polydomain states. Further, in the case of pyroelectric response, we also investigate a secondary effect that arises from a piezoelectric contribution that results from thermal expansion mismatch with the substrate which can be significant in thin film ferroelectrics. We identify that these extrinsic and secondary contributions, which have been neglected in earlier calculations for thin films, can significantly impact the response and may offer new pathways to improve the susceptibility of ferroelectric thin films to electric fields and temperature.
Ferroelectric materials such as PZT and BST have been a subject of intense theoretical and experimental study due to their robust and tunable ferroelectric properties that enable a wide variety of applications such as mechanical transducers, thermal sensors, and dielectric capacitors \[1\]. As bulk crystals these materials possess a rich composition dependent phase diagram and the dielectric, piezoelectric, and pyroelectric properties of these materials which enable such applications can be adjusted with composition. In thin films, the ferroelectric properties can also be engineered with epitaxial strain, thickness, electrical boundary conditions, and more \[12, 44, 45\]. Recent work on strain engineering of ferroelectrics, for instance, has demonstrated spectacular results including strain induced ferroelectricity in SrTiO$_3$ \[23\], rotational phases in ultrathin PbTiO$_3$ \[46\], and strain driven morphotropic phase boundary-like features in BiFeO$_3$ \[25\]. Thus, epitaxial strain has become one of the most powerful tools for enhancing and controlling the properties in complex oxide systems and a route to harnessing phenomena that may be absent in bulk materials.

Since most practical applications utilize “thick” ferroelectric films (generally in excess of 200 nm), it is important to understand the dielectric and pyroelectric susceptibilities in these systems and explore new mechanisms for improving them. Epitaxial ferroelectric thin films in this range of thickness offer an exciting potential for such a study but a comprehensive theoretical understanding is currently unavailable. Pyroelectric properties of ferroelectric thin films have been calculated using GLD models in the past but most studies have concentrated on monodomain films at a few chosen compositions \[47, 48\]. It is known, however, that monodomain states are stable only in ultrathin films of PZT \[49, 50\] and thicker films that are more technologically relevant, form polydomain states in equilibrium \[51–53\]. GLD theory has been modified to accurately predict the formation and properties of these polydomain states in strained films \[54, 55\]. In this Chapter, we develop a GLD phenomenological model to study dielectric and pyroelectric properties of polydomain structures that form in epitaxially strained films of the technologically relevant PZT system. We develop a design algorithm that will allow researchers to maximize the susceptibilities in epitaxial thin films as a function of composition, temperature, and thin-film strain.

### 2.1 The Model: Free Energy and Boundary Conditions

We consider the case of single-crystal epitaxial thin films of a ferroelectric grown in the cubic paraelectric state on a much thicker (001)-oriented cubic substrate. Typical thin films used in ferroelectric devices are 0.1-1 μm thick on 0.1-1 mm thick substrates. During cooling from the growth temperature, the paraelectric to ferroelectric transition takes place resulting in the formation of a mono or polydomain ferroelectric state at lower temperatures. The monodomain states consists of homogeneous polarization and strains throughout
the film while the polydomain state consists of two alternating domains with different polarization separated
by planar domain walls. To identify the equilibrium state of the films which is either a monodomain
or a polydomain state, we use the thermodynamic theory of ferroelectric thin films with dense domain
structures as developed in Refs. [54] and [55]. We assume that the polarization and strain fields inside the
individual domains are homogeneous and the domain wall self-energies are negligible. Such an assumption
is justified for thick PZT films where the theoretically predicted domain structures have been observed
experimentally [51,53] and the condition that the domain wall width is much less than the film thickness is
satisfied so that the domain wall self-energy may be neglected [56,57].

We use the generalized Helmholtz free energy density ($\tilde{G}$) for a ferroelectric thin film to obtain the
equilibrium domain structure and the ferroelectric susceptibilities. In the crystallographic reference frame
($x_1, x_2, x_3$) of the paraelectric phase $\tilde{G}$ can written in terms of the polarization $P_i$ and stresses $\sigma_i$ as [54]

$$\tilde{G} = \alpha_1 (P_1^2 + P_2^2 + P_3^2) + \alpha_{11} (P_1^4 + P_2^4 + P_3^4) + \alpha_{111} (P_1^6 + P_2^6 + P_3^6)
+ \alpha_{112} \left\{ P_1^4 (P_2^2 + P_3^2) + P_2^4 (P_1^2 + P_3^2) + P_3^4 (P_1^2 + P_2^2) \right\} + \alpha_{123} P_1^2 P_2^2 P_3^2
+ \frac{1}{2} s_{11} (\sigma_1^2 + \sigma_2^2 + \sigma_3^2) + s_{12} (\sigma_1 \sigma_2 + \sigma_2 \sigma_3 + \sigma_3 \sigma_1) + \frac{1}{2} s_{44} (\sigma_1^2 + \sigma_2^2 + \sigma_3^2)
- \frac{1}{2} \epsilon_0 (E_1^2 + E_2^2 + E_3^2) - E_1 P_1 - E_2 P_2 - E_3 P_3$$

(2.1)

where $P_i$ are the polarization components. The primary stiffness coefficient ($\alpha_1$) is given by the Curie-
Weiss law as $\alpha_1 = \frac{T - T_c}{2\epsilon_0 C}$ and $\alpha_{ij}$ and $\alpha_{ijk}$ are the higher order stiffness coefficients. $\sigma_i$ are the mechanical
stresses, $s_{ij}$ are the elements of the elastic compliance tensor at constant polarization, $E_i$ are the components
of the internal electric field, $C$ is the Curie constant, and $T_c$ is the ferroelectric Curie temperature. The
phenomenological coefficients for the PZT system were obtained from Refs. [58] and [59]. The stresses $\sigma_i$ are
related to the polarization components and lattice strains through the electrostrictive coefficients as shown
in the equations of state below. Thus, $\tilde{G}$ takes the coupling between the strain and polarization into full
account and the transformation of $\tilde{G}$ into a function of $P_i$ and strains $S_i$ restores these coupling terms. The
free energy neglects the energies associated with the tilting of the oxygen octahedra and the anti-ferroelectric
polarization states. These are valid assumptions for $x > 0.5$ and $T > 300$ K which are considered in this
Chapter [60]. For the thick films considered here, we can also neglect the depolarization field due to the
finite conductivity of the PZT thin films and the presence of symmetric epitaxial electrodes [61].

The free energy is supplemented by the relevant mechanical boundary conditions for the mono/polydomain
structures [54,60]. For the monodomain ferroelectric states, the mechanical boundary conditions give the
in-plane strain components as

\[ S_1 = S_2 = S_m, \quad S_6 = 0 \]

where the misfit strain \( S_m = \frac{a_s - a_0}{a_s} \) is defined by the substrate lattice parameter \( a_s \) and the lattice constant \( a_0 \) of the free standing film. Since there are no forces acting on the free surface of the film, we also have

\[ \sigma_3 = \sigma_4 = \sigma_5 = 0 \]

The remaining three strains \((S_3, S_4, S_5)\) depend on the polarization \( P_i \) in the film as \( S_n = -\frac{\partial G}{\partial \sigma_n} \). In the absence of an external electric field, for the case of short-circuited PZT films, we set \( E_i = 0 \) along all three directions. This enables the description of the free energy of the monodomain states in terms of the polarizations \( P_i \) and the epitaxial misfit strain \( S_m \). Minimizing the free energy gives the equilibrium polarization as a function of strain, composition, and temperature.

For the polydomain states, the average free energy density \( \langle \tilde{G} \rangle \) can be written as \( \langle \tilde{G} \rangle = \phi' \tilde{G}' + (1 - \phi') \tilde{G}'' \) where \( \phi' \) is the domain fraction of the first domain type and \( \tilde{G}' \) and \( \tilde{G}'' \) are the energy densities within the domains of first and second type, respectively. Using mechanical boundary conditions it is possible to eliminate the stresses \( \sigma'_i, \sigma''_i \) from the expression of \( \langle \tilde{G} \rangle \) similar to the single domain case. From the epitaxial relationship determined by the substrate we can express the mean in-plane strains as

\[ \langle S_1 \rangle = \langle S_2 \rangle = S_m, \quad \langle S_6 \rangle = 0 \]

The absence of forces acting on the free surfaces implies

\[ \langle \sigma_3 \rangle = \langle \sigma_4 \rangle = \langle \sigma_5 \rangle = 0 \]

The strain components inside each domain are related to the free energy as \( S_n = -\frac{\partial G}{\partial \sigma_n} \). In polydomain films, these must be supplemented by the microscopic boundary conditions on the domain walls. In the reference frame \((x_1, x_2, x_3)\) with \( x_3 \) perpendicular to the domain walls, the strain compatibility in the neighboring domains implies \( S'_i = S''_i \) where \((i = 1, 2, 6)\) and the mechanical equilibrium of the domains implies that the stress components are related as \( \sigma'_i = \sigma''_i \) where \((i = 3, 4, 5)\). Also, the local internal fields \( E'_i \) in a polydomain film are not necessarily equal to the externally applied field. In the absence of depolarizing fields, however, we can set the average electric field \( \langle E_i \rangle \) to zero along all three directions in the case of
short-circuited ferroelectric films considered here. The microscopic electric field continuity equations yield

\[ E'_1 = E''_1, \quad E'_2 = E''_2, \quad \epsilon_0 E'_3 + P'_3 = \epsilon_0 E''_3 + P''_3. \]

Using these relationships the average free energy density \( \langle \tilde{G} \rangle \) can be written as a function of seven variables \( P'_i, P''_i \) and \( \phi' \). Performing the minimization of \( \langle \tilde{G} \rangle \), we can find the equilibrium polarizations and domain populations as a function of epitaxial strain, composition, and temperature.

### 2.2 Temperature-Strain Phase Diagram of PZT

In this study, the free energy of five monodomain phases and six polydomain phases were evaluated numerically and the state with the minimum free energy was chosen as the equilibrium state. The monodomain states considered were the paraelectric phase \( (P_1 = P_2 = P_3 = 0) \), \( c \) phase \( (P_1 = P_2 = 0, P_3 \neq 0) \), \( r \) phase \( (P_1 = P_2 \neq 0, P_3 \neq 0) \), \( ca \) phase \( (P_1 \neq 0, P_2 = 0, P_3 \neq 0) \), and the \( aa \) phase \( (P_1 = P_2 = 0, P_3 = 0) \). It has already been shown that these are the only stable monodomain states in PZT thin films \[60\]. Near zero strain, the monodomain \( r \) phase is replaced by the polydomain \( c/a/c/a \) phase in thick PZT films for Ti-rich compositions [Fig. 2.1]. In the \( c/a/c/a \) phase, we have pseudotetragonal \( c \) domains (with polarization along [001]) separated from the pseudotetragonal \( a \) domains (with polarization along [100]) by 90° domain walls that are parallel to 101 in the cubic substrate. For this phase, the equilibrium spontaneous polarization \( (P_s) \) has the same magnitude within the \( c \) and \( a \) domains and is calculated as

\[ P_s^2 = -\frac{\alpha_{33}^{**}}{3\alpha_{111}} + \left( \frac{\alpha_{33}^{**} - \alpha_{33}^{**}}{3\alpha_{111}} \right)^{1/2} \]

where \( \alpha_{33}^{**} = \alpha_1 - (Q_{12}/s_{11})S_m \) and \( \alpha_{33}^{**} = \alpha_{11} + (Q_{12}/2s_{11}) \) are the renormalized GLD coefficients for \( c/a/c/a \) phase. The equilibrium fraction of the \( c \) phase in this structure is given by

\[ \phi_c = 1 - \frac{(s_{11} - s_{12})(S_m - Q_{12}P_s^2)}{s_{11}(Q_{11} - Q_{12}P_s^2)} \]

Similarly, in the positive misfit strain region, the monodomain \( aa \) phase breaks up into the polydomain \( a_1/a_2/a_1/a_2 \) phase with \( a_1 \) and \( a_2 \) domains having the same magnitude of polarization and volume fractions but with polarization along [100] and [010], respectively. The \( a_1 \) and \( a_2 \) domains are separated by domain walls parallel to 110 in the substrate as shown in Fig. 2.1. For this phase, we can calculate the equilibrium
spontaneous polarization within the domains as

$$P_s^2 = -\frac{\alpha_{11}^{**}}{3\alpha_{111}} + \left(\frac{\alpha_{111}^{**2}}{9\alpha_{111}^2} - \frac{\alpha_{11}^{**}}{3\alpha_{111}}\right)^{1/2}$$

where $\alpha_{11}^{**} = \alpha_1 - (Q_{11} + Q_{12})S_m/(s_{11} + s_{12})$ and $\alpha_{111}^{**} = \alpha_{11} + (Q_{11} + Q_{12})^2/[4(s_{11} + s_{12})]$. Near the morphotropic phase boundary, we observe a polydomain version of the monodomain $ca$ phase as $ca^*/aa*/ca^*/aa^*$ due a $P_2$ instability in thick films. This polydomain state can be understood as $c/a/c/a$ phase with a non-zero $P_2$ in both the $ca^*$ and $aa^*$ domains. In neighboring domains, the polarization component $P_2$ has the same magnitude and direction and the magnitude of polarization along the $c$ direction in the $ca^*$ domain is equal to that in the $aa^*$ domain along the $a_1$ direction (both equal to $P_s$) [Fig. 2.1]. For this phase, we can calculate the equilibrium volume fractions in terms of the polarization components in the $ca^*$ phase as

$$\phi_{ca^*} = \frac{(s_{11} - s_{12})S_m - (s_{12}Q_{12} - s_{11}Q_{11})P_3^2 + (s_{12}Q_{11} - s_{11}Q_{12})P_2^2}{s_{11}(Q_{11} - Q_{12})P_3^2}$$

The values of polarization ($P_2$ and $P_3$) were obtained by numerical minimization of the free energy. Further,
for compositions $x < 0.6$ and near zero strain, we also observe equilibrium polydomain phases due to a $P_3$ instability. They are termed $ca_1/ca_2/ca_1/ca_2$ and $r_1/r_2/r_1/r_2$ and these reduce the region of stability of the $c/a/c/a$ phase at such compositions. In these domain structures, the in-plane polarization components and domain fractions retain the characteristics of the parent $a_1/a_2/a_1/a_2$ or $aa_1/aa_2/aa_1/aa_2$ phase but they exhibit a non-zero out-of-plane polarization $P_3$. The polarization component in neighboring domains in these structures is related as $P_3' = -P_3''$. The in-plane and out-of-plane polarization components in the $ca_1/ca_2/ca_1/ca_2$ and $r_1/r_2/r_1/r_2$ structures were obtained by numerical minimization of the free energy. Thus, we obtain a complex domain stability map as a function of strain, composition and temperature as shown in Fig. 2.1. We observe that a large fraction of the phase diagram is occupied by the $c/a/c/a$ domain structure with $90^\circ$ domain walls separating the $c$ and $a$ domains and this is consistent with prior observations of such domain structures in tetragonal PZT thin films. This multi-component phase diagram results in a non-intuitive variation of the dielectric and pyroelectric susceptibilities as discussed below.

2.3 Pyroelectric and Dielectric Susceptibilities of PZT Films

2.3.1 Pyroelectric Susceptibility

The pyroelectric properties of a ferroelectric material under short-circuit conditions (i.e., $E = 0$) is comprised of three components: intrinsic, extrinsic, and secondary contributions. In general, the total pyroelectric coefficient is the sum of the pyroelectric coefficients at constant strain (intrinsic + extrinsic, sometimes called the primary pyroelectric effect) and the piezoelectric contribution from thermal expansion (secondary pyroelectric effect). The intrinsic contribution to the pyroelectric response arises from a temperature dependent change in the polarization in the bulk of a ferroelectric domain. The extrinsic contribution (or a domain wall contribution) to the pyroelectric response arises due to the temperature dependent movement of the domain walls in the polydomain states. Finally, the secondary contribution to the pyroelectric response arises from a piezoelectric contribution that results from thermal expansion. In thin-film samples, the secondary contribution is related to the difference in thermal expansion between the film and the substrate. Since pyroelectric measurements are usually performed at zero external electric fields, we can neglect the contribution of temperature dependent dielectric constant to the pyroelectric coefficient and the effect of leakage. To date, both the extrinsic and secondary contributions have generally been neglected in theoretical calculations but in the current treatment we systematically investigate the impact of all three contributions. We begin by investigating the primary pyroelectric effect before exploring the secondary pyroelectric effect for specific thin film heterostructures.
Figure 2.2: Dependence of the pyroelectric coefficient with epitaxial strain for PZT thin films with $x = (a) 1.0, (b) 0.9, (c) 0.8, (d) 0.7, (e) 0.6, and (f) 0.5$. The red line indicates the total pyroelectric coefficient (intrinsic + extrinsic) while the blue line shows the pyroelectric coefficient assuming pinned domain walls, i.e. zero extrinsic contribution.
Using the GLD model we have investigated the primary pyroelectric coefficient along the substrate normal \((\pi_3 = \frac{d(P_3)}{dT})\) of PZT as a function of composition \((x)\) and strain at room temperature (300 K) [Fig. 2.2 a-f]. At large compressive strains the monodomain \(c\) phase is the equilibrium phase at all compositions studied and the pyroelectric coefficient of the \(c\) phase can be obtained as

\[
\pi_3 = \frac{-\alpha_0}{4P_3\sqrt{\alpha_{33}^2 - 3\alpha_{111}\alpha_3^*}}
\]

where \(\alpha_{33}^* = \alpha_{11} - Q_{12}^2/(s_{11} + s_{12})\) and \(\alpha_3^* = \alpha_1 - 2S_m Q_{12}/(s_{11} + s_{12})\). The magnitude of the pyroelectric coefficient is observed to decrease with increasing compressive strain. This can be understood as resulting from an increase in \(T_c\) with increasing compressive strain which thereby progressively removes the enhancement that comes with proximity to \(T_c\). As the compressive strain is lowered, at a critical strain this monodomain \(c\) phase forms a polydomain \(c/a/c/a\) phase. Further variations in the strain result in the \(c/a/c/a\) phase transforming into either a \(a_1/a_2/a_1/a_2\) phase (for \(x > 0.62\)) or a \(ca^*/aa^*/ca^*/aa^*\) phase (for \(x < 0.62\)). Additionally, for \(x < 0.62\), the \(ca^*/aa^*/ca^*/aa^*\) phase transforms to the \(a_1/a_2/a_1/a_2\) phase through the polydomain \(r\) phase and the \(ca_1/ca_2/ca_1/ca_2\) phases [Fig. 2.2 a-f]. Among the polydomain phases, we observe that the \(c/a/c/a\) and \(ca^*/aa^*/ca^*/aa^*\) polydomains possess non-zero pyroelectric coefficients along the out-of-plane direction. For these domain structures, the average out-of-plane polarization is \(P_3 = \phi_c P_s\), where \(\phi_c\) is the fraction of domains with an out-of-plane polarization \(P_s\). The primary pyroelectric coefficient can be calculated as \(\pi_3 = \phi_c \frac{dP_s}{dT} + P_s \frac{d\phi_c}{dT}\). The first term represents the intrinsic pyroelectric response due to a temperature dependent change in the magnitude of the polarization within the domains. Since the equilibrium domain population \(\phi_c\) also depends on temperature, we have an extrinsic contribution to the primary pyroelectric coefficient as shown in the second term. Physically, this term arises due to the rotation of the polarization in the region swept by the domain wall as it moves under the influence of the changing temperature. The thermodynamic theory enables us to quantify this effect and calculate the intrinsic and extrinsic contribution individually. For the \(c/a/c/a\) phase, the extrinsic contribution can be calculated from the equilibrium domain fractions using

\[
\frac{d\phi_c}{dT} = \frac{2(s_{11} - s_{12})S_m}{s_{11}(Q_{11} - Q_{12})P_s^3} \frac{dP_s}{dT}
\]

For the compositions considered here, the sign of the extrinsic contribution for the \(c/a/c/a\) phase depends on the sign of \(S_m \frac{dP_s}{dT}\) only. Since \(\frac{dP_s}{dT}\) is always negative, the extrinsic pyroelectric coefficient is positive for compressive strains and negative for tensile strains. Therefore, the extrinsic contribution opposes the intrinsic effect for compressive strains and enhances the intrinsic effect for tensile strains in the \(c/a/c/a\) phase.
as shown in Figs. Fig. 2.2 a-f. Physically, this can be understood as follows: the c/a/c/a phase is confined by the c phase (with a larger $P_3$) in the compressive regime and the $a_1/a_2/a_1/a_2$ phase (with a lower $P_3$) in the tensile regime; therefore, the fraction of the c phase in the polydomain state shows opposing trends with temperature in the tensile and compressive regimes [Fig. 2.3]. With increasing temperature, the fraction of the c phase increases under compressive strains but decreases under tensile strains. The spontaneous polarization, however, decreases with temperature under both compressive and tensile strains. Thus, at compressive strains, $P_s$ decreases but the fraction $\phi_c$ increases and the two contributions oppose one another. Under tensile strains, $P_s$ decreases and the fraction $\phi_c$ also decreases, therefore the two effects support each other. In ferroelectric thin films, the out-of-plane polarization typically increases under compressive strain and decreases under tensile strain [54] so this effect of strain on the extrinsic pyroelectric coefficient in polydomain states is likely to be a general feature in ferroelectric thin films. From Fig. 2.2, it is clear that this extrinsic effect significantly alters the intrinsic pyroelectric response and, therefore, the pyroelectric coefficient can be significantly enhanced in tensile strained films. This analysis also serves to explain the giant pyroelectric effect observed in thick self-supported BaTiO$_3$ films at a critical elongation between 2-4% [62]. In that case, the authors noted that the large pyroelectric coefficient that was observed could not be attributed to the intrinsic or the dielectric contributions (due to a change in dielectric constant with temperature). It was surmised that the c–a domain switching mediated by 90° domain walls could be responsible for this observed effect, but no explanation was provided for the presence of a critical tensile strain or the actual mechanism involved. Our theoretical calculations present a mechanism for the observed effect and provide a physical basis for the presence of a critical tensile strain. A quantitative comparison with theory is, however, not possible here since the poled polycrystalline BaTiO$_3$ films were buckled and the exact value of the tensile strain under the electrical contacts (that corresponds to the 2-4% elongation) is difficult to estimate.

Further, in the case of PZT thin films, since the c/a/c/a phase persists into tensile strain only for Ti-rich compositions [Fig. 2.1], we see that the large pyroelectric coefficients are obtained for Ti-rich films at the boundary between the c/a/c/a and $a_1/a_2/a_1/a_2$ phases. At Ti compositions closer to the morphotropic phase boundary ($x<0.6$), the polydomain c/a/c/a persists only in the compressive regime and the domain wall effects result in a low pyroelectric coefficient. Instead of the c/a/c/a phase, near the morphotropic phase boundary, we observe the ca*/aa*/ca*/aa* phase with a non-zero $\pi_3$. For this phase, we can calculate the extrinsic contribution using temperature dependence of the volume fractions for this phase as

$$\frac{d\phi_c}{dT} = \frac{2(s_{11}-s_{12})S_m}{s_{11}(Q_{11}-Q_{12})P_3^2} \frac{dP_3}{dT} + \frac{2(s_{11}Q_{11}-s_{12}Q_{12})P_2}{s_{11}(Q_{12}-Q_{11})P_3^3} \left[ P_3 \frac{dP_2}{dT} - P_2 \frac{dP_3}{dT} \right]$$
where $P_2$, $P_3$ are polarization components in the $ca^*$ domain.

Upon a complete optimization of the pyroelectric coefficient with strain and composition [Fig. 2.4] a clear picture begins to emerge. We find that the room temperature (300 K) pyroelectric coefficient is maximum ($\pi_3 = -0.045 \, \mu\text{C/cm}^2\text{K}$) at a composition of $x = 0.62$ and a tensile strain of 0.1% corresponding to multicritical point at the boundary between five polydomain phases. Large pyroelectric coefficients exceeding $0.03 \, \mu\text{C/cm}^2\text{K}$ in magnitude can be obtained at the boundary between the $c/a/c/a$ and the $a_1/a_2/a_1/a_2$ phases at tensile strains over a wide range of composition in the Ti-rich region due to the additive contributions from intrinsic and extrinsic effects. This reveals the complexity of predicting the optimum value of pyroelectric coefficient in such systems and suggests that neither proximity to $T_c$ nor the magnitude of polarization alone provide enough information to completely maximize the pyroelectric coefficient. In reality, other factors such as strain driven polarization transitions and the susceptibility of domain walls to temperature can greatly impact the properties of these materials and in turn, dominate responses in epitaxial thin films. In fact, as shown in Fig. 2.2, the domain wall effects can dominate the intrinsic response and one needs to take into account domain wall displacements to completely understand and estimate the properties of ferroelectric films.

We note that this calculation assumes that the domain walls are free to move without any energy barriers. In reality lattice imperfections or defects can pin domain walls, hinder their movement, and reduce the extrinsic contribution. The extrinsic contribution to pyroelectric response will be zero in the case of completely pinned domain walls and our calculation, in effect, places an upper bound on the extrinsic
contribution to the pyroelectric properties. The energy barriers for the 90° domains considered here are much smaller than the 180° domain walls [63] and the 90° domain walls are expected to move quite freely at $T \geq 300$ K in epitaxial thin films. Since the extrinsic contribution reduces the total pyroelectric coefficient for compressively strained films, one could also increase the pyroelectric coefficient for compressively strained films using some form of nanoscale domain wall pinning (possible through focused ion-beam patterning of defects) or lowering the temperature, thereby rendering the domain walls immobile. Similarly, any form of domain pinning will serve to reduce the pyroelectric coefficients in tensile strained films.

Thus far, we have focused only on the primary pyroelectric coefficient in materials and have excluded secondary contributions. In a real system, temperature dependent changes in crystal shape will result in piezoelectric contributions to the pyroelectric response known as the secondary pyroelectric effect. For thin films, the substrate is usually considered to be a passive medium that influences the pyroelectric properties of the film through the epitaxial strain alone; however, the difference in thermal expansion between the substrate and the ferroelectric thin film can also influence the pyroelectric properties due the thermal strain from the mismatch. Again, this contribution is referred to as the secondary pyroelectric coefficient ($\pi_s$) and has generally been neglected since early estimates suggested that it should be considerably smaller than the primary effect in epitaxial thin films that are clamped in-plane to a thick substrate. In prior work, such secondary contributions have been estimated to play a minor role in the pyroelectric response of thin films.

Figure 2.4: Strain - composition phase diagram of PZT thin films showing the pyroelectric coefficient at 300 K for the various equilibrium polydomain states.
(<10% of the total response, except near the morphotropic phase boundary) [64]. Such models, however, have only investigated monodomain ferroelectric thin films. Here, we calculate the secondary contribution to the pyroelectric coefficient in polydomain films and show that it can enhance the primary pyroelectric effect. Since the polarization also depends on the strain due to the thermal expansion mismatch, we can write the secondary contribution as

$$\pi_s = (S_m - 1)(\alpha_f - \alpha_s) \left[ \phi_c \frac{\partial P_s}{\partial S_m} - P_s \frac{\partial \phi_c}{\partial S_m} \right]$$

where $\alpha_f$ and $\alpha_s$ are the thermal expansion coefficients of the film and the substrate, respectively and $\phi_c$ is the fraction of domains with an out-of-plane polarization $P_s$. This can be used to calculate the secondary contribution to the pyroelectric coefficient of polydomain thin films from the strain dependence of $P_s$ and $\phi_c$. We immediately see that the secondary pyroelectric coefficient depends on the thermal and mechanical properties of the substrate and an estimation of this contribution requires intimate knowledge of the substrate that is used to impart the strain. This is in stark contrast to the primary pyroelectric coefficient which depends only on the ferroelectric material. General guidelines towards optimizing the pyroelectric susceptibilities utilizing the secondary effects can be gleaned from the equation above. Since $S_m \ll 1$ and $P_s$, $\phi_c$ usually decrease with increasing strain, we can immediately see that the secondary effect adds to the intrinsic effect only if $\alpha_f < \alpha_s$. As a result, a substrate with larger thermal expansion coefficient than PZT is required to increase the intrinsic pyroelectric effects. Further, the sensitive strain dependence of $\phi_c$ [Fig. 2.2] leads us to believe that this could be a significant addition to the primary pyroelectric effects for polydomain thin films. We will consider this contribution in greater detail in Chapter 4 when we use specific substrates to impart the epitaxial strain in PZT thin films.

Thus, when attempting to analyze a large phase space in materials (i.e., the large strain and composition phase space undertaken here), it is reasonable to focus on the primary (intrinsic and extrinsic) pyroelectric effect to provide a strong foundation for the physics of the materials. Once research is focused on a specific film-substrate system, however, addition of the secondary effect will provide a more complete picture and accurate prediction of pyroelectric coefficients in such systems.

2.3.2 Dielectric Susceptibility

The GLD model discussed above was extended to finite electric fields to calculate the dielectric properties of PZT thin films. In order to keep the model analytically tractable, the dielectric properties of the PZT system was calculated for the Ti-rich region of the phase diagram with $x > 0.65$. For this region, the phase
diagram is comprised of three phases - the monodomain c phase and two polydomain phases - the c/a/c/a phase and a1/a2/a1/a2 phases. The free energy of the c phase is modified trivially in the presence of an electric field along the substrate normal (with an additional term equal to $-EP_3$) and the energy of the a1/a2/a1/a2 phase is unaffected. For the c/a/c/a phase, the volume fraction of the c phase is modified at finite electric fields as [54, 65]

$$\phi_c = 1 - \frac{(s_{11} - s_{12})(S_m - Q_{12}P_s^2)}{s_{11}(Q_{11} - Q_{12}P_s^2)} + \frac{E(s_{11}^2 - s_{12}^2)}{s_{11}(Q_{11} - Q_{12})^2P_s^2}$$

where $E$ is the magnitude of the electric field along the substrate normal and $P_s$ is the spontaneous polarization within the c domains of the polydomain phase such that the average polarization along the substrate normal $\langle P_3 \rangle = \phi_cP_s$. The out-of-plane polarization in the c domains in the c/a/c/a polydomain state was evaluated numerically from the resulting free energy. The energies of these three phases was compared at finite electric fields to obtain the equilibrium phase and dielectric susceptibilities. The out-of-plane dielectric permittivity ($\epsilon_{33}$) can be evaluated as

$$\epsilon_{33} = \frac{d\langle P_3 \rangle}{dE} = \phi_c\frac{dP_s}{dE} + P_s\frac{d\phi_c}{dE}$$

Therefore, the dielectric permittivity for the a1/a2/a1/a2 vanishes by definition. The first term above represents the intrinsic permittivity and the second term is the extrinsic contribution to the permittivity arising from the reversible displacement of the domain walls which changes the domain fractions. Further, it is clear that the monodomain c phase has a purely intrinsic contribution and no extrinsic contribution. The c/a/c/a phase, however, has an intrinsic and extrinsic response to the motion of the 90° domain walls. In the linear approximation (valid at low electric fields), neglecting the effect of small domain wall displacement on the polarization within the domains, we can calculate the extrinsic contribution to the permittivity in the c/a/c/a phase as

$$\epsilon_{ex} = \frac{(s_{11}^2 - s_{12}^2)}{s_{11}(Q_{11} - Q_{12})^2P_s^2}$$

Calculating the dielectric permittivity of PbZr$_{0.2}$Ti$_{0.8}$O$_3$ as a typical example of a PZT thin film in this range of composition (0.65 < x < 1.0), we find that the intrinsic permittivity [dashed line, Fig. 2.5] of the polydomain c/a/c/a state is < 100 and that the total permittivity [solid line, Fig. 2.5] (intrinsic plus extrinsic contributions) is expected to be enhanced to ~200. We observe that the extrinsic contributions from electric field induced 90° domain wall displacements result in a significant enhancement of the
dielectric permittivity in the polydomain c/a/c/a phase. Furthermore, the extrinsic contribution increases with increasing fraction of the a domains (and tensile strain) until the film transforms to the completely in-plane polarized a$_1$/a$_2$/a$_1$/a$_2$ state. Therefore, the maximum permittivity is obtained for Ti-rich PZT films at the polydomain transition to the a$_1$/a$_2$/a$_1$/a$_2$ phase at tensile strains - similar to the case for the pyroelectric coefficient discussed earlier. In contrast to the pyroelectric coefficient considered previously, the extrinsic contribution to the dielectric permittivity is always positive (i.e., it increases the intrinsic effect) and is independent of the sign of epitaxial strain. Furthermore, unlike the pyroelectric effect, there are no secondary contributions to the dielectric permittivity since the substrate are typically electrical insulators and are usually at constant temperature during dielectric measurements.

### 2.3.3 Electrocaloric Effects

Utilizing the polydomain GLD models developed thus far, we can also analyze the electrocaloric properties of PZT thin films. The electrocaloric effect refers to the change in temperature of a ferroelectric under adiabatic conditions in response to an applied electric field [2, 66]. Since the spontaneous polarization in a ferroelectric is temperature dependent, an electric field that influences ferroelectric ordering can cause a change in temperature by raising or lowering the entropy associated with the order parameter. Early studies of this effect focused on bulk or single crystal materials where very high voltages (> 500 V) were required.
to achieve modest temperature changes of 1-2 K [66, 67]. Recent studies, however, suggest that thin film ferroelectrics can possess superior electrocaloric performance because it is possible to achieve large electric fields (using considerably lower voltages) while taking advantage of the enhanced breakdown strength of thin film specimens.

It has been shown in the previous two sections that the presence of domain walls can significantly affect the dielectric and pyroelectric properties. It is thus important to understand the effect of domain structures on the electrocaloric properties since the presence of large electric fields during this process can further enhance domain wall mobility. We utilize the polydomain GLD formalism developed in Section 2.2 to investigate the electrocaloric properties of polydomain PZT thin films. For Ti-rich PZT (0.65 < x < 1) thin films at 300 K and for the range of electric fields investigated here (10 kV/cm < E < 1000 kV/cm), the equilibrium domain structure can possess any of three different phases as a function of strain and composition: one monodomain (c phase) and two polydomain (c/a/c/a and a1/a2/a1/a2) phases.

The electrocaloric and pyroelectric coefficients of a ferroelectric material are related by a Maxwell’s relations as [66]

\[ \left( \frac{\partial S}{\partial E} \right)_T = \left( \frac{\partial P}{\partial T} \right)_E \]

Therefore electrocaloric change in temperature upon application of an electric field can thus be calculated using the pyroelectric coefficient at finite electric fields as [68–70]

\[ \Delta T = -T \int_{E_a}^{E_b} \frac{1}{C_E(T, E)} \left( \frac{\partial P}{\partial T} \right)_E dE \]

where \( C_E(T, E) \) is the heat capacity per unit volume at constant electric field, \( \left( \frac{\partial P}{\partial T} \right)_E \) is the pyroelectric coefficient of the ferroelectric, and \( \Delta E = E_b - E_a \) (\( E_a = 10 \text{kV/cm throughout this section} \)) is the range of the applied electric field. In the temperature range of interest (300-550 K), the absolute value of the heat capacity is approximately constant across composition for Ti-rich films at 2.7x10^6 J/m^3K [68]. Since the peak in the heat capacity associated with the polarization transition is \( \sim 10\% \) of the background [68,69], we neglect the contribution of the polarization to the heat capacity in our calculations.

Among the three stable phases, the c phase and the c/a/c/a phase possess a finite electrocaloric temperature change for applied fields along [001]. The a1/a2/a1/a2 phase has a vanishing electrocaloric response due to zero polarization along the substrate normal. In contrast to monodomain 1D GLD models which have been used in prior theoretical studies and suggest an increasing electrocaloric performance with increasing tensile strain (due to a reduced ferroelectric transition temperature), in a polydomain system the transition to an in-plane polarized state completely negates the effect of any electric field in the out-of-plane direction.
Figure 2.6: Dependence of the electrocaloric temperature change ($\Delta T$) with epitaxial strain for PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films with $\Delta E = 100$ kV/cm at 300 K. The solid line indicates the total $\Delta T$ (intrinsic + extrinsic) while the dotted line shows $\Delta T$ assuming zero extrinsic contribution.

for films with large tensile strains. Thereby reducing the electric field induced temperature change to zero.

In order to calculate the electrocaloric temperature change in response to the applied electric fields we calculated the pyroelectric susceptibilities as shown in Section 2.2. Similar to the dielectric and pyroelectric properties, we see that the electrocaloric effect has an extrinsic contribution due to electric field induced domain wall displacements in polydomain PZT thin films. Using such a GLD model, we have investigated the adiabatic temperature change for a PbZr$_{0.2}$Ti$_{0.8}$O$_3$ film with $\Delta E = 100$ kV/cm (2 V drop across a 200 nm thick film) at 300 K [Fig. 2.6] as a typical example. As shown in the figure, when excluding the effect of domain walls, the intrinsic electrocaloric effect is maximized at mild compressive strains corresponding to the monodomain ($c$) to polydomain ($c/a/c/a$) transition. Including the effects of temperature and electric field on the motion of domain walls in the models, shifts the maximum response to a critical tensile strain that corresponds to the disappearance of the out-of-plane polarization (i.e., the boundary between $c/a/c/a$ and $a_1/a_2/a_1/a_2$ phases). We observe that the extrinsic effects are observed to significantly alter the total electrocaloric response and in general, the extrinsic contribution adds to and subtracts from the intrinsic electrocaloric effect at mild tensile and compressive strains respectively, similar to the pyroelectric effects discussed in Section 3.2.1.

Upon a complete optimization of the electrocaloric response including the extrinsic effects for $0.65 <$
Figure 2.7: Electrocaloric temperature change as a function of strain and composition for the PZT thin film system for \( 0.65 < x < 1.0 \) at 300 K for the various equilibrium polydomain states with \( \Delta E = 100 \text{kV/cm} \).

\( x < 1 \), a complete picture of the electrocaloric properties emerges [Fig. 2.7]. The electrocaloric temperature change is seen to be high along the two polarization phase transitions due to the large pyroelectric coefficients corresponding to these transitions. The maximum electrocaloric effect is obtained along the phase boundary between the \( c/a/c/a \) and \( a_1/a_2/a_1/a_2 \) phases at small tensile strains. The maximum \( \Delta T \) for \( \Delta E = 100 \text{kV/cm} \) at 300 K is \( \Delta T = 0.36 \text{K} \) at \( x = 0.73 \). With high electric fields corresponding to \( \Delta E = 1000 \text{kV/cm} \) (20 V drop across a 200 nm thick film), adiabatic temperature changes as large as \( \Delta T = 2.9 \text{K} \) can be obtained at 300 K in PZT films with \( x = 0.73 \) and \( S_m = 0.3\% \). This is can be further improved by moving slightly closer to the ferroelectric transition temperature of PZT. At a temperature of 500 K a temperature change of \( \sim 6 \text{K} \) can be obtained in a \( \text{PbZr}_{0.27}\text{Ti}_{0.73}\text{O}_3 \) thin film at an applied field of \( \sim 1000 \text{kV/cm} \) [Fig. 2.8]. This temperature is still significantly less than the Curie temperature of this composition of PZT at this electric field, therefore the ferroelectric breakdown strength should be high and such temperature changes feasible. Thus, large electrocaloric responses can be obtained at temperatures much below the Curie temperature by harnessing extrinsic contributions to the electrocaloric effect.

As noted in Section 3.2.1, the pyroelectric properties of thin films are also modified by secondary effects due to thermal expansion mismatch the film and the substrate. Once a suitable substrate has been chosen
to impart the tensile epitaxial strain, one can obtain more reliable estimates of the electrocaloric effects by including the secondary effects. Consequently, we can also maximize the electrocaloric temperature change by choosing a substrate with a larger thermal expansion coefficient than PZT to increase the secondary pyroelectric effects. Large electrocaloric effects have been observed in ferroelectric thin films but operating in close proximity to the Curie temperature under the large applied electric fields necessary for such effects is technically difficult in films. This study shows another pathway, in which by leveraging extrinsic factors such as domain wall displacement in ferroelectric thin films one can significantly alter the intrinsic response and obtain large electrocaloric responses in strain engineered epitaxial thin films at $T \ll T_c$. This should provide experimentalists with a new mechanism to engineer ferroelectric thin films with the excellent electrocaloric properties at any desired temperature.

### 2.4 Conclusions

In this Chapter, we have developed a phenomenological GLD model to study the dielectric and pyroelectric susceptibilities of polydomain PZT thin films as a function of epitaxial strain, temperature, and composition. We have shown, that apart from the intrinsic dielectric and pyroelectric responses, thin films with complex domain structures also have an extrinsic contribution to these susceptibilities. This is due to the
electric field or temperature induced movement of domain walls and can be a significant contribution to the intrinsic response of thin films. Further, since pyroelectric susceptibilities involve temperature changes in the ferroelectric film and the substrate, differences in thermal expansion between them can result in a secondary contribution to the pyroelectric properties of thin films. Through a careful optimization of the dielectric and pyroelectric responses, we have shown that large susceptibilities can be obtained at room temperature in Ti-rich thin films under tensile strain due the large density of 90° domain walls. These GLD studies give an invaluable insight into the evolution of these properties in polydomain ferroelectric thin films and provide a sound theoretical platform for a systematic experimental optimization of the dielectric and pyroelectric susceptibilities in tetragonal ferroelectric thin films.
Chapter 3

Growth and Characterization of

Epitaxial PbZr$_{0.2}$Ti$_{0.8}$O$_3$ Thin Films

In the previous Chapter, the dielectric and pyroelectric susceptibilities of tetragonal ferroelectric materials exhibiting complex polydomain structures were investigated for the PZT system using a phenomenological GLD formalism. It was demonstrated that large responses can be obtained at room temperature in Ti-rich thin films at tensile strains due to extrinsic contributions from 90° domain wall displacements and secondary contributions from thermal expansion mismatch with the substrate. In order to explore this experimentally, PbZr$_{0.2}$Ti$_{0.8}$O$_3$ was chosen as a model system for the electrical characterization. In this Chapter, we present a detailed report on the growth of epitaxial PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films via pulsed-laser deposition on a variety of single crystal oxide substrates and a characterization of their crystal and ferroelectric domain structures using a combination of x-ray diffraction, atomic force microscopy, and piezoresponse force microscopy. We show that the evolution of ferroelectric domain structures in epitaxial PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films as a function of epitaxial strain is in agreement with the predictions of the GLD model and PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thus serves as an excellent model system to study the effect of 90° domain walls on ferroelectric susceptibilities.
3.1 Growth of Epitaxial PbZr$_{0.2}$Ti$_{0.8}$O$_3$ Thin Films

PbZr$_{0.2}$Ti$_{0.8}$O$_3$ is a prototypical member of the tetragonal PZT ferroelectric family with lattice constants (at 300 K) of $a = 3.94 \text{ Å}$ and $c = 4.12 \text{ Å}$ [27, 28]. It has been used extensively for a variety of applications such as ferroelectric memories, piezoelectric actuators, and electro-optic devices [7, 9]. This is primarily due to its high Curie temperature ($\sim 420^\circ\text{C}$) and a robust spontaneous polarization at room temperature ($P_s \sim 65 - 70 \mu\text{C/cm}^2$). In thin-film form, the lattice constants of PbZr$_{0.2}$Ti$_{0.8}$O$_3$ make it particularly attractive for an experimental study as it enables convenient growth of predominantly $c$ axis oriented thin films with a strain in the range of 1% using commercially available oxide single crystal substrates [12, 71]. Since epitaxial strain has been shown to tune the domain structure and the ferroelectric properties of the PZT thin films in Chapter 2, PbZr$_{0.2}$Ti$_{0.8}$O$_3$ presents a convenient model system. Epitaxial thin films utilized in this work were deposited by PLD.

![Figure 3.1: Schematic of the pulsed-laser deposition system used for the deposition of complex oxide heterostructures used in this study.](image)

PLD has gained widespread popularity in the past decade for the deposition of complex oxide materials such as PZT due to its high throughput and the high-quality of the resulting thin films and heterostructures. The schematic of the PLD process utilized for the growth of PbZr$_{0.2}$Ti$_{0.8}$O$_3$ is shown in Fig. 3.1. In this technique, thin films are deposited by the ablation of a target with the desired composition using an UV ($\lambda = 248 \text{ nm}$) laser with a pulse width of 10-50 ns and an energy of 50 - 100 mJ resulting in a power of $\sim 10^7 \text{ W}$. 

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The intense power of the laser pulse produces a plasma plume that is directed towards a hot substrate on which the material is deposited. The deposition occurs in an oxidizing atmosphere (with a partial pressure of 1 - 500 mTorr oxygen) at temperatures ranging from 400 - 800 °C. Control of the film composition, growth rate, and morphology is achieved by controlling the energy density of the pulse, the pulse repetition rate, oxygen pressure, and growth temperature. Following growth, the samples are cooled at 5-10°C/min. to room temperature in 1 atm of oxygen to achieve complete oxidation of the thin films and prevent the formation of oxygen vacancies. Details of the PLD growth process including the growth conditions utilized in this work are described in Appendix A.

In order to measure the ferroelectric properties of the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films, an epitaxial bottom electrode that can be deposited in-situ prior to the deposition of the ferroelectric layer is necessary. In this study, SrRuO$_3$ was used as a lattice matched bottom electrode for the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ layer. SrRuO$_3$ is an oxide metal with orthorhombic unit cell and an in-plane pseudocubic lattice constant of 3.93 Å [32]. Due to the excellent structural compatibility with PbZr$_{0.2}$Ti$_{0.8}$O$_3$ and the substrates, thin layers of SrRuO$_3$ (20-30 nm thick) served as lattice matched bottom electrodes. In this range of thickness, SrRuO$_3$ can be grown in a coherently strained fashion within a 1% strain regime investigated here [72]. The use of oxide metals such as SrRuO$_3$ is also desirable due to its excellent chemical compatibility with PZT which enables space charge free interfaces and excellent ferroelectric properties including large switchable polarization and superior fatigue endurance [31–33, 35, 36, 44, 73]. In order to obtain robust ferroelectric properties and to accurately measure the susceptibilities, it is also desirable to have an epitaxial top electrode of SrRuO$_3$ for the ferroelectric capacitor structures. Patterning epitaxial top electrodes is a significant challenge facing the ferroelectrics community and this issue will be considered in greater detail in the next Chapter when we discuss the ferroelectric properties of the strained PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films.

In order to tune the ferroelectric domain structures with the substrate induced epitaxial strain, the PbZr$_{0.2}$Ti$_{0.8}$O$_3$/SrRuO$_3$ heterostructures were fabricated on SrTiO$_3$ (001), DyScO$_3$ (110), TbScO$_3$ (110), and GdScO$_3$ (110) single crystal substrates (Crystec GmbH, Berlin). The chosen substrates provide lattice mismatches with the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ of -0.8%, 0.3%, 0.7%, and 0.9% for SrTiO$_3$, DyScO$_3$, TbScO$_3$, and GdScO$_3$, respectively, and enable us to probe the region with the increased dielectric and pyroelectric responses as predicted by GLD theory.

The heterostructures used in this study were fabricated by depositing a 20 nm thin layer of SrRuO$_3$ as the bottom electrode on the substrate at 635°C in 100 mTorr of oxygen. A laser fluence of 1-1.2 J/cm$^2$ at a repetition rate of 10-14 Hz was used for the growth of the SrRuO$_3$ layer. Following the growth of SrRuO$_3$, the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ layer of thickness 150 nm was deposited at 635°C in 200 mTorr of oxygen. For PbZr$_{0.2}$Ti$_{0.8}$O$_3$,
a laser fluence of 1.2-1.4 J/cm² and a repetition rate of 3 Hz was used. The PbZr₀.₂Ti₀.₈O₃ targets were fabricated with 10% excess lead to compensate for the Pb loss, if any, during the growth. A growth rate of ~9 nm/min. for SrRuO₃ and 3.5 nm/min. for PbZr₀.₂Ti₀.₈O₃ were typically obtained. Following growth, the films were cooled to room temperature at 5°C/min. in 700 Torr of oxygen and characterized using a variety of techniques such as atomic force microscopy, x-ray diffraction (XRD), and piezoresponse force microscopy (PFM) prior to the deposition of top electrodes for the dielectric and pyroelectric characterization. In the rest of this Chapter, we will discuss the characterization of the structure and ferroelectric domains in the strained thin films.

3.2 Structural Characterization of PbZr₀.₂Ti₀.₈O₃ Thin Films

Detailed XRD θ – 2θ scans of the heterostructures reveal single-phase (00l)-oriented thin films on all four substrates [Fig. 3.2 a]. Off-axis reciprocal space maps (RSMs) about the 103-pseudocubic diffraction condition were performed to investigate the in-plane epitaxial relationship between the film and the substrate and they revealed that the c domain portions of the heterostructures are coherently strained to the un-
underlying substrate in all cases [Fig. 3.2 b-e]. The GLD models predict that the fraction of \(a\) domains will increase with increasing tensile strain and this increase in the fraction of \(a\) domains was observed in the XRD studies. Since the \(a\) domains are tilted away from the substrate normal, specular rocking curves about the 200 diffraction condition [Fig. 3.3 a] revealed the presence of these tilted \(a\) domains and the intensity of the 200 peaks (indicative of the fraction of \(a\) domains) increased from SrTiO\(_3\) to GdScO\(_3\) as predicted from theory. The RSM studies of the 002-diffraction peaks of all films also revealed peaks corresponding to the tilted \(a\) domains (tilted at \(\sim 2^\circ\)) [Fig. 3.3 b-e]. This increase in the fraction of \(a\) domains (\(\phi_a\)) was quantified using the XRD rocking curves by using the integrated intensity of under the 200 and 002 peaks as [74] \(\phi_a = I_{200}/(I_{002} + I_{200})\) where \(I_{200}\) represents the sum of integrated rocking curve intensities of the four 200-reflections and \(I_{002}\) is the integrated rocking curve intensity of the 002-reflection [Table 3.1].

3.3 Ferroelectric Domain Structures of PbZr\(_{0.2}\)Ti\(_{0.8}\)O\(_3\) Thin Films

Atomic force microscopy (AFM) of as-grown films revealed smooth surfaces on all four substrates with rms roughness < 0.5 nm [Fig. 3.4 a-d]. The presence of \(a\) domains was also observable in the AFM images as
Figure 3.4: AFM images of 150 nm PbZr$_{0.2}$Ti$_{0.8}$O$_3$/ 20 nm SrRuO$_3$ films grown on (1a) SrTiO$_3$ (001), (b) DyScO$_3$ (110), (c) TbScO$_3$ (110), and (d) GdScO$_3$ (110) substrates. Vertical (amplitude) piezoresponse force microscopy images of heterostructures grown on (e) SrTiO$_3$ (001), (f) DyScO$_3$ (110), (g) TbScO$_3$ (110), and (h) GdScO$_3$ (110).

regular twinned patterns representative of tilted $a$ domains and these features were particularly prominent on TbScO$_3$ and GdScO$_3$ substrates with a high density of 90° domain walls. In order to probe the evolution of the $a$ domains, PFM studies were performed on all four substrates [Fig. 3.4 e-h]. Typical vertical PFM images (amplitude) reveal clear contrast contrast between the $c$ and $a$ domains. From these and numerous other PFM images, we have extracted measures of the average domain spacing ($D$) [Table 3.1]. Accurate values of the domain fractions were obtained from the areal fractions in the vertical PFM images where the contrast between the $c$ and $a$ domains is clearly visible and the PFM images were particularly useful in obtaining domain fractions on TbScO$_3$ and GdScO$_3$ where a large number of vertical PFM images with the appropriate contrast could be obtained in a reasonable scan size (5 - 10 um). For these two substrates, the XRD estimate from the area under the rocking curves was less accurate in determining the volume fractions due to satellite reflections around the 002 rocking curve, possibly due to the regular periodicity of the $c$ domains at the nanoscale. It should be emphasized that no evidence of 180° domain walls were found in the PFM investigation of the as-grown heterostructures. This is consistent with prior observation of a preferential out-of-plane polarization direction in ferroelectric thin films with SrRuO$_3$ as the bottom electrode [75, 76].

The observations of the XRD and PFM studies are summarized in Table 3.1. We see that as we move from
Table 3.1: Fraction of $a$ domains ($\phi_a$) and domain periodicity ($D$) as measured for film grown on various substrates. The numbers in parentheses represent the standard deviation from measurements.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\phi_a$(%)</th>
<th>$D$ [$\sigma_D$] (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTiO$_3$(001)</td>
<td>4.2</td>
<td>3.02 [0.55]</td>
</tr>
<tr>
<td>DyScO$_3$(110)</td>
<td>9.3</td>
<td>2.72 [1.37]</td>
</tr>
<tr>
<td>TbScO$_3$(110)</td>
<td>11.2</td>
<td>1.80 [1.04]</td>
</tr>
<tr>
<td>GdScO$_3$(110)</td>
<td>20.2</td>
<td>0.59 [0.44]</td>
</tr>
</tbody>
</table>

The compressively strained SrTiO$_3$ (-0.8%) to the tensile strained GdScO$_3$ (0.9%) we increase the fraction of inplane oriented $a$ domains from $\sim$ 4% to $\sim$20%. This is accompanied by a reduction in the average domain periodicity size from $\sim$ 3 µm to $\sim$ 0.6 µm.

We note that the $\phi_a$ observed experimentally deviates slightly from those predicted by the polydomain GLD model which predicts the onset of the $a_1/a_2/a_1/a_2$ domain structure for films grown on GdScO$_3$. This is likely due to the simplifying assumptions applied in the polydomain GLD model and to the finite thickness of our films. Phase-field models, which account for inter-domain electrostatic interactions and make no $a$ priori assumptions about the domain structure, predict a transition to the fully in-plane oriented $a_1/a_2/a_1/a_2$ state at larger tensile strains than the current models [55,77]. Further, the lack of complete local charge compensation at the domain walls could lead to an increased stability of the $c$ domains [77]. Charge compensation mechanisms are dependent on the processing conditions thus it is unreasonable to expect theoretical models to exactly predict the experimentally observed strain-dependence. It is also possible that thermal expansion mismatch between the film and the substrate could influence the distribution of the domains as they form during the cool-down after the growth of the film in the paraelectric state. $\phi_a$ is also a function of the film thickness and it is expected to increase with increasing thickness, but we have focused here on 150 nm thick films in order to maintain coherently strained $c$ domains in the films. However, the trends predicted by the GLD model (i.e., variation of domain structure with strain) are indeed accurate. Since we can directly measure $\phi_a$ and $D$ we can relate the effect of domain structure on physical properties (such as spontaneous polarization and ferroelectric susceptibilities) without any $a$ priori assumptions about the domain distributions.
3.4 Conclusions

In this Chapter, we have shown that high quality epitaxial thin films of PbZr$_{0.2}$Ti$_{0.8}$O$_3$ can be synthesized via PLD on a variety of single crystal oxide substrates in the range of epitaxial strain of 1% with lattice matched SrRuO$_3$ as a bottom electrode. XRD and PFM investigations of the as-grown thin films reveal that the fraction of in-plane oriented $a$ domains and the density of 90° domain walls increase with increasing tensile strain as predicted by GLD theory. These films serve as model systems to investigate the extrinsic and secondary contributions to dielectric and pyroelectric susceptibilities which will be undertaken in the next Chapter.
Chapter 4

Ferroelectric Properties of Strained

$\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ Thin Films

In the previous Chapter, the growth of $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ thin films via pulsed-laser deposition and the characterization of their crystal structure and ferroelectric domains were discussed in detail. In order to tune the density of $90^\circ$ domain walls, $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ thin films were grown on four single crystal oxide substrates - $\text{SrTiO}_3$ (001), $\text{DyScO}_3$ (110), $\text{TbScO}_3$ (110), and $\text{GdScO}_3$ (110) which impart epitaxial strains of -0.8%, 0.3%, 0.7%, and 0.9% respectively. The as-grown films were found to be single phase (00l) oriented through XRD $\theta - 2\theta$ scans and they revealed smooth surfaces with < 0.5 nm rms roughness in AFM. The XRD and PFM characterization showed that the fraction of $a$ domains increased from $\sim$ 4% on the compressively strained $\text{SrTiO}_3$ to $\sim$ 20% on the tensile strained $\text{GdScO}_3$. In this Chapter, we present a detailed report of the ferroelectric properties of the strained $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ thin films including polarization hysteresis, leakage, fatigue, and ferroelectric susceptibilities (dielectric and pyroelectric). After a brief introduction to the fabrication of the epitaxial ferroelectric capacitors required for this study, we show the ferroelectric characteristics of strained $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ heterostructures. Finally, we report on experimental measurements of the dielectric and pyroelectric susceptibilities and compare the results to the predictions of the GLD model from Chapter 2.
4.1 Fabrication and Ferroelectric Characterization of Epitaxial PbZr$_{0.2}$Ti$_{0.8}$O$_3$ Capacitors

The combination of excellent thermal stability, mechanical toughness, radiation hardness, and electrical properties (e.g., fast switching speeds, low power consumption, and high permittivity) has made ferroelectric materials candidates for a variety of applications [7, 12, 13, 78]. A number of scientific and technological challenges including electrical characteristics such as fatigue, retention, and imprint have had to be addressed to enable such advances [34]. These effects have been shown to be dominated by defects (especially oxygen vacancies) and exacerbated by the choice of electrodes [31,33,34]. As we look to make ferroelectric materials with improved susceptibilities and integrate functional oxide materials such as ferroelectrics into electronic devices, it will be necessary to improve both contact materials and the processes by which we define them.

Certain electrodes are also known to reduce the permittivity and remnant polarization and increase the coercive field due to the appearance of a dead layer at the metal-ferroelectric interface [31,35,36,44]. While the intrinsic critical thickness for the occurrence of ferroelectricity is just a few unit cells (< 5 nm) [35,79,80] the lack of perfect charge compensation in some metal electrodes often increases the practical usable thickness. A large number of experimental and theoretical studies have shown that oxide metals perform significantly better than elemental metals as contacts due to their structural and chemical compatibility [31–33,35,36,44,73]. Such oxide metals improve fatigue and retention, can help to minimize imprint [32], prevent the formation of ferroelectric dead layers, and result in large permittivity and remnant polarization even in ultrathin ferroelectric layers [35,36,44]. For the present study, in particular, oxide electrodes are essential to reliably measure the susceptibilities and correlate the effect of epitaxial strain and domain structures on the ferroelectric properties.

At the same time, the use of ferroelectrics at high temperature and reliable measurements of the temperature dependent properties such as pyroelectric coefficients have also been severely restricted by the lack of high-temperature compatible electrodes and contact-based experimental measurements of ferroelectric thin film properties at temperatures above room temperature are therefore rarely reported. Increased leakage, diminished chemical stability, and poor adhesion of electrodes at elevated temperatures has made this difficult. Furthermore, electrode asymmetry has also been shown to affect temperature dependent properties adversely [81]. As a result, researchers have focused on non-contact techniques (e.g., second harmonic generation [22,82] and XRD) to probe temperature dependent properties of thin films, but quantitative measures of ferroelectric properties are hard to obtain with these techniques. Thus, the practical utility of ferroelectric materials is, in many cases, limited by the electrodes used to contact them and the intrin-
sic properties of ferroelectrics can be completely obscured by the extraneous effects originating from the metal-ferroelectric interface [31, 36]. Therefore, the fabrication of capacitor structures with nearly ideal metal-ferroelectric interfaces is crucial for optimizing the performance of ferroelectrics, extending their temperature of operation, reliably measuring ferroelectric properties, and in obtaining fundamental insights into their structure-property relationships.

4.1.1 Fabrication of Epitaxial Top Electrodes

To create fully epitaxial capacitor device structures, we have developed a process that differs considerably from traditional techniques. In prior work, following the growth of an oxide metal bottom electrode and ferroelectric layer, elemental or oxide metal top electrodes are typically deposited at room temperature through a standard photoresist mask, unwanted material is removed via lift-off, and, in some cases, the capacitor structure is post-annealed. Even in capacitors with the same top and bottom electrode material, the resulting contacts are not identical. In some cases, a tri-layer stack is grown in-situ and top contacts have been defined by ion-milling [36]. Ion-milling however, can induce mechanical damage and over-milling is difficult to avoid due to the lack of chemical selectivity. High temperature metal oxide deposition through a shadow mask has also been explored [83] but shadow masks suffer from large feature sizes and poor registry. Thus, existing methods for defining top electrodes are not adequate for fabricating epitaxial metal-ferroelectric-metal structures for advanced applications. A lithography based technique would be ideal, but defining features with photoresist prevents further epitaxial growth due to the poor high-temperature stability of photoresists. In this work, we use a novel MgO hard-mask process to fabricate epitaxial all-oxide heterostructures and utilize this process to make nearly ideal, symmetric capacitor structures with excellent ferroelectric properties and high-temperature stability.

The new process is described in Fig. 4.1. Following the growth of the PbZr$_{0.2}$Ti$_{0.8}$O$_3$/SrRuO$_3$ heterostructures, we spin coat photoresist and expose/develop the inverse of the desired final device pattern. Then a 200 nm layer of amorphous MgO is deposited at room temperature by e-beam evaporation. The unwanted photoresist and MgO are lifted off in acetone. The remaining MgO layer serves as the hard mask for the subsequent deposition of the epitaxial top SrRuO$_3$ electrode in the desired pattern since MgO is high-temperature compatible. Before proceeding to the high-temperature deposition of the top oxide metal, we perform an oxygen-plasma cleaning step to remove any remaining photoresist residue on the surface of the ferroelectric layer. The MgO hard mask/PbZr$_{0.2}$Ti$_{0.8}$O$_3$/SrRuO$_3$ heterostructure is then pumped to a base pressure of $\sim 10^{-6}$ Torr, the chamber is filled to 760 Torr of oxygen, and the sample is heated to a deposition temperature of 500-600$^\circ$C. Before deposition, the chamber is quickly evacuated to a growth pressure of
100 mTorr and 80 nm of SrRuO$_3$ is deposited. Following growth, films are cooled to room temperature at an oxygen pressure of 700 Torr.

After growth, the SrRuO$_3$ is lifted off by etching the MgO in a 15% solution of phosphoric acid. The phosphoric acid etches the MgO at a rapid rate (~7.5 nm/sec.) [Fig. 4.1 b], but does not appear to impact the other oxides (etching rates for PbZr$_{0.2}$Ti$_{0.8}$O$_3$ and SrRuO$_3$ are measured to be < 0.1 nm/sec.). Using this technique and traditional optical lithography, features down to 5 µm in lateral dimension have been fabricated. The process also results in well defined, abrupt edges [Fig. 4.1 c]. Thus far we have been limited by the temperature of decomposition of the ferroelectric layer and not by that of the hard-mask. We have investigated the stability and etchability of the MgO after higher temperature treatments and have found that even after annealing the MgO features at 1200°C for 1 hour [Fig. 4.2] we observe similar etch rates for the MgO. Work to date suggests that the MgO process described here is compatible with any modern
nanolithography process and thus, we anticipate this process could be extended to smaller feature sizes with ease. The ultimate minimum feature sizes will be dependent not on the MgO process, but on the minimum feature size achievable by the given patterning technique. The MgO process described herein can be thought to be complementary to the recent use of anodic aluminum oxide (AAO) masks used to fabricate nano-features of ferroelectrics at high temperature [84] and subsequent use of AAO and electron-beam lithography/lift-off techniques to define nanoscale top-contacts for ferroelectrics [85]. The current approach provides addition high-temperature stability for the fabrication of epitaxial oxide contacts and since it does not rely on the AAO process, it allows for the generation of arbitrary shapes and feature sizes. We anticipate that this process can be widely applicable in other exciting oxide systems too, such as colossal magnetoresistive oxides, high-temperature superconductors, and in the study of novel properties of oxide interfaces across a wide range of length scales and temperatures.

### 4.1.2 Ferroelectric Properties of Epitaxial Ferroelectric Capacitors

We have investigated the ferroelectric properties of the capacitor structures fabricated using the MgO process using a wide range of techniques. To demonstrate the importance of top contacts in controlling the ferroelectric properties, we have created four different ferroelectric capacitors for comparison using the same PbZr_{0.2}Ti_{0.8}O_{3}/SrRuO_{3}/DyScO_{3} (110) heterostructure but different top electrodes. We have used the film on DyScO_{3} as a representative ferroelectric sample to compare the effect of top electrodes and in turn, we have investigated the following top contacts: 1) 100 nm Au / 5 nm Cr, 2) 100 nm Pt / 5 nm Cr, 3) room-temperature deposited 100 nm Pt / 80 nm SrRuO_{3} followed by annealing at 600°C for 30 minutes in oxygen, and 4) high-temperature deposited 80 nm SrRuO_{3} electrodes using the MgO hard-mask process described above. Ferroelectric polarization hysteresis loops measured on these samples [Fig. 4.3a] reveal that while
elemental metal contacts exhibit hysteresis loops dominated by leakage, hysteresis loops improve significantly with the annealed Pt/SrRuO$_3$ contacts. The capacitors fabricated with epitaxial SrRuO$_3$ electrodes, however, exhibit the best performance with symmetric and square loops.

The effect of the various electrodes on the current-voltage and leakage characteristics of the capacitors was also studied [Fig. 4.3 b]. The metal-ferroelectric-metal structure can be understood as back-to-back Schottky diodes (with a Schottky barrier at each ferroelectric-metal interface) [81, 83] and at any applied voltage the Schottky diode that is under reverse-bias will dominate the leakage characteristics. Here, the bottom electrode was fixed at ground and the drive voltage was applied to the top electrode. Thus, for positive and negative voltages, the bottom and top interfaces dominate the leakage characteristics, respectively. Since the
bottom electrode is essentially identical for all samples, the leakage current at positive voltages is expected
to be similar. For negative voltages, however, the leakage is dominated by the top electrode interface with
transition metals such as Cr (with a low work function and high electronegativity) exhibiting a poor rectifying
contact [83] that gives rise to asymmetric leakage characteristics and lossy hysteresis loops. Noble metals
such as Au and Pt should give rise to better electrical performance but exhibit poor adhesion without an
adhesion layer of Cr, Ti, etc. The SrRuO$_3$ electrodes dramatically reduce the leakage and imprint due to
the higher work function (4.5-5 eV) [86] and the chemical compatibility of the interface.

We have also investigated the room-temperature ferroelectric response of the capacitors with epitaxial
SrRuO$_3$ electrodes between 1 and 2x10$^4$ Hz [Fig. 4.3 c]. Generally, low frequency hysteresis loops are difficult
to measure due to the dominance of leakage currents and one usually resorts to high frequencies (>1 kHz)
to measure reliable loops. This has made the frequency-dependent study of ferroelectric properties difficult,
especially for undoped PbZr$_{0.2}$Ti$_{0.8}$O$_3$ films. The combination of high-quality PbZr$_{0.2}$Ti$_{0.8}$O$_3$ films and
symmetric epitaxial electrodes results in robust ferroelectric response with square ferroelectric hysteresis
loops, large remnant polarization ($P_r$ $\sim$ 79 µC/cm$^2$), negligible polarization offsets and loop closure even at
measurement frequencies of 10 Hz. Even at 1 Hz, the films reveal evidence of ferroelectric switching (although
somewhat convoluted by leakage). These measurement frequencies are one to two orders-of-magnitude lower
than measurements typically done using traditional contacts for similar films. From these measurements,
we can extract the frequency dependence of coercive voltage [Fig. 4.3 d]. We have determined the coercive
voltage as $E_c = (E_c^+ + E_c^-)/2$ where $E_c^+$ and $E_c^-$ are the positive and negative coercive fields from the
hysteresis loop. We see that coercive voltage can be described in terms of the frequency ($f$) by a power law
of the form $E_c \sim f^\beta$ as predicted from domain wall motion limited models of ferroelectric switching [87].
This is consistent with earlier work [7, 88, 89] which demonstrated that domain wall growth rather than
nucleation should play an important role in ferroelectric switching in epitaxial films. We observe two scaling
regimes with different $\beta$ and a crossover frequency of $\sim$ 300 Hz. The presence of two scaling regimes is
likely due to the presence of two frequency dependent regimes of domain wall switching [88, 89]. At low
frequencies thermally activated creep of domain walls controls switching but at high frequencies, in the
absence of sufficient time for the creep to completely switch the polarization, the viscous flow of the domain
wall dominates.

We have also probed the switching and fatigue properties of the epitaxial capacitors via pulsed meas-
urements. Polarization fatigue is the process by which switchable ferroelectric polarization is reduced by
repetitive electrical cycling and is among the most serious device failure mechanisms in ferroelectric films.
Traditionally, it has been suggested that ferroelectric capacitors with elemental metal electrodes suffer sig-
significant fatigue and that simply replacing the elemental metal with an oxide metal improves the fatigue performance [31, 32, 34, 73, 90–94]. Since oxygen vacancy accumulation at the metal-ferroelectric interface is a major cause of fatigue, the oxide metals perform better since they serve to compensate for the oxygen vacancies. To investigate the switching characteristics, we begin with PUND switching measurements with bipolar pulses which were completed as a function of applied voltage [Fig. 4.4 a] and pulse width [Fig. 4.4 b]. For these capacitors, we observe symmetric and complete switching for positive and negative biases occurring at +/- 1.4 V (93.3 kV/cm), 1.6 V (106.6 kV/cm), and 2.5 V (166.6 kV/cm), for 1 ms, 0.1 ms, and 0.01 ms pulses, respectively. Likewise, we observe the onset of switching only for voltages in excess of 1 V and critical pulse durations ranging from 0.002 - 0.016 ms for voltages ranging from 3.75 to 1.5 V. This shows

Figure 4.4: PUND measurement as a function of (a) voltage for various pulse widths and (b) pulse width for various pulse voltages. (c) Fatigue data showing the loss of remnant polarization ($P_r$) with repeated cycling. (d) Ferroelectric hysteresis loops of the capacitor shown in (c) in the as grown state ($N = 1$) and after $N = 1.25 \times 10^9$ cycles; data taken five minutes after the fatigue measurement.
that complete switching can be obtained in these films at 10 µs with voltage pulses as small as 2.5 V. This information was used to complete a study of the fatigue properties of these capacitors using a bipolar pulse train (described in the inset of Fig. 4.4 c) with a 4V pulse at a frequency of 10 kHz with a 20% duty cycle. The samples are found to possess essentially no fatigue even after $10^8$-$10^9$ cycles. Furthermore, after $1.25 \times 10^9$ cycles the measured remnant polarization was $69 \mu C/cm^2$ just five minutes after completion of the fatigue and returned to essentially the same pre-fatigue levels after a few days [Fig. 4.4 d].

Temperature dependent ferroelectric characterization was also performed between 296 - 430 K [Fig. 5] - atleast roughly 100 K higher than measurements reported previously. The temperature stable top electrodes enabled square hysteresis loops to be obtained up to 430 K [Fig. 4.5 a]. Elemental metals or room-temperature deposited SrRuO$_3$ are known to give lossy hysteresis loops or to completely fail at temperatures $>373$ K [81]. This makes the temperature dependence of polarization (or pyroelectric coefficient) and coercive field very difficult to obtain. Often, one resorts to phase sensitive techniques to measure the temperature dependence of polarization to offset the problems of DC leakage and thermally stimulated currents [41]. Further, the temperature dependence of coercive field [Fig. 4.5 b] shows that the coercive field decreases roughly linearly with temperature in this regime with a slope of 0.6 kV/cmK. The frequency and temperature dependent characterization give useful insights into the behavior of PbZr$_{0.2}$Ti$_{0.8}$O$_3$ films and show that ferroelectric film performance can be greatly improved with the choice of electrodes.

We now proceed to investigate the ferroelectric characterization of strained PbZr$_{0.2}$Ti$_{0.8}$O$_3$ heterostructures. The capacitors on all four substrates reveal symmetric leakage characteristics and ferroelectric hys-
Polarization-electric field hysteresis loops of the various heterostructures measured at 10 kHz. (b) PUND measurements of the switched polarization in the system completed as a function of pulse width. Hysteresis on all four substrates reveal square loops with a large spontaneous polarization in excess of 60 $\mu$C/cm$^2$ [Fig. 4.6 a]. It was also observed that the out-of-plane remnant polarization as measured by the hysteresis loops decreased with increased tensile strain from SrTiO$_3$ to GdScO$_3$ due to the increased fraction of in-plane oriented $a$ domains. This was further confirmed by measuring the switchable polarization via PUND measurements [Fig. 4.6 b]. These switching studies confirm the predictions of GLD model and the PFM characterization reported in Chapter 3 and reveal that as the epitaxial strain increases from -0.8% to +0.9%, the remnant polarization decreases from $\sim$ 90$\mu$C/cm$^2$ to $\sim$ 61$\mu$C/cm$^2$. The relationship between the out-of-plane polarization and the fraction of $a$ domains is also plotted to summarize the characterization of the domain structure and ferroelectric properties in the strained thin films [Fig. 4.7]. In the rest of the Chapter, we will describe the measurements of dielectric and pyroelectric susceptibilities on the strained thin films with varying density of in-plane oriented domains and compare the results with the predictions of the GLD model.

### 4.2 Dielectric Permittivity of Strained PbZr$_{0.2}$Ti$_{0.8}$O$_3$ Thin Films

In order to measure the out-of-plane dielectric permittivity ($\epsilon_{33}$) of the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ heterostructures, the sample capacitance was measured at 1-100 kHz and the dielectric permittivity was extracted from the capacitance as $C = (\epsilon_0 \epsilon_{33} A)/t$, where $A$ is the area of the capacitor and $t$ is the thickness of the film. In order to measure the dielectric permittivity in the reversible regime, a small AC excitation of 0.1 V was used and capacitors with showing symmetric leakage and low loss tangents ($< 0.1$) were chosen for the measurements.
Figure 4.7: The variation of remnant polarization ($P_r$), spontaneous polarization ($P_s$) within the domains, and the fraction of $a$ domains ($\phi_a$) with epitaxial strain for 150 nm thick PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films.

AC voltage dependent capacitance measurements (or Rayleigh analysis) [Fig. 4.8] was performed to confirm that the measurements were performed in the reversible regime.

Before discussing the results of the dielectric permittivity measurements, let us summarize the results of the polydomain GLD model here. For the $c/a/c/a$ domain structure, the out-of-plane permittivity ($\epsilon_{33}$) can be evaluated as

$$\epsilon_{33} = \frac{d\langle P_3 \rangle}{dE} = \phi_c \frac{dP_s}{dE} + P_s \frac{d\phi_c}{dE}$$

where $P_s$, $\phi_c$, and $E$ represent the out-of-plane polarization within the $c$ domain, the fraction of the $c$ domains, and the electric field along the substrate normal, respectively. The first term represents the intrinsic permittivity of the polydomain state and the second term is the extrinsic contribution to the permittivity arising from the reversible displacement of the domain walls that changes the domain fractions. In the linear approximation (valid at low electric fields), neglecting the effect of small domain wall displacement on the polarization within the domains, we can calculate the extrinsic contribution to the permittivity analytically as

$$\epsilon_{ex} = \frac{(s_{11}^2 - s_{12}^2)}{s_{11}(Q_{11} - Q_{12})^2P_s^2}$$

where $s_{ij}$ are the elastic compliances, and $Q_{ij}$ are the electrostrictive coefficients. For PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films at 300 K, we find that the intrinsic permittivity [dashed line, Fig. 4.9 a] of the polydomain $c/a/c/a$ state is $< 100$ and that the total permittivity [solid line, Fig. 4.9 a (intrinsic plus extrinsic contributions)]
Figure 4.8: Detailed Rayleigh studies of the strained PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films showing the small signal dielectric permittivities and the loss tangents on all four substrates.

is expected to be enhanced significantly. Furthermore, the extrinsic contribution increases with increasing fraction of the $a$ domains with increasing tensile strain.

Proceeding to the results of the dielectric measurements, we find that the permittivity increases with increasing $\phi_a$ as per the predictions of the GLD model [Fig. 4.9 a]. This shows that the 90° domain walls do indeed contribute significantly to the room temperature dielectric permittivity. Further, on all four substrates the permittivity shows a significant frequency dispersion [Fig. 4.9 b]. The frequency dependence of the dielectric constant is likely due to two important factors. First, although some reports suggest that the domain wall contribution should be frequency independent up to the domain wall resonance (1-10 GHz), in practice, the finite depinning time of the domain walls gives rise to logarithmic frequency dependence in the low-frequency regime [95–97]. Second, point defects such as oxygen vacancies, are also known to contribute significantly to the low-frequency (<100 kHz) permittivity and their contribution decreases with increasing frequency [97–99]. Since these two effects are intimately connected and almost always present in any real material (be it films, bulk ceramics, or single crystals), it is very difficult to separate these two effects in any study of these materials. We note, however, that the trends in the measured permittivity agree well with the predictions of the GLD theory [solid line, Fig. 4.9 a].

To gain a deeper understanding into the observed dielectric behavior and of the domain wall motion, one can describe the field induced vibrations of the domain walls using standard equations of motion [100, 101]. Generally, for a 90° domain wall at low frequencies, the mass of the domain wall is neglected and
the restoring force can be written in terms of a domain wall stiffness $k$ defined as $F_r = -kl$ and $l$ is the amplitude of the field induced domain wall oscillations. Thus, the domain wall contribution to the permittivity can be written as \[ \epsilon_x = \frac{\sqrt{2l^2}}{\epsilon_0 k l} \]. The idea of domain wall stiffness has been invoked for many years [100–103] to understand the behavior of domain walls, but it is usually treated as an adjustable parameter which is fitted to the experimental results. Our measurements allow us to estimate the domain wall stiffness in PbZr\textsubscript{0.2}Ti\textsubscript{0.8}O\textsubscript{3} for the first time [Table 4.1]. Early theoretical studies suggested that $k$ should not vary with domain size, but later models suggested otherwise [102, 104]. To date, no experimental values for $k$ have been reported in the literature and it is difficult to find values even from theoretical treatments. Provided enough information, however, one can estimate values of $k$ from parameters such as domain size, grain size, spontaneous polarization, permittivity, elastic stiffness, etc. From prior studies [102], we can estimate $k$ values of $10^{14}$ N/m\textsuperscript{3}. This is consistent with what we observe for samples with low densities of domain walls. We note, however, that $k$ values increase with increasing density of domain walls and could be dramatically underestimated (by at least an order of magnitude) in samples possessing $> 20\%$ $a$ domains. This has considerable implications for estimates of thermodynamic quantities near the tensile strain induced phase boundary and for overall estimates of domain wall contributions to physical properties. These measurements of dielectric permittivity also offer unique insight into the microscopic coupling between electric fields and domain walls in ferroelectrics. In tetragonal ferroelectrics that can have both 180° (ferroelectric) and 90° (ferroelastic) domain walls, it has been suggested that 180° domain wall motion will affect only the permittivity and 90° domain wall motion will affect both dielectric and
Table 4.1: Fraction of a domains ($\phi_a$), domain periodicity ($D$), remnant polarization ($P_r$), and domain wall stiffness ($k$) as measured for film grown on various substrates. The numbers in parentheses represent the standard deviation from measurements.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\phi_a$ (%)</th>
<th>$D$ [$\sigma_D$] ($\mu$m)</th>
<th>$P_r$ ($\mu$C/cm$^2$)</th>
<th>$k$ [$\sigma_k$] ($10^{15}$N/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrTiO$_3$(001)</td>
<td>4.2</td>
<td>3.02 [0.55]</td>
<td>90</td>
<td>0.67 [0.12]</td>
</tr>
<tr>
<td>DyScO$_3$(110)</td>
<td>9.3</td>
<td>2.72 [1.37]</td>
<td>78</td>
<td>0.56 [0.28]</td>
</tr>
<tr>
<td>TbScO$_3$(110)</td>
<td>11.2</td>
<td>1.80 [1.04]</td>
<td>73</td>
<td>0.84 [0.48]</td>
</tr>
<tr>
<td>GdScO$_3$(110)</td>
<td>20.2</td>
<td>0.59 [0.44]</td>
<td>61</td>
<td>1.76 [1.30]</td>
</tr>
</tbody>
</table>

piezoelectric properties. Although some work has been done concerning the effect of 90° domain walls on piezoelectric properties in films [105–107], prior studies of effects on permittivity were obscured by complex polycrystalline structures and the resulting complex interplay of domain walls and grain boundaries. We have generated a model set of epitaxial thin films that closely match polydomain GLD models and have observed the unambiguous contribution of 90° domain walls to the dielectric response at room temperature and utilized these measurements to experimentally probe the stiffness of 90° domain wall to applied electric fields.

4.3 Pyroelectric Susceptibility of Strained PbZr$_{0.2}$Ti$_{0.8}$O$_3$ Thin Films

The pyroelectric susceptibility of a ferroelectric is typically characterized by measuring the pyroelectric current generated in response to a known temperature change. The pyroelectric current ($i_p$) from a ferroelectric capacitor depends on the rate of change of temperature as $i_p = \pi AdT/dt$ where $\pi$ is the pyroelectric coefficient and $A$ is the area of the capacitor. Measuring this response of thin films is difficult and this has restricted the understanding of pyroelectricity as compared to other ferroelectric susceptibilities such as dielectric permittivity and piezoelectric constants. Most techniques currently utilized to measure pyroelectric properties were developed to probe bulk ceramics or single crystals, including laser induced heating [39] and constant ramp-rate heating induced current [40]. These techniques are adequate to identify pyroelectricity or to estimate the pyroelectric coefficients of large samples but lack precision as a consequence of poor temperature accuracy, non-uniform heating, and contributions from thermally stimulated currents [41,42,108]. Thermally stimulated currents due to a temperature induced release of charge from trap sites within ferroelectrics is a
Figure 4.10: A typical measurement of the pyroelectric coefficient using a linear temperature ramp at 10 K/min showing the non-pyroelectric currents generated in response to the temperature change.

particularly significant problem for characterizing thin-films and these techniques have been applied, with limited success, to characterize thin films [30, 109–111]. A typical experiment with a linear temperature ramp on a PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin film shows this clearly [Fig. 4.10]. Here, we apply a 10 K/min temperature ramp on the thin films and monitor the resulting current. If the response was purely pyroelectric, we should observe a constant current corresponding the pyroelectric coefficient but however, we observe a temperature dependent non-constant current most likely due to the release of trapped charges (i.e. thermally stimulated currents). This makes a reliable estimate of pyroelectric coefficient impossible to infer and illustrates the problems associated with such DC measurement techniques. In contrast to the pyroelectric current which depends on the rate of change of temperature, within a narrow temperature interval (a few degrees K), the thermally stimulated current ($i_s$) depends on the temperature linearly as $i_s = i_{so} + \lambda T$ where $i_{so}$ is the room temperature thermally stimulated current and $\lambda$ is a constant related to the activation energy of the trap states that give rise to the thermally stimulated currents [42]. However, even though the thermally stimulated currents make measurements of pyroelectricity difficult, the difference in the nature of these two responses can be utilized to make accurate measurements via phase sensitive techniques [41, 42]. In such measurements which typically utilize sinusoidal temperature oscillations, the component of the current in-phase with the temperature is related to the thermally stimulated current and the current out-of-phase with the temperature is the pyroelectric current. Such a phase-sensitive technique is typically used to overcome the limitations due to thermally stimulated currents and provide an accurate measure of pyroelectricity. This method is, however, difficult to implement on small-area (< 200µm diameter) thin-film ferroelectric
capacitors whose pyroelectric current can be small ($\sim 100$ fA for $dT/dt=1-10$ K/min).

In order to measure the pyroelectric susceptibilities of the strained thin films, we have implemented a low-noise phase-sensitive technique to accurately measure the small pyroelectric currents ($< 1$ pA) generated in response to a sinusoidal temperature oscillations. Phase-sensitive measurements of the pyroelectric coefficient were completed by measuring the current induced in response to sinusoidal temperature oscillations using a current preamplifier (Femto DLPCA-200) mounted in close proximity to the sample [Fig. 4.11 a]. Temperature variations of the form $T = T_b + T_0 \sin(\omega t)$ with a background temperature $T_b = 320$ K and oscillations of magnitude $T_0 \sim 1.25 K$ at an angular frequency $\omega \approx 0.125 \text{rad/s}$ were utilized to obtain a clean sinusoidal oscillation in a stable temperature near room temperature while producing a pyroelectric current that can be measured accurately [Fig. 4.11 b-c]. The pyroelectric coefficient was extracted from the out-of-phase component of the measured sinusoidal current as $\pi = \frac{i_0 \sin(\theta)}{AT_0 \omega}$ where $i_0$ is the amplitude of the current oscillation and $\theta$ is the measured phase difference between the current and the temperature oscillations. The pyroelectric coefficient was extracted from a large number ($n = 32$) of capacitors from a minimum of two identically prepared samples on each substrate. The measured phase difference $\theta$ between the temperature and current oscillations is close to -90$^\circ$ all samples as expected [Fig. 4.12]. Deviations from -90$^\circ$ phase difference between the temperature and current oscillations likely arise due to the presence of thermally stimulated currents in these samples; however, our ability to precisely measure the phase difference allows us to unequivocally identify the purely pyroelectric contribution.

Before discussing the results of the pyroelectric measurements, we will summarize the results of the
polydomain GLD model for the PbZr\(_{0.2}\)Ti\(_{0.8}\)O\(_3\) thin films here. For the c/a/c/a domain structure, the
pyroelectric coefficient along the substrate normal can be defined as \(\pi_3 = \frac{\langle P_3 \rangle}{dT}\) where \(\langle P_3 \rangle = \phi_c P_s\), \(\phi_c\) is the volume fraction of the c domains, and \(P_s\) is the spontaneous polarization with the c domains. The
total pyroelectric coefficient can thus be expressed as \(\pi_3 = \phi_c \frac{dP_s}{dT} + P_s \frac{d\phi_c}{dT}\) where the first and second terms
represent the intrinsic and extrinsic contribution to the pyroelectric coefficient, respectively. Using such
a model, the pyroelectric coefficient of a PbZr\(_{0.2}\)Ti\(_{0.8}\)O\(_3\) thin film at 320 K was calculated. The intrinsic
response [dashed orange line, Fig. 4.13] is found to decrease (in magnitude) with an increasing density of
a domains. Additionally, the primary (intrinsic + extrinsic contributions due to the temperature-induced
motion of 90\(^\circ\) domain walls) pyroelectric coefficient was calculated. As noted in Chapter 2, including the
extrinsic effects, the primary pyroelectric coefficient is found to increase with increasing fraction of a domains
[blue dashed line, Fig. 4.13]. As a result, similar to dielectric and piezoelectric response, the 90\(^\circ\) domain
walls are predicted to have a significant effect on the pyroelectricity even at temperatures far below the
Curie temperature and completely reverse the trend with \(\phi_a\) in this case.

The phase sensitive pyroelectric measurements reveal that, as \(\phi_a\) increases from \(\sim 4\%\) to \(\sim 20\%\), the mea-
sured pyroelectric coefficient increases from \(\sim -200\) to \(\sim -300\) \(\mu C/m^2K\) [filled red squares, Fig. 4.13]. This
is consistent with the predictions that the primary pyroelectric response should increase with the density of
90\(^\circ\) domain walls (since there are more domain walls to provide extrinsic contributions). This indicates that
Figure 4.13: The measured pyroelectric coefficient (red squares) as a function of percentage \(a\)-domains in polydomain \(\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3\) thin films. The dashed orange line is the intrinsic response and the dashed blue line is the primary response (intrinsic + extrinsic) calculated using polydomain GLD theory. The open green squares indicate the sum of primary + secondary contributions to the pyroelectric coefficient for each film-substrate combination and the dashed green line indicates the trend expected assuming an average thermal expansion coefficient of \(10.9 \times 10^{-6} \text{ K}^{-1}\) for all the substrates.

the monodomain models of intrinsic response are inadequate to explain the observed pyroelectric response in polydomain films. The measured pyroelectric coefficient, however, shows a minor, but systematic, deviation from the values predicted for the primary contribution (i.e., measured values are consistently larger). While it is unrealistic to expect the GLD theory to provide a precise prediction of the actual pyroelectric coefficients, it is possible that the systematic deviation arises from other mechanisms active in thin-film ferroelectrics. As discussed previously, thin films are susceptible to secondary effects due to thermal expansion mismatch between the film and substrate. The average in-plane thermal expansion coefficients of \(\text{SrTiO}_3\), \(\text{DyScO}_3\), and \(\text{GdScO}_3\) are \(11.1 \times 10^{-6} \text{ K}^{-1}\), \(9.3 \times 10^{-6} \text{ K}^{-1}\), and \(12.1 \times 10^{-6} \text{ K}^{-1}\), respectively [112, 113]. Experimental measurement of the thermal expansion coefficient of \(\text{TbScO}_3\) is not available in the literature.

We can observe general trends by using an average thermal expansion coefficient for all substrates studied here \(10.9 \times 10^{-6} \text{ K}^{-1}\) and PZT \((5.4 \times 10^{-6} \text{ K}^{-1})\). Using these values, we estimated the average secondary contribution to the pyroelectric coefficient [dashed green line, Fig. 4.13]. We observe that the measured values agree well with the predictions of the GLD model including the secondary effects and the secondary pyroelectric coefficient provides an important correction to the primary pyroelectric coefficient calculated previously. Alternatively, we can consider each film-substrate combination independently (done here for films on \(\text{SrTiO}_3\), \(\text{DyScO}_3\), and \(\text{GdScO}_3\) substrates) [green squares, Fig. 4.13]. This approach helps explain the fine-structure observed in the data (i.e., the relative vertical shifts of data points). Nevertheless, the addition
of the secondary effect seems to systematically exceed the values of the measured pyroelectric coefficients. This could arise for a number of possible reasons: 1) Domain wall effects are overestimated due to domain wall pinning resulting in a lower extrinsic contribution than expected from GLD theory. The diminished extrinsic contributions push responses closer to the intrinsic values, thereby increasing the magnitude of the response in the region of interest. 2) The secondary effects require further corrections (due to, for example, anisotropic thermal expansion coefficients). Nonetheless, this work has provided the first comprehensive study of pyroelectricity in polydomain ferroelectric thin films with $c/a/c/a$ domain structures.

These measurements dramatically improves the current understanding of extrinsic (domain wall) and secondary contributions to pyroelectricity in thin films and reveals how thin film epitaxy can be used to generate model systems for the study of pyroelectricity. Using epitaxial thin film strain and domain engineering we have systematically identified important contributions to the pyroelectric properties of ferroelectric thin films and utilized the insight to improve the pyroelectric susceptibilities in PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films at room temperature.

4.4 Novel Techniques to Measure Pyroelectric Susceptibilities

Thus far, we have considered the phase-sensitive measurements of pyroelectric coefficient in PbZr$_{0.2}$Ti$_{0.8}$O$_3$ to investigate the effect of 90° domain walls and thermal expansion mismatch on the pyroelectric properties. Due to the low-frequency of the temperature oscillations that are achievable with a bulk sample heater (< 0.05 Hz), however, the pyroelectric currents are small and an ultra-low noise measurement set-up is necessary. Higher signal-to-noise is possible by increasing the frequency of the temperature oscillations since the pyroelectric current is proportional to the frequency of the temperature oscillation. Increasing the frequency is also desirable from a practical standpoint since most pyroelectric materials operate in devices at significantly higher frequencies (0.1-1 kHz) than the measurements reported here [109]. Furthermore, high frequency pyroelectric characterization will also provide fundamental insights into the response of the ferroelectric to heat at shorter time scales. However, prior attempts to characterize the pyroelectric properties at high frequencies (using a laser based heat source, say) have met with limited success since they are typically not quantitative. A thorough characterization of the thermal properties of the pyroelectric materials is necessary to obtain accurate quantitative measures of the pyroelectric coefficient via high frequency measurements. Such independent thermal property measurements are not necessary for the low frequency measurements reported earlier since the sample is assumed to be at thermal equilibrium with the heater at such low frequencies.
Figure 4.14: High-frequency phase sensitive pyroelectric measurements of PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films on DyScO$_3$ using the low-frequency technique (LFP), $2\omega$ method with microfabricated Pt heaters, and laser intensity modulation (LIM) methods.

The phase-sensitive pyroelectric characterization techniques reported previously at 0.02 Hz was extended to higher frequencies on PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films using a $2\omega$ based technique with a microfabricated Pt heater line (upto 1 kHz) and a laser-based heat source (upto 1 MHz). These measurements were performed in collaboration with B. Bhatia and W. P. King (for the $2\omega$ measurements) and T. Trong and Prof. D. G. Cahill (for the laser intensity modulation method). Independent measurements of the thermal properties of the film and the substrate were performed using $3\omega$ and time-domain thermoreflectance [114,115]. The thermal properties were utilized to model the temperature distribution within the ferroelectric layer at various frequencies and the measured pyroelectric currents were fitted to the thermal models to extract the pyroelectric coefficient. These measurements indicate that the pyroelectric coefficient is approximately constant from 0.02 Hz to 1 MHz [Fig. 4.14]. However, more accurate measurements were possible at higher frequencies due to the higher signal-to-noise ratio. These measurements represent a significant advance in the measurement of pyroelectric properties and open the doors for the pyroelectric characterization of thin film ferroelectric across a wide range of temperatures and frequencies. They also provide an independent confirmation of the low-frequency phase-sensitive techniques implemented in this work. Current work utilizing these novel
techniques attempts to extend these high-frequency measurements to study high-temperature pyroelectric properties (where leakage necessitates high signal-to-noise) and direct measurements electrocaloric properties in thin films.

4.5 Conclusions

In this Chapter, we have presented a detailed investigation of the ferroelectric, dielectric, and pyroelectric properties of epitaxially strained PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films. An MgO based hard-mask process was developed for the fabrication of fully epitaxial capacitor structures of PbZr$_{0.2}$Ti$_{0.8}$O$_3$ with SrRuO$_3$ metallic electrodes. Detailed measurements of the dielectric and pyroelectric susceptibilities of the strained heterostructures revealed that the susceptibilities increased with increasing tensile strain as predicted by the GLD models due to extrinsic contributions from domain wall displacements. Further, the pyroelectric measurements show that secondary effects due to thermal expansion mismatch could also play a significant role in determining the total pyroelectric susceptibility at room temperature. These measurements show the crucial role played by the domain walls and the choice of substrates on the ferroelectric susceptibilities and have important implications for the optimization of ferroelectric susceptibilities for a variety of functional devices.
Chapter 5

Growth and Characterization of Compositionally Graded PZT Thin Films

In the previous Chapters, we have systematically identified important contributions to dielectric and pyroelectric susceptibilities in tetragonal PZT thin films with complex domain structures using a combination of GLD models, epitaxial strain engineering, and low-noise measurement techniques. In this Chapter, we explore a new route to tune ferroelectric properties via composition gradients in thin films. We show that compositionally graded films of PZT exhibit unique structural and ferroelectric properties that are not found in single layer thin films. This includes a substantially reduced tendency for strain relaxation, the presence of large built-in electric fields, and a substantially reduced dielectric permittivity. Using a combination of XRD, PFM, and ferroelectric measurements we investigate the novel properties of such compositionally graded systems and firmly establish composition gradients as a unique and powerful tool for manipulating ferroelectricity.
5.1 Introduction to Compositionally Graded Ferroelectric Thin Films

Compositionally graded thin films, which possess a smooth variation in the composition throughout the thickness of the film, have shown considerable promise for improved functional properties in traditional semiconductor systems. Compositional gradients have been utilized in semiconductor epitaxy (in systems such as Si$_x$Ge$_{1-x}$ and In$_{1-x}$Ga$_x$As) as buffer layers for the growth of dislocation-free epilayers, as virtual substrates for achieving epitaxial integration of widely mismatched materials, and for bandgap control in optoelectronic devices [116–119]. As a result, in the past decade compositional gradients have become a well established and successful route to fabricate advanced semiconductor devices on silicon such as two-dimensional electron gases, high efficiency light emitting diodes, and solar cells. While a similar motivation (i.e., inhibiting strain relaxation) also applies to complex oxide epitaxy, ferroelectric materials offers additional challenges and new opportunities. Traditional ferroelectric materials have been epitaxially strained to only with ~2%, beyond which dislocation formation prevents strained thin films and as a result, structurally relaxed bulk-like phases are formed. Prior work on semiconductor thin films, however, suggests that strain much beyond this regime is possible in compositionally graded films thereby enabling strain to exert a more prominent effect. The gradients in composition, however, also result in gradients in strain and as a result, the ferroelectric properties could be drastically altered due to electrostrictive and flexoelectric coupling (i.e. coupling between polarization and strain gradients) effects.

Prior work on compositionally graded ferroelectric thin films in systems including PZT and BST has revealed a range of novel phenomena such as the presence of built-in electric fields, shifted hysteresis loops, and large susceptibilities [120–124]. Recent theoretical work has also suggested that compositionally graded thin films could show geometric frustration [125] and experimental efforts have explored flexoelectric effects associated with strain gradients such films [126, 127]. Despite a longstanding scientific interest and an immense potential for applications, the origin of the novel properties and the structure-property relationships in compositionally graded films is still unclear. In turn, this has limited the adoption and utilization of these graded materials as compared to more traditional epitaxial strain approaches to engineer and control functionality in thin-film ferroelectrics.

In this Chapter we utilize PZT as a model system to systematically study the effect of composition gradients on the crystal structure, ferroelectric domain structure, and the resulting ferroelectric properties of graded thin films by investigating single layer, bilayer, and compositionally graded PZT thin films. After a brief introduction to the growth and structural analysis of the heterostructures, we present a detailed report
Figure 5.1: Schematic illustrations of the six sample variants studied in this work including (a) single-layer PbZr_{0.2}Ti_{0.8}O_3, (b) single-layer PbZr_{0.8}Ti_{0.2}O_3, (c) up-bilayer, (d) down-bilayer, (e) up-graded, and (f) down-graded.

of their ferroelectric properties using PFM and ferroelectric measurements. We observe that both bilayer and compositionally graded heterostructures have ferroelectric domain structures that are largely determined by the structural evolution at the film-substrate interface. By minimizing the lattice misfit at the interface, large residual strains can be generated in the heterostructures which gives rise to exotic ferroelectric domain structures (that are not found in single layer versions of these materials) and corresponding novel dielectric and ferroelectric properties including the observation of built-in electric fields and two different zero-field stable states with the same net polarization, but different small-signal dielectric permittivity.

5.2 Growth of Compositionally Graded PZT Thin Films

We focus our attention on 100 nm thick films of PZT with compositions between $x = 0.2 - 0.8$. The two end-members are PbZr_{0.2}Ti_{0.8}O_3 (a tetragonal ferroelectric with lattice parameters $a = 3.94 \, \text{Å}$ and $c = 4.12 \, \text{Å}$) and PbZr_{0.8}Ti_{0.2}O_3 (a rhombohedral ferroelectric with lattice parameter $a = 4.118 \, \text{Å}$ and $\alpha = 89.73^\circ$) [27, 28, 128]. Considering the bulk lattice parameters of PbZr_{0.2}Ti_{0.8}O_3 and PbZr_{0.8}Ti_{0.2}O_3, GdScO_3 (110) single crystal substrates (with a pseudocubic lattice parameter $a = 3.97 \, \text{Å}$ that is between the two phases) are used for this study. Six variants of heterostructures were studied: 1) single-layer PbZr_{0.2}Ti_{0.8}O_3 [Fig. 5.2 a], 2) single-layer PbZr_{0.8}Ti_{0.2}O_3 [Fig. 5.2 b], 3) up-bilayer heterostructures (a 50 nm
PbZr\textsubscript{0.8}Ti\textsubscript{0.2}O\textsubscript{3} layer grown on a 50 nm layer of PbZr\textsubscript{0.2}Ti\textsubscript{0.8}O\textsubscript{3}) [Fig. 6.2 c], 4) down-bilayer heterostructures (a 50 nm PbZr\textsubscript{0.2}Ti\textsubscript{0.8}O\textsubscript{3} film grown on a 50 nm layer of PbZr\textsubscript{0.8}Ti\textsubscript{0.2}O\textsubscript{3}) [Fig. 6.2 d], 5) compositionally up-graded heterostructures (which smoothly transition from PbZr\textsubscript{0.2}Ti\textsubscript{0.8}O\textsubscript{3} to PbZr\textsubscript{0.8}Ti\textsubscript{0.2}O\textsubscript{3}) from the substrate to the film surface) [Fig. 6.2 e], and 6) compositionally down-graded heterostructures (which smoothly transition from PbZr\textsubscript{0.8}Ti\textsubscript{0.2}O\textsubscript{3} to PbZr\textsubscript{0.2}Ti\textsubscript{0.8}O\textsubscript{3} from the substrate to the film surface) [Fig. 6.2 f]. In all cases, the PZT heterostructures are grown with a 30 nm SRO bottom electrode. The laser fluence and repetition rate were maintained at 1.9 J/cm\textsuperscript{2} and 3 Hz for all PZT growths and 1.8 J/cm\textsuperscript{2} and 13 Hz for the growth of the SRO. Compositionally graded heterostructures were synthesized by continuously varying the composition from PbZr\textsubscript{0.2}Ti\textsubscript{0.8}O\textsubscript{3} to PbZr\textsubscript{0.8}Ti\textsubscript{0.2}O\textsubscript{3} and vice versa using a programmable target rotator (Neocera, LLC) that was synced with the excimer laser. The up-bilayer and compositionally up-graded heterostructures were grown at 600\textdegree C. The down-bilayer and compositionally down-graded heterostructures were grown at 560\textdegree C. For all the samples, films were grown at oxygen pressures of 200 mTorr and were cooled in 700 Torr pressure of oxygen.

The variation in composition across the thickness of the film was confirmed using time-of-flight secondary ion mass spectrometry (TOF-SIMS) analysis with both single-layer PbZr\textsubscript{0.2}Ti\textsubscript{0.8}O\textsubscript{3} [Fig. 5.2 a] and PbZr\textsubscript{0.8}Ti\textsubscript{0.2}O\textsubscript{3} [Fig. 5.2 b] films revealing essentially constant Zr and Ti ion concentrations across the thickness of the films and compositionally graded samples revealing a gradual change in the Zr and Ti ion concentration across the thickness of the films [Fig. 5.2 c-d]. The TOF-SIMS analysis confirms that the compositionally graded variants have smoothly varying Zr- and Ti-contents across the thickness of the film.

5.3 Crystal and Ferroelectric Domain Structure of Compositionally Graded PZT Thin Films

5.3.1 Structural Analysis \textit{via} X-ray Diffraction

The structure of these heterostructures was studied using XRD RSMs about the 103 and 332 diffraction conditions for the film and substrate, respectively. These studies reveal that single-layer PbZr\textsubscript{0.2}Ti\textsubscript{0.8}O\textsubscript{3} films are coherently strained to the GdScO\textsubscript{3} (110) substrates [Fig. 5.3 a] while single-layer PbZr\textsubscript{0.8}Ti\textsubscript{0.2}O\textsubscript{3} films are partially relaxed [Fig. 5.3 b]. We observe a similar asymmetry in strain relaxation in the bilayer heterostructures where the up-bilayer variants possess a majority tetragonal-like structure with some indication of partial strain relaxation [Fig. 5.3 c] while the down-bilayer variants possess peaks for both the
Figure 5.2: Time-of-flight secondary ion mass spectra for (a) PbZr$_{0.2}$Ti$_{0.8}$O$_3$ (b) PbZr$_{0.8}$Ti$_{0.2}$O$_3$ (c) upgraded (d) down-graded variants.

rhomboedral (PbZr$_{0.8}$Ti$_{0.2}$O$_3$, referred to as PZT$_R$ in the figure) and tetragonal (PbZr$_{0.2}$Ti$_{0.8}$O$_3$, referred to as PZT$_T$ in the figure) phases including evidence of in-plane $a$ domain formation in the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ [Fig. 5.3 d]. Furthermore, in the compositionally graded heterostructures the up-graded variants are found to possess a nearly coherently-strained tetragonal-like structure with lattice parameters $a = 3.97$ Å and $c = 4.136$ Å [Fig. 5.3 e] while the down-graded variants exhibit peaks corresponding to relaxed versions of the rhombohedral phase and $a$ domains of the tetragonal phase [Fig. 5.3 f].

The asymmetry in the strain relaxation and the observed crystal structures is fairly straightforward to understand. The lattice mismatch between PbZr$_{0.2}$Ti$_{0.8}$O$_3$ and the substrate (0.9% tensile) is considerably smaller than the lattice mismatch between the PbZr$_{0.8}$Ti$_{0.2}$O$_3$ and the substrate (3.5% compressive). As a result, the 100 nm thick films of PbZr$_{0.2}$Ti$_{0.8}$O$_3$ are more susceptible to strain relaxation as compared to PbZr$_{0.2}$Ti$_{0.8}$O$_3$ films of the same thickness. Therefore, the down-bilayer and down-graded variants are expected to undergo rapid strain relaxation and present the subsequent Ti-rich phase with an effectively larger in-plane lattice parameter than the GdScO$_3$ substrate. The Ti-rich (tetragonal) material will, in turn, accommodate the large tensile strain via the formation of $a$ domains. This is consistent with the observed diffraction patterns in down-bilayer [Fig. 5.3 d] and down-graded [Fig. 5.3 f] variants. On the other hand, when the Ti-rich material is grown at the substrate interface, the small lattice mismatch with the substrate is easily accommodated and the subsequent Zr-rich material is presented with in-plane lattice parameters that are more favorable for generating a compressively strained variety of the Zr-rich phases. In this case,
Figure 5.3: Reciprocal space mapping about the 103 and 332-diffraction conditions for (a) single-layer PbZr$_{0.2}$Ti$_{0.8}$O$_3$, (b) single-layer PbZr$_{0.8}$Ti$_{0.2}$O$_3$, (c) up-bilayer, (d) down-bilayer, (e) up-graded, and (f) down-graded variants. Expected peak positions for bulk (black) and strained (orange) versions of the parent phases are labeled in each graph. Note that when appropriate and distinct, we distinguish between peaks arising from Zr-rich and Ti-rich PZT as PZT$_R$ and PZT$_T$, respectively.

akin to what has been observed in compositionally graded semiconductor heterostructures, large strains can be achieved across the film thickness because locally the lattice mismatch throughout the film is considerably smaller.
Figure 5.4: Piezoresponse force microscopy images of (a) single-layer PbZr$_{0.8}$Ti$_{0.2}$O$_3$ (vertical phase), (b) single-layer PbZr$_{0.8}$Ti$_{0.2}$O$_3$ (vertical phase), (c) up-bilayer (vertical phase), (d) down-bilayer (lateral amplitude), (e) up-graded (vertical phase), and (f) down-graded (lateral amplitude) variants.

5.4 PFM Analysis of Ferroelectric Domain Structure

The XRD observations are further supported by imaging the ferroelectric domain structure of these variants using PFM. Analysis of the single-layer PbZr$_{0.8}$Ti$_{0.2}$O$_3$ variants [Fig. 5.4 a] confirms the presence of out-of-plane and in-plane oriented domains consistent with 90° domain structures typically observed in such tetragonal ferroelectrics. The single-layer PbZr$_{0.8}$Ti$_{0.2}$O$_3$ variants, however, display a much more complex domain structure [Fig. 5.4 b] indicative of the rhombohedral structure and reminiscent of the mosaic domains observed in BiFeO$_3$ thin films. Up-bilayer variants [Fig. 5.4 c] (with PbZr$_{0.8}$Ti$_{0.2}$O$_3$ at the top of the film) display a complex domain structure similar to the single-layer PbZr$_{0.8}$Ti$_{0.2}$O$_3$ variants while the down-bilayer variants [Fig. 5.4 d] reveals the presence of $a_1$ and $a_2$ domains consistent with a tensile strained Ti-rich (tetragonal) phase. Finally, the up-graded variants exhibit domain structures consisting of $c$ and $a$ domains (generally found in Ti-rich, tetragonal phases of PZT) [Fig. 5.4 e] despite the fact that the top 50 nm of this heterostructure is made up of Zr-rich (rhombohedral) phases. On the other hand, the down-graded variants exhibit a domain structure much like that in the down-bilayer variants where there are $a_1$ and $a_2$ domains as expected from a tensile strained Ti-rich (tetragonal) phase [Fig. 5.4 f].
Both the RSMs and the PFM images confirm an unexpected observation - the ability to produce a tetragonal-like version of Zr-rich PZT. Such a tetragonal variant of the parent rhombohedral compositions has been predicted previously but was thought to be challenging to obtain due to the difficulty in retaining such large strains in thin films [129]. It appears, however, that compositional gradients can be used to dramatically extend the range of strain (similar to the approaches used in traditional group IV and III-V semiconductors) and thereby enable Zr-rich phases to be strained considerably more than is possible in a single layer film. These XRD and PFM studies suggest that the ultimate structure of the bilayer and compositionally graded heterostructures is determined by the initial phase that grows thereby producing an asymmetry in the observed structures.

### 5.5 Ferroelectric Properties of Compositionally Graded PZT Thin Films

We proceeded to probe the impact of this complex structural evolution on the dielectric and ferroelectric properties of the graded heterostructures at room temperature. Symmetric capacitor structures (circular capacitors, diameter 25-100 µm) with epitaxial SrRuO$_3$ electrodes were fabricated using an MgO-based hard-mask process described in Chapter 4. Capacitance-voltage and polarization hysteresis studies were performed as a function of frequency and excitation voltage to compare the response across the different heterostructures.

We begin with the polarization hysteresis of the different heterostructures [Fig. 5.5]. Two distinct behav-
iors were observed; that for down-bilayer and down-graded and that for up-bilayer and up-graded variants. The down-bilayer and down-graded variants [Fig. 5.5 a] both show symmetric hysteresis loops with greatly diminished remnant and saturation polarization compared to single-layer films of both PbZr$_{0.2}$Ti$_{0.8}$O$_3$ and PbZr$_{0.8}$Ti$_{0.2}$O$_3$. This is likely explained by the fact that both variants possess a large fraction of in-plane polarized $a$ domains of the tetragonal phase (which cannot be switched to be out-of-plane polarized) and thus nearly half of the film is essentially ferroelectrically inactive in this device geometry. The up-bilayer and up-graded variants, on the other hand, show very different behavior [Fig. 5.5 b] with significantly shifted (along the field axis) hysteresis loops and large saturation and remnant polarization (commensurate with that measured in the single-layer films). In the case of the up-bilayer and up-graded variants, the stabilization of tetragonal-like structures means that the entire thickness of the film can produce switchable polarization (thus the large saturation and remnant polarization). More interestingly, the up-bilayer and (more so) the up-graded variants show large horizontal shifts of the hysteresis loops (along the electric field axis) of up to $\sim 200$ kV/cm that are not observed in any of the other sample variants. We note that by reversing the polarity of the hysteresis measurements (i.e., with the drive-voltage applied to the bottom electrode and the top electrode grounded) we observed that the hysteresis loop was shifted in the opposite direction, as expected [Fig. 5.6]. Although reminiscent of imprint which can occur due to a variety of extrinsic factors such as space charge accumulation due to asymmetric electrodes or the presence of defect dipoles within the ferroelectric [130, 131], the observed shifts of the hysteresis loop are indeed intrinsic to the sample.
Figure 5.7: Rayleigh analysis of the six PZT heterostructures showing the low-field dielectric response and tanδ for (a) single-layer PbZr$0.2$Ti$0.8$O$_3$, (b) single-layer PbZr$0.8$Ti$0.2$O$_3$, (c) up-bilayer, (d) down-bilayer, (e) up-graded, and (f) down-graded variants.

Classic imprint can be easily eliminated with symmetric capacitor structures and oxide electrodes (such as the SrRuO$_3$ electrodes used here) and the fact that only the up-bilayer and up-graded variants show the shift indicates a different driving force for this effect. Prior work on single-layer thin films, however, has highlighted the role of strain gradients (or flexoelectricity) within the film as a possible mechanism for the formation of a built-in electric field [132–134]. Our structural studies have revealed significant retention of compressive strain in the up-graded variant resulting in strain gradients as large as $4.3 \times 10^5$ m$^{-1}$ (corresponding to a 4.3% strain gradient over a 100 nm thick film) which could be responsible for the observed voltage offsets. A detailed theoretical investigation of the origin of the voltage offset and its relation to the structural relaxation is performed in the next Chapter using a phenomenological GLD model.

The observed built-in electric fields also have a large effect on the small signal dielectric permittivity ($\epsilon_{33}$) of the heterostructures. Detailed Rayleigh studies [Fig. 5.7] were used to determine the measurement voltage and confirm the absence of irreversible contributions to the permittivity. The frequency-dependent permittivity falls into three distinct regimes. The single-layer PbZr$0.8$Ti$0.2$O$_3$, the down-bilayer, and the down-graded variants exhibit permittivity values in excess of 300 across all frequencies studied [Fig. 5.8 a, b] which is consistent with what is expected for samples possessing polydomain structures and large extrinsic contribution from domain walls. The single-layer PbZr$0.2$Ti$0.8$O$_3$ variants show intermediate permittivity with a value around 250 across all frequencies studied. This is consistent with the value reported in polydomain films with similar domain structures in Chapter 4. Finally, the up-bilayer and up-graded variants
Figure 5.8: (a) Dielectric permittivity and (b) loss tangent for each of the six sample variants as a function of frequency.

exhibit considerably reduced permittivity between 80-120 at all frequencies studied. This is comparable to the intrinsic dielectric constant of single-domain PZT [71].

It has been shown previously that inhomogeneous strain or strain gradients can lead to significant reduction in dielectric permittivity [132–134]. Our studies confirm this observation exactly with the variants exhibiting the lowest permittivity corresponding to those variants observed to have the largest strain gradients. These prior studies, however, do not comment on the microscopic mechanism giving rise to reduced dielectric response. We contend that the presence of built-in fields can reduce the extrinsic contribution from domain walls due to an effective stiffening or pinning of the domain walls due to the increased stability of a single polarization variant at zero bias. In other words, the presence of a built-in potential pointing parallel to the \( c \) domains of these heterostructures, could potentially skew the energy landscape such that the small signal susceptibility is greatly diminished. We have further extracted values of the Rayleigh coefficient for each sample variant which supports these observations [Table 5.1]. The Rayleigh coefficient is a quantitative measurement of the irreversible domain wall contribution to the permittivity. We observe larger Rayleigh coefficients for single-layer \( \text{PbZr}_{0.8}\text{Ti}_{0.2}\text{O}_3 \), down-bilayer, and down-graded variants as compared to up-bilayer and up-graded variants suggesting that domain wall motion in the later variants is suppressed and could be playing a role in decreasing the overall permittivity of the samples.

We have also performed a detailed characterization of the pyroelectric properties of the six heterostructures at 320 K using the low-frequency phase-sensitive technique presented in Chapter 4 [Table 5.1]. These measurements indicate that the up-graded and the up-bilayer variants possess the highest pyroelectric coefficient, comparable in magnitude to the single layer \( \text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3 \) variant. We observe that the down-bilayer
Table 5.1: Rayleigh coefficient and pyroelectric susceptibility for the six graded PZT sample variants.

<table>
<thead>
<tr>
<th>Heterostructure</th>
<th>$\alpha$ (cm/kV)</th>
<th>$\pi$ ($\mu$C/m²K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbZr$<em>{0.2}$Ti$</em>{0.8}$O$_{3}$</td>
<td>1.4</td>
<td>-300</td>
</tr>
<tr>
<td>PbZr$<em>{0.8}$Ti$</em>{0.2}$O$_{3}$</td>
<td>2.06</td>
<td>-229</td>
</tr>
<tr>
<td>Up-bilayer</td>
<td>0.33</td>
<td>-299</td>
</tr>
<tr>
<td>Down-bilayer</td>
<td>1.87</td>
<td>-77</td>
</tr>
<tr>
<td>Up-graded</td>
<td>0.28</td>
<td>-291</td>
</tr>
<tr>
<td>Down-graded</td>
<td>0.59</td>
<td>-185</td>
</tr>
</tbody>
</table>

and down-graded variants possess a significantly reduced pyroelectric coefficient, possibly due to the small fraction of out-of-plane oriented domains. The large pyroelectric coefficients and reduced permittivity in up-graded and up-bilayers is particularly important in devices since a large number of applications such as pyroelectric energy harvesting and infrared radiation detection have figures of merit proportional to $\pi/\sqrt{\varepsilon}$. As a result, compositional gradients can be utilized to improve the pyroelectric properties while reducing the dielectric constant and thus enabling better pyroelectric device performance. In fact, the up-graded PZT heterostructures have figures of merit a factor of 1.75 and 2.5 better than the single layer variants of PbZr$_{0.2}$Ti$_{0.8}$O$_{3}$ and PbZr$_{0.8}$Ti$_{0.2}$O$_{3}$, respectively.

Finally, we have explored capacitance - voltage butterfly loops and interesting differences were observed between sample variants that do and do not exhibit built-in electric fields in the ferroelectric hysteresis. For example, the up-graded variants [Fig. 5.9 a] exhibit two distinct small-signal permittivities and asymmetric butterfly loop shape whereas down-graded variants [Fig. 5.9 b] exhibit a single value of small-signal permittivity and a symmetric loop shape. This could have potential for new modalities of non-volatile, low-power memories. Unlike traditional ferroelectric memories which require multiple capacitors to store a single data bit and destructive read/write operations, a new configuration based on the measurement of zero-bias capacitance would offer smaller feature size and non-destructive read operations. Additionally, other applications (e.g., piezoelectric vibrational energy scavenging) that require a constant and known polarization direction to enable repeatable and consistent device operation could utilize such materials. In particular, to improve the performance of a material in piezoelectric vibrational energy scavenging applications, one needs a material which simultaneously exhibits large piezoelectric response, low dielectric constant, and improved robustness to depolarization/aging. Traditionally this has been achieved in ferroelectrics by utilizing imprint or built-in electric fields that arise from the use of asymmetric electrodes. The use of compositionally graded materials could provide a new pathway to improved performance in each of these areas.
5.6 Conclusions

Bilayer and compositionally graded PZT variants have been observed to possess exotic structural and ferroelectric properties that are largely determined by the structure of the initial growth layer. We have observed that up-bilayer and up-graded variants exhibit nearly coherently strained, tetragonal-like crystal and ferroelectric domain structures despite having large fractions of the film with compositions on the rhombohedral side of the bulk PZT phase diagram. Analogous to prior work in traditional semiconductor systems, the compositional grading of the film gives rise to a gradual increase in the magnitude of strain from the substrate and a reduced susceptibility to strain relaxation. This results in heterostructures which possess ferroelectric hysteresis loops with large voltage offsets, large remnant polarization, and low permittivity compared to other sample variants. Composition and strain gradients are, in turn, demonstrated as a powerful new tool to tune the properties of ferroelectric thin films and further evolution of this concept could represent a new direction in epitaxial thin film manipulation of complex oxide materials.
In the previous Chapter, we presented a detailed experimental study of the structural and ferroelectric properties of compositionally graded PZT thin films. We observed that the compositional gradients give rise to a number of novel properties which are not found in the single layer variants including large voltage offsets and reduced dielectric permittivities. The physical origin of these behavior, however, is unclear.

In this Chapter we perform a detailed investigation of the voltage offsets in compositionally graded PZT thin films using a GLD theory which includes the effects of structural relaxation via dislocation formation. Our work indicates that the observed physical properties of such films are the result of a delicate interplay between strain relaxation, the polarization distribution within the film, and flexoelectric interactions. The experimentally observed ferroelectric hysteresis and comparisons to GLD models reveal that the built-in electric field is intrinsic to the graded thin film and is a direct consequence of the strong flexoelectric coupling between the out-of-plane polarization and the in-plane epitaxial strain.
6.1 Graded Ferroelectric Thin Films: Prior Work

Ferroelectric materials have broken inversion symmetry at the unit cell level. Bilayer and compositionally graded thin-film ferroelectric heterostructures additionally have macroscopic broken inversion symmetry across the thickness of the material. Such macroscopic inversion symmetry breaking and the associated novel physical properties have attracted widespread experimental and theoretical attention in the past decade. In contrast to single component ferroelectrics, the degeneracy between the two polarization states in these materials is broken by a built-in electric field which has been shown to result in self-poling, shifted hysteresis loops, enhanced susceptibilities, and signatures of geometric frustration [120,122–124,135–137]. Such a built-in bias within the material is typically generated by an inhomogeneous strain through lattice engineering (via multicomponent superlattices) [138,139], or a global composition gradient [120,122,123,135–137]. Since the built-in fields can result in enhanced susceptibilities and directly affect the polarization switching characteristics, understanding the origin of the observed behavior is key to utilizing it in practical applications such as non-volatile memories, piezoelectric sensors, and thermal imaging systems. In spite of extensive theoretical and experimental studies on compositionally graded ferroelectric heterostructures over the last two decades, the physical mechanism behind the built-in fields has been difficult to identify due to a plethora of intrinsic and extrinsic factors that have been proposed to give rise to the observed behavior.

Early experiments on compositionally graded heterostructures reported a shift in the polarization (vertical) axis of the hysteresis loop and gradients in the polarization within the material were believed to cause the observed offsets [123,137]. The measured vertical offsets, however, were explicitly dependent on the measurement circuit (i.e., the reference capacitor of the Sawyer-Tower circuit and the applied voltage) [137,140] with an exponential approach to a stable equilibrium after the application of an electric field and corresponded to physically unrealistic values of polarization (> 250 µC/cm²) in compositionally graded PZT films) [120,141]. Later work [121] indicated that these observed shifts should, in fact, be along the voltage (horizontal) axis due to a built-in electric field, but can manifest itself as a polarization offset in a hysteresis measurement under certain measurement configurations. These shifts are distinctly different from shifts in hysteresis loops that arise from extrinsic effects such as asymmetric electrodes or the inhomogeneous distribution of oxygen vacancies in the capacitor [141,142]. The effects of interest are intrinsic to the material and result from the macroscopic broken inversion symmetry. Further, theoretical work has also pointed out that apart from a polarization gradient, inhomogeneities in composition and strain can also play a role in generating a symmetry breaking internal field [132,143–145]. In particular, flexoelectric coupling (which relates polarization and strain gradients in a material) has been recently shown to significantly affect the
properties of ferroelectrics, particularly in thin films with large strain gradients due to structural relaxation via misfit dislocation formation and near surfaces and interfaces [126, 127, 133, 134, 146]. This is primarily due to the much larger strain gradients that can be sustained in thin films (\(>10^5 \text{m}^{-1}\)) as compared to that which is possible in bulk crystals or sintered ceramic materials (\(<1 \text{m}^{-1}\)) [127, 144]. The effects of composition variation, structural relaxation, strain gradients, and flexoelectric coupling, however, have not been addressed in any study of compositionally graded ferroelectric thin films although these effects are certainly present and likely greatly impact the properties of such systems.

6.2 GLD Theory of Compositionally Graded Ferroelectric Thin Films

We focus on 100 nm thick, compositionally up-graded and down-graded heterostructures of PZT with end members \(x = 0.2\) and \(x = 0.8\). The thin films grown on GdScO\(_3\) (110) substrates, whose structural and ferroelectric properties have been extensively characterized in the previous Chapter, form the focus of this theoretical study. On GdScO\(_3\) (110) the lattice mismatch with the PbZr\(_{0.2}\)Ti\(_{0.8}\)O\(_3\) and PbZr\(_{0.8}\)Ti\(_{0.2}\)O\(_3\) end-members are +0.8% (tensile) and -3.5% (compressive), respectively. Ferroelectric hysteresis loops of the two different compositionally graded heterostructures reveal dramatically different behavior [Fig. 6.1]. Hysteresis loops obtained from compositionally up-graded films reveal large saturation and remnant polarization, square hysteresis loops, and a large voltage offset while those from compositionally down-graded samples reveal low saturation and remnant polarization, slanted hysteresis, and no voltage offsets. At first glance, the films should both possess the same magnitude of composition and polarization gradient across the thickness of the film and, therefore, the presence of a voltage offset in the compositionally up-graded thin film alone is unexpected. In reality, vastly different compatibility between the various phases and the substrate, changes in crystal structure and symmetry, and corresponding variations in polarization likely combine to result in a complex and potentially unexpected manifestation of unusual structural and ferroelectric properties. The current Chapter is meant to develop a physical picture of the interplay of strain and strain relaxation, structural evolution, and polarization in these novel heterostructures and to provide insights as to the driving force for voltage offsets in some heterostructures and not others.
6.3 The Model: Free Energy and Boundary Conditions

To rationalize the observed ferroelectric properties and understand the origin of the built-in fields, we utilized a GLD phenomenological model including the effects of local inhomogeneities in polarization ($P$) and stresses ($\sigma$), flexoelectric coupling between polarization and stress gradients, and misfit dislocation formation to provide a realistic theoretical foundation to understand compositionally graded ferroelectric heterostructures. For the case of 2D clamped thin films, the correct thermodynamic description is provided by a Legendre transformation of the Gibbs free energy density ($G$) as [43]

$$\tilde{G} = G + u_1 \sigma_1 + u_2 \sigma_2 + u_6 \sigma_6$$

(6.1)

where $u_i$ and $\sigma_i$ represent the strains and stresses, respectively (in the Voigt notation, with $x_3$ perpendicular to the film-substrate interface). For the case of monodomain (001)-oriented thin films grown on cubic substrates, $G$ can be written as [146,147]

$$G(x_3) = \alpha_i P_i^2 + \alpha_{ij} P_i^2 P_j^2 + \alpha_{ijk} P_i^2 P_j^2 P_k^2 - s_{ijkl} \sigma_{ij} \sigma_{kl} - Q_{ijkl} \sigma_{ij} P_k P_l$$

$$+ g_{ijkl} \left( \frac{\partial P_i}{\partial x_j} \right) \left( \frac{\partial P_k}{\partial x_l} \right) + \frac{1}{2} \mu_{ijkl} \left( \sigma_{ij} \frac{\partial P_k}{\partial x_l} - P_k \frac{\partial \sigma_{ij}}{\partial x_l} \right)$$

(6.2)
where $P_i$ are the polarization components, $\sigma_{ij}$ are the components of the stress tensor, $\alpha_i$, $\alpha_{ij}$, and $\alpha_{ijk}$ represent the bulk stiffness coefficients, $s_{ijkl}$ are the components of the elastic compliance tensor, $Q_{ijkl}$ are the electrostrictive coefficients, $g_{ijkl}$ are the gradient energy coefficients, and $\mu_{ijkl}$ are the flexoelectric coefficients. The stiffness coefficients, elastic compliances, and electrostrictive coefficients for the PZT system were obtained from Refs. [58] and [59]. The composition dependence of the material constants and the stiffness coefficients is reflected in a position dependence of all quantities except for the flexoelectric coupling and the gradient energy coefficients in Eq. 6.2. In the absence of experimental measurements of flexoelectric coupling in PZT across the composition, a constant value was used for the entire range of compositions studied here [147]. The gradient energy coefficients were taken as $g_{11} = 2 \times 10^{-10} \text{C}^{-2} \text{m}^4 \text{N}$ and $g_{44} = 1 \times 10^{-10} \text{C}^{-2} \text{m}^4 \text{N}$ [148].

The depolarizing fields within the film are neglected due to the thickness of our films [in this case 100 nm which is much larger than the screening length of standard oxide electrodes ($\sim 1 \text{Å}$)] [149], the presence of symmetric electrodes, and the finite conductivity of PZT [61]. The free energy was supplemented by the relevant mechanical and electrical boundary conditions as shown below and minimized numerically to obtain the equilibrium state of the polarization and stress/strain within the film.

The stress components in Eq. 6.1 are obtained using $u_1 = u_2 = u$ and $u_6 = \sigma_3 = \sigma_4 = \sigma_5 = 0$, where $u_i = \frac{\partial G}{\partial \sigma_i}$. The total in-plane strain ($u$) within the film is a function of the distance $x_3$ away from the substrate interface and is different from the misfit strain ($u_m(x_3)$) with the substrate due to strain relaxation. It should be noted that the misfit strain itself varies with $x_3$ due to the composition dependence of lattice constants in PZT and is calculated as $u_m(x_3) = 1 - \frac{a_f(x_3)}{a_s}$ where $a_f$, $a_s$ are the film and substrate lattice parameters, respectively. The lattice constants of PZT as a function of composition were obtained from Ref. [27] and [28].

Including the effect of misfit dislocation formation at a temperature $T_g$, the total strain can be obtained by minimizing the total strain energy. This total strain energy per unit area ($U$) is given as [51,117,119]

$$U = \int_0^t \left[ Y \left( u_m \pm \frac{x_3}{\rho b \cos \lambda} \right)^2 + G \frac{\rho |b|^2}{2 \pi} \ln \left( \frac{t - x_3}{|b|} \right) \right] dx_3$$

where the first term represents the reduction in energy due to misfit dislocation formation and the second term represents the energy cost of forming dislocations. In this equation $Y$ is the biaxial modulus, $G$ is the shear modulus, $t$ is the thickness of the film, $\rho$ is the dislocation density, and $b$ is the Burgers vector for the lowest energy dislocations (i.e., $\langle 110 \rangle$ dislocations inclined at $\lambda = 45^\circ$ to the substrate [51]. The sign of $b$ in the first term is chosen to reduce the misfit strain at that location with $|b| = \sqrt{2a}$. The equilibrium density of misfit dislocations and the total strain were obtained by minimizing $U$ using a modified look-ahead
Figure 6.2: Evolution of strain in compositionally graded thin films including the theoretical lattice misfit strain ($u_m$) at 300 K (black dashed line) and 800 K (grey dash-dot line) as well as the total strain ($u$) at 300 K (as calculated by the various model variants) for compositionally (a) up-graded and (b) down-graded thin films. The magnitude of the strain relieved by dislocation formation ($|u - u_m|$) is also shown for compositionally (c) up-graded and (d) down-graded films. The four model variants considered are $Y = G$, $T_g = 300$ K (red), $Y > G$, $T_g = 300$ K (green), $Y = G$, $T_g = 800$ K (blue), and $Y > G$, $T_g = 800$ K (orange) and the striped grey regions represent the values bounded by the various models.

Strain relaxation via misfit dislocation formation, as described above, has been studied previously for perovskite ferroelectrics assuming complete relaxation at the growth temperature and no further dislocation formation at lower temperatures [51]. Complementary work on semiconductor systems, however, typically assumes evolution of equilibrium dislocation distributions down to room temperature [119]. In reality, the actual distribution is bounded by these two extremes as dislocation formation is often kinetically limited and is not well understood for complex perovskite ferroelectrics grown in their paraelectric state such as the compositionally graded films used in this study. The equilibrium distribution of dislocations calculated minimizing scheme [119]. Details of the minimization procedure are included in Appendix B.
above provides a good starting point for the theoretical analysis of the strain relaxation during the synthesis of such compositionally graded heterostructures [117]. To tackle this ambiguity in our understanding of the relaxation processes, we calculated the dislocation density and strain distribution at \( T_g = 800 \text{K} \) and \( 300 \text{K} \). Additionally, there are different approaches to the definition of the elastic moduli (\( Y \) and \( G \)) for the different defect formation processes. As per existing models of strain relaxation two cases were considered for the elastic stiffness: 1) \( Y = C_{11} + C_{12} - 2C_{12}^2/C_{11}, G = (C_{11} - C_{12})/2 \) (henceforth referred as \( Y > G \)) and 2) \( Y = G = C_{11} + C_{12} - 2C_{12}^2/C_{11} \) (henceforth referred to as \( Y = G \)) where \( C_{ij} \) are the components of the elastic stiffness tensor. Finally, the strain distribution for dislocation formation at \( T_g = 300 \text{K} \) is given by \( u(x_3) = u_m(x_3) \pm \int_0^{x_3} \rho_b \cos \lambda \). It should be noted that calculations at \( T_g \neq 300 \text{K} \) must be appropriately scaled due to thermal expansion of the substrate and the film. In this case, the misfit strain at \( T_g \) is relaxed by dislocation formation at that temperature and the final total strain at room temperature (\( T_r \)) is calculated as

\[
u(x_3, T_r) = 1 - \frac{\alpha_g(x_3)}{\alpha_s(x_3, T_r)} \text{ where } \alpha_s(x_3, T_r) = \alpha_s(x_3, T_g)[1 + \alpha_s(T_r - T_g)] \text{ and } \alpha_s = \text{the thermal expansion coefficient of the substrate.}
\]

The thermal expansion coefficients for the GdScO\(_3\)(110) substrate and PbZr\(_{1-x}\)Ti\(_x\)O\(_3\) film were taken as \( 12 \times 10^{-6} \text{K}^{-1} \) and \( 5.4 \times 10^{-6} \text{K}^{-1} \) respectively [112, 113]. Thus, we considered four model variations: 1) strain relaxation at high-temperatures only with equivalent moduli (\( Y = G, T_g = 800 \text{K} \)), 2) strain relaxation at high-temperatures with different moduli (\( Y > G, T_g = 800 \text{K} \)), 3) strain relaxation down to room temperature with equivalent moduli (\( Y = G, T_g = 300 \text{K} \)), 4) strain relaxation down to room-temperature with different moduli (\( Y > G, T_g = 300 \text{K} \)) [Fig. 6.2]. For comparison, the unrelaxed lattice misfit strain (\( u_m(x_3) \)) calculated both at 300 K and 800 K is provided.

For all model variations studied, we find that the overall trends follow, unsurprisingly, the nature of the lattice mismatch. The shaded areas in [Fig. 6.2] represent the range of expected results as bounded by the various models. For the compositionally up-graded heterostructure [Fig. 6.2 a] there is a significant substrate induced compressive strain retained throughout the thickness of the film. In contrast, the formation of a high density of dislocations at the film-substrate interface (calculated dislocation densities are as large as \( 10^{16} \) – \( 10^{17} \) m\(^{-2}\)) results in significant strain relaxation in the compositionally down-graded heterostructure [Fig. 6.2 b]. As a result, a large fraction of the down-graded film is placed under tensile strain due to the large in-plane lattice parameter of the relaxed Zr-rich underlayer which screens the Ti-rich region from the substrate lattice. This trend is further clarified by examining the magnitude of the strain relieved via dislocation formation (i.e., \( |u(x_3) - u_m(x_3)| \)) for both the up- and down-graded thin films [Fig. 6.2 c-d]. A significantly smaller amount of the strain is relieved near the substrate interface for the up-graded film (\( \sim 0.2\% \)) as compared to the down-graded film (\( \sim 2\% \)). This is supported by the dislocation density
extracted from the models which suggests that the down-graded films possess a dislocation density nearly two orders-of-magnitude larger than that of the up-graded films in the near interface limit. Furthermore, despite minor variations in the calculated strain distribution between the various models, the simulations identify an important trend - the structural compatibility of the bottom-most layer and the substrate plays a crucial role in determining the overall strain distribution in the heterostructure. From this analysis, it is found that the compositionally up-graded heterostructures possess an overall compressive strain and are generally less relaxed due to the better structural compatibility with the substrate. The compositionally down-graded heterostructures, on the other hand, relax rapidly near the substrate (due to a large misfit strain) through misfit dislocation formation and as a result, have an overall tensile strain over the majority of the film. This insight is confirmed by structural characterization of the heterostructures by X-ray reciprocal space mapping studies presented in the previous Chapter which revealed that the compositionally up-graded heterostructures are more coherently strained to the substrate throughout the film thickness while the compositionally down-graded heterostructures reveal relaxed phases.

To understand how this strain distribution affects the polarization within the films, the GLD free energy in Eq. 6.1 was minimized numerically with the total strain distribution. The usual boundary condition for the polarization components $P_i$ is modified by flexoelectricity and for the case of short-circuited thin films,
acquires the form \[146,147,150\]

\[n_3 g_{44} \frac{\partial P_i}{\partial x_3} + n_3 \mu_{12} P_i (Q_{11} + Q_{12}) \frac{\partial}{\partial x_3} \left( \frac{P_i}{s_{11} + s_{12}} \right) + g_{44} \frac{P_i}{\delta} = 0; i = 1, 2\]

\[n_3 \left( g_{11} + \mu_{12} \frac{u_s}{s_{11} + s_{12}} \right) \frac{\partial P_3}{\partial x_3} + n_3 \mu_{12} u_s \frac{P_3}{s_{11} + s_{12}} + g_{11} \frac{P_3}{\delta} - n_3 \frac{\mu_{12} (Q_{11} + Q_{12}) (P_1^2 + P_2^2) + 2Q_{12}P_3^2}{2(s_{11} + s_{12})} = 0\]

where \(n_3\) is the unit vector along the surface normal, \(\delta\) is the extrapolation length at the surface, and \(u_s\) is the value of the in-plane strain at the boundary (i.e., \(x_3 = 0, 100 \text{ nm}\)). Upon solving the equations of state for polarization in three dimensions, we observe that for compositionally up-graded heterostructures that as one transitions from the film-substrate interface to the film surface, the increasing compressive strain in the film causes the in-plane polarization \(P_1 = P_2\) [Fig. 6.3 a] to reduce and the out-of-plane polarization \(P_3\) [Fig. 6.3 b] to increase. This is unexpected since the top-most portion of the film should possess a rhombohedral-like crystal structure with strong in-plane polarization components. The models suggest that compositionally grading the heterostructure allows one to quench the in-plane polarization at the expense of out-of-plane polarization in these heterostructures. In the case of compositionally down-graded heterostructures, on the other hand, as one transitions from the film-substrate interface to the film surface, the increasing tensile strain in the film causes the in-plane polarization \(P_1 = P_2\) [Fig. 6.4 a] to increase and the out-of-plane polarization \(P_3\) [Fig. 6.4 b] to decrease. In fact, the effect of tensile strain

Figure 6.4: Evolution of (a) in-plane \((P_1 = P_2)\) and (b) out-of-plane \((P_3)\) polarization across the thickness of a 100 nm thick compositionally down-graded film at 300 K. For comparison, the same polarization components are calculated for coherently strained films (black dashed line labeled no relaxation). Again results from all four variations of the strain relaxation model are provided including \(Y = G, T_R = 300 \text{ K}\) (red), \(Y > G, T_R = 300 \text{ K}\) (green), \(Y = G, T_R = 800 \text{ K}\) (blue), and \(Y > G, T_R = 800 \text{ K}\) (orange).
is so strong, that the top-most portion of the film possessing tetragonal-like crystal structure must orient its long axis of polarization in the plane-of-the-film to accommodate this lattice mismatch and strain. This observation is consistent with piezoresponse force microscopy of the as-grown heterostructures presented in Chapter 5 and helps explain the diminished remnant polarization values reported herein [Fig. 6.1] since a considerable fraction of heterostructure cannot be switched upon application of electric field along the substrate normal.

![Figure 6.5: Evolution of out-of-plane polarization across the thickness for a 100 nm thick compositionally (a) up-graded and (b) down-graded films at 300 K including the effect of depolarization fields. For comparison, the out-of-plane polarization component is calculated for coherently strained films (black dashed line labeled no relaxation). The results from all four models variants $Y = G, T_g = 300\,\text{K}$ (red), $Y > G, T_g = 300\,\text{K}$ (green), $Y = G, T_g = 800\,\text{K}$ (blue), and $Y > G, T_g = 800\,\text{K}$ (orange) are included.](image)

As stated above, prior modeling approaches to similar systems have suggested that depolarization effects may not be required in these models to accurately predict the properties. Nonetheless, because of the complexity of the continuously changing polarization throughout the thickness of the film and based on recent reports showing the potential importance of such effects in compositionally graded films we completed additional models including depolarization effects [151]. We extended the GLD simulations detailed in the manuscript with an added depolarization energy term to the free energy of the form $-\frac{1}{2}E_dP_3$ where $E_d = -(P(x_3) - \langle P_3 \rangle)/(\epsilon_0\epsilon_b)$ and $\langle P_3 \rangle = \frac{1}{t} \int_0^t P(x_3)dx_3$. Here, $\epsilon_b$ is the background dielectric permittivity ($\epsilon_b = 50$ for the simulations performed here) and $t$ is the thickness of the film. Including the effect of such a depolarization energy term, the result of the simulations are shown above [Fig. 6.5 a,b]. Such models reveal two main effects: 1) a reduction in the overall value of the polarization in the film and 2) significant flattening in the polarization profile across the thickness for both compositionally up-graded and down-graded heterostructures. Models including depolarization effects predict a nearly uniform polarization
through the thickness and an almost identical polarization values for compositionally up-graded and down-graded heterostructures. This is in incompatible with both the ferroelectric hysteresis loop measurements and the piezoresponse force microscopy imaging of the domain structures in the heterostructures. It appears that even in a system where the polarization is changing continuously, the fact that these films are “thick” (i.e., much thicker than the screening length of standard oxide electrodes) and that the PZT films possess finite conductivity renders the inclusion of depolarization effects unnecessary.

6.4 Origin of the Built-in Fields

The free energy, when supplemented with the boundary conditions and simplified to eliminate the stress components, generates symmetry breaking terms (proportional to odd powers of $P_3$ and the flexoelectric coefficient) within the thickness which manifest as a built-in field. This flexoelectric contribution to the free energy density ($G_\mu$) is directly proportional to the flexoelectric coefficient as $G_\mu = -\frac{\mu_{12} P_3}{s_{11} + s_{12}} \frac{\partial u}{\partial x_3}$. To further illuminate the role of flexoelectricity in determining the properties of this system, we performed simulations both with and without the flexoelectric coefficient. These studies reveal that while the flexoelectric coupling does impact the built-in field (and the macroscopic voltage offset) it does not affect the average value of polarization within the film (although it can slightly adjust the values near the film surfaces). As a result, the flexoelectric coupling is found to be responsible for the shifts of the hysteresis loops horizontally, but does not affect the absolute values of the polarization within the material. From the form of the free energy, it is clear that the built-in field requires the presence of both a gradient in the in-plane strain and also the presence of a non-zero polarization along the out-of-plane direction. In the compositionally up-graded heterostructures, the presence of a non-zero $P_3$ throughout the thickness results in a finite internal bias and it can be estimated that for a system with $\mu_{12} = -10^{-10} \text{m}^3$, $s_{11} + s_{12} = 5 \times 10^{-12} \text{m}^2 / \text{N}$, and $\frac{\partial u}{\partial x_3} = -5 \times 10^5 \text{m}^{-1}$ (or a 5% strain gradient across the 100 nm film such as in the case of the coherently strained compositionally up-graded heterostructure) the built-in field is $\approx 100 \text{kV/cm}$ close to the observed value of 200 kV/cm. It should be noted that at the present time, the flexoelectric coefficients and the elastic coefficients are not known accurately enough (both in magnitude and as a function of composition) to calculate a more reliable value theoretically. In the case of compositionally down-graded heterostructures, the lack of an internal bias is also consistent since it has a relaxed rhombohedral layer near the substrate (which reduces the effective strain gradients) and tensile strained tetragonal regions near the surface which have negligible out-of-plane polarization (but a finite strain gradient). As a result, it is clear that the internal bias in compositionally up- and down-graded heterostructures originates from the flexoelectric coupling between the strain gradients and
out-of-plane polarization within the film. Thus, flexoelectricity could play a large effect in nanoscale systems such as thin films which can support large strain gradients. Additionally, our work suggests that these effects may be manifested in counterintuitive manners due to complex stain relaxation and concomitant polarization evolution that occurs in these materials.

6.5 Conclusions

In conclusion, we have performed a detailed study of compositionally graded ferroelectric heterostructures using novel GLD phenomenological models that shed light on the origin of built-in electric fields in these materials. The models indicate that flexoelectric coupling between the out-of-plane polarization and the in-plane epitaxial strain is responsible for the built-in fields and the observed voltage offsets in the hysteresis loops. The interplay of structural compatibility between the film and the substrate, strain relaxation, and polarization distribution, however, results in a complex evolution of properties with gradients in composition. Further theoretical and experimental work is necessary to develop more realistic models of strain relaxation and polarization evolution in the presence of flexoelectricity in these materials. This work has established the importance of flexoelectricity in compositionally graded ferroelectric heterostructures and shown that through a careful consideration of strain and polarization distributions, large built-in electric fields can be obtained in such systems.
Chapter 7

Pyroelectric Energy Conversion

In the previous Chapters we have systematically investigated various pathways including epitaxial strain engineering and composition gradients to control the dielectric and pyroelectric susceptibilities of thin film ferroelectrics using PZT as a model system. In this Chapter, we will leverage the insights from these studies to investigate the effectiveness of ferroelectric thin films for a practical device application of thermal energy harvesting via pyroelectric energy conversion. We present a detailed introduction to reversible energy conversion cycles using ferroelectrics and present preliminary results obtained in microfabricated energy harvesting devices employing thin film ferroelectrics. This Chapter is derived from work in progress with B. Bhatia, H. Cho, and W. P. King.
7.1 Introduction to Pyroelectric Energy Conversion

The pyroelectric effect in ferroelectric materials can be used for electrical power generation from temperature changes via reversible thermodynamic cycles similar to gas phase carnot engines [152–154]. In an ideal carnot engine, the working fluid undergoes a reversible process via two adiabatic and two isothermal steps which enable a conversion of heat to mechanical work. Analogously, in a pyroelectric cycle with a ferroelectric material, the polarization of the ferroelectric is cycled through changes in temperature ($T$) and electric field ($E$). The changes in polarization can be converted to electrical power via the pyroelectric effect through a current in the external circuit. Depending on the path chosen in the $P - E - T$ phase space, different reversible cycles are possible to convert heat to electrical energy [154]. For any such cycle, the total electrical work can be calculated as the area under the $P - E$ curve as

$$W = \oint PdE$$

The direction of the path i.e. clockwise or counterclockwise determines if electrical energy is produced or dissipated. Clockwise cycles correspond to net electrical work output and counterclockwise cycles correspond to energy dissipation.

One commonly used reversible cycle is the Ericsson cycle which consists of two isotherms (at $T_L$ and $T_H$ - for low and high temperatures) and two constant electric field (at $E_L$ and $E_H$ - for low and high fields) steps [Fig. 7.1]. Starting at $T_L$ and $E_H$, the material is exposed to the heat bath bringing the sample to $T_H$ and lowering the polarization of the system. Next, the electric field is decreased to $E_L$, resulting in a decrease in the polarization. From here the material is cooled back to $T_L$ at constant electric field $E_L$, increasing the polarization in the system. And finally the electric field is increased to $E_H$, again increasing the polarization in the system. Each polarization change associated with an electric field or temperature change results in a current flow through the external circuit and conversion of thermal energy to electrical energy. For such a cycle, the efficiency of the energy conversion can be calculated as

$$\eta = \frac{W_{tot}}{Q_{in}}$$

Where $W_{tot}$ is the total work done by the ferroelectric and $Q_{in}$ is the net heat input. Here, $W_{tot}$ is the area under the thermodynamic cycle minus the electrical losses. The electrical losses consists of two major contributions - hysteretic losses and joule heating. The hysteretic losses can be estimated by the area enclosed by minor hysteresis loops at the two temperatures $T_L$ and $T_H$ for the applied range of electric fields and the
leakage of the ferroelectric governs the joule heating. As a result, the work output is maximized for materials with large pyroelectric coefficients and large applied electric fields. At the same time, the electrical losses can be minimized with increased resistivity and reduced hysteresis (i.e., lower frequency and lower electric field amplitudes). In the absence of thermal losses to the surroundings, \( Q_{in} \) is simply equal to \( C \Delta T \), where \( \Delta T = T_H - T_L \) assuming a constant heat capacity \( (C) \) in this range of electric fields and temperature. This is a realistic approximation since the heat capacity of most ferroelectric materials is dominated by the contribution from the lattice and even near the ferroelectric transition, the contribution from the polarization order parameter is \(< 15\%\) of the background lattice contribution \([68, 69]\). As a result, it is clear that even in the absence of any losses, the ultimate efficiency of pyroelectric energy conversion could be low (\(< 10\%\)) and much smaller than the corresponding carnot limit \((= 1 - (T_L/T_H))\). In situations where large temporal fluctuations in temperature exist such as automobiles for example, pyroelectric conversion could, however, be very useful in scavenging wasted thermal energy. In order to reduce the thermal losses and achieve maximal efficiencies, we need materials with large polarization contribution to entropy and careful attention to thermal management issues while cycling.

From the discussion above, it is apparent that efficient pyroelectric energy conversion requires the following characteristics of the ferroelectric

- Large pyroelectric coefficient
- Large polarization (as compared to the lattice) contribution to heat capacity
- Low leakage at high operation temperatures
• Low dielectric constants and hysteretic losses

• Ability to withstand large temperature and electric field fluctuations

In most materials, the requirements above are not independent and as a result, a careful materials optimization is necessary for optimal performance. Early theoretical and experimental studies that investigated pyroelectric energy conversion in ferroelectric ceramics were met with limited success due to the low efficiencies (< 0.1%), low power densities (~10⁻⁴ J/cm³), and small output power (~100 µW) [154, 155]. Pyroelectric energy harvesting has been the subject of renewed interest recently due to the advancement of thin-film epitaxy and an improved prospect for an efficient energy harvester [156, 157].

Epitaxial ferroelectric films offer a number significant advantages over more traditional sintered ceramic samples - they possess exceptional ferroelectric properties (low leakage, high remnant polarization, and tunable ferroelectric susceptibilities), they have a very low thermal mass enabling high frequency operation and a high power output, they operate at low external voltages and possess large breakdown strengths, and they can be easily integrated into modern microfabricated devices. As a result, pyroelectric energy conversion with ferroelectric thin films offers an enormous potential for a disruptive energy technology but there exists no working demonstration of such a device. In the rest of the Chapter, we will present preliminary results from microfabricated ferroelectric energy conversion devices using ferroelectric thin films such as PZT and BST and employing lithographically defined metallic line heaters for fast temperature oscillations.

7.2 Microfabricated Ferroelectric Thin Film Energy Harvesting Devices

7.2.1 Device Design

The schematic of a typical energy harvesting device is shown in Fig. 7.2. Here, the SrRuO₃ / ferroelectric / SrRuO₃ thin film capacitor is fabricated using a two-step MgO based hard-mask process - one for the bottom electrode and one for the ferroelectric and top SrRuO₃ electrode. 200 nm thick PZT or BST thin films were used for the ferroelectric layer and symmetric SrRuO₃ capacitors were utilized to obtain symmetric robust ferroelectric response and to reduce the possibility of contact related measurement artifacts described in Section 4.3. After the deposition of the epitaxial capacitor structure an SiO₂ isolation layer is deposited by plasma-enhanced chemical vapor deposition at 300° C. Finally, Cr-Pt layers are deposited for the 20 µm wide heater line (on top of SiO₂) and to contact the top and bottom SrRuO₃ electrodes for the electrical measurements. The heater lines are used to locally heat the ferroelectric and the SiO₂ prevents
electrical shorting between the heater line and the top or bottom electrodes. Cr is used as an adhesion layer for all the Pt layers.

### 7.2.2 Energy Conversion Cycles

In order to study pyroelectric energy conversion in such a microfabricated platform, an Ericsson-like cycle was applied to the sample using simultaneous control of the electric field and temperature across the samples. The temperature on the ferroelectric was modulated at high frequency ($\omega = 1 - 25$ kHz) using the resistive heater lines with an applied electrical excitation voltage at $\omega/2$. Since the thermal penetration depth is much larger than the film thickness ($\sim 200$ nm) the amplitude of the temperature oscillation in the ferroelectric was calculated for the applied heating voltage using a one-dimensional thermal diffusion model. The electric field across the ferroelectric was modulated simultaneously by voltages applied to the top SrRuO$_3$ electrode. The pyroelectric current generated during the temperature or electric field modulation was collected from the bottom electrode and was used to monitor the changes in the polarization of the ferroelectric.

In a typical cycle, the electric fields and temperature applied across the ferroelectric is modulated as in Fig. 7.3 a with $\Delta T \sim 10 - 100$°C and $\Delta E \sim 10 - 100$ kV/cm. The heating voltage and the electric fields are synced in frequency and phase so as to take the material through an Ericsson-like cycle. Here,
Figure 7.3: (a) Heater strip input voltage, applied out-of-plane electric field applied across the PZT layer, and the resulting current measured using a current amplifier during a typical Ericsson cycle measurement. (b) The Ericsson cycle plotted on the $P - E$ hysteresis loop acquired at the two operation temperatures showing the minor loops for the range of electric fields.

Smooth variations of the temperature and electric fields are utilized and simultaneously minor loops are also acquired at the two operation temperatures to estimate the hysteretic losses during the cycle [Fig. 7.3 b]. As described previously, the net work output per cycle is calculated as the area under the cycle minus the one half the total area of the two minor loops. Due to the large magnitude of the pyroelectric currents during such cycling ($\sim 1 \mu A$) the effect of joule heating is negligible. The contribution of leakage at such frequencies is expected to be $< 0.1 \mu A$ for these measurement conditions. Depending on the area under the minor loops, the total electrical work output ($W_{tot}$) is either positive or negative (corresponding to dissipation). Depending on the electric field and temperature amplitudes, both energy production and dissipation are observed. For a given amplitude of the temperature oscillation and $E_h$, we observe that large $\Delta E$ results in $W_{tot} < 0$ due to the dominance of hysteresis near zero field [Fig. 7.4 a]. As a result, positive work output is observed only for $E_L$ greater than a minimum value. A similar crossover is also observed in frequency dependent experiments for a given $\Delta E$ and $\Delta T$ [Fig. 7.4 b]. At high frequencies, the ferroelectric becomes more hysteretic at a given electric field sweep and as a result large $\Delta E$ results in net energy dissipation. This is in agreement with observations in Chapter 4, where the hysteretic contribution to the $P - E$ loops was found to be more prominent at higher frequencies. The total work output shows an increase at low frequencies, possibly due to the frequency dependence of thermal diffusion lengths. At the same time, due
Figure 7.4: Ericsson cycles acquired for different range of (a) electric field amplitudes and (b) frequencies for $\Delta T \sim 100^\circ C$ on a BaTiO$_3$ ferroelectric thin film. Red and blue cycles correspond to energy harvesting and dissipation respectively.

to the temperature dependence of the pyroelectric coefficients, a higher overall power output could also be obtained at higher $\Delta T$, for a given $T_L$ and $\Delta E$. The effects of leakage could, however, be more important at higher operation temperatures.

Overall, high temperature ramp rates ($> 10^5$ K/s) and large power densities ($> 100$ kW/cm$^3$) are obtained in these microfabricated energy harvesting devices [Fig. 7.5]. An estimate of the overall conversion efficiency of the pyroelectric material (neglecting thermal losses) is $\sim 0.3\%$. These observations have significant implications for the future prospects of pyroelectric energy harvesting. Prior experiments on pyroelectric energy conversion cycles utilized bulk samples and slow (almost quasi-static) heating rates. Therefore, the frequency dependence of the material properties (and hysteresis) was unimportant and the power outputs were low. In our experiments, the high frequency of temperature oscillation results, most importantly, in proportionally higher power outputs. Further, due to the large dependence of ferroelectric polarization and hysteresis on the frequency, the cycling rates have significant effects on the power output. Higher frequencies result in lower leakage but higher hysteretic losses. As a result, a careful choice of the range of operation in terms of electric fields and temperature oscillation is necessary to maximize the power outputs for a given ferroelectric material. Current work aims to perform detailed measurements of these energy conversion cycles and establish design rules for increasing the operating efficiency and the output power. These experiments will establish a new paradigm for thermal to electrical energy conversion utilizing the pyroelectric properties of ferroelectric thin films and pave the way for novel energy harvesting devices utilizing
Figure 7.5: A comparison of the power densities and temperature ramp rates obtained in this work as compared to prior work on energy conversion cycles in ferroelectric ceramics.

the concepts developed here.

7.3 Hysteretic losses and Joule Heating Effects

As noted above, the ultimate goal for the materials discussed in this thesis is to utilize them in a waste-heat energy conversion unit. In this spirit, here we present a brief overview of the losses and challenges associated with the utilization of these materials in such an application. In the pyroelectric energy conversion systems described in this work, we anticipate two major sources of loss: 1) Energy dissipated due to ferroelectric hysteresis and irreversible domain wall motion during electric field cycling and 2) Joule heating effects due to leakage across the ferroelectric layer due to its finite resistivity. These two electrical losses will impact the power outputs and operating temperatures of the energy conversion device as discussed below. Apart from the possibility of temperature rise due to these two electrical losses, the temperature of the ferroelectric changes at the cycling frequency due to reversible electrocaloric effects due to electric field. A careful consideration of all the above effects is essential to reliably estimate the device efficiency and optimize the
thermal management issues for improved performance. In the following sections we explore briefly each of these possible loss mechanisms.

### 7.3.1 Energy Dissipated During Electrical Field Cycling

The hysteretic nature of the ferroelectric polarization response to applied electric fields results in energy dissipation during electric field cycling. This loss can be broken into two regimes - 1) cycling with unipolar electric field within a regime of fields less than the coercive voltage (or non-switching cycling) and 2) cycling with bipolar electric fields with amplitudes comparable to or larger than the coercive voltage giving rise to ferroelectric switching in these materials (or switching cycling). In both cases, the total energy dissipated in one electric field cycle can be calculated as the area within the hysteresis loop for the applied range of electric fields. In general, this energy is dissipated as heat within the ferroelectric and could result in self-heating of the film depending on the thermal contact between the film and its surroundings. For a hysteresis loop enclosing an area \( H \) for applied electric fields at a frequency \( \omega \), the total rate of heat generation \( \dot{q}_E \) per unit volume of the ferroelectric (in the absence of any heat loss to the surroundings) is given as

\[
\dot{q}_E = \frac{H \omega}{2\pi}
\]

For a ferroelectric thin film capacitor undergoing switching cycling, this is the switching hysteresis area and can be simplified using \( H = 4E_cP_r \) for square hysteresis loops where \( E_c \) is the coercive field, and \( P_r \) is the remnant polarization of the ferroelectric. In the case of non-switching cycles, \( H \) is the area of the minor loops corresponding the applied range of electric fields. Typically, the minor loops enclose a small fraction (typically less than 0.1) of the switching hysteresis area. For the case of the PZT thin films utilized in this study \( E_c \sim 250 \text{kV/cm} \) and \( P_r \sim 50-75 \mu \text{C/cm}^2 \).

### 7.3.2 Joule Heating

The application of electric field to the sample also results in joule heating due to the leakage currents across the ferroelectric capacitor. The rate of energy dissipated (typically as heat) due to joule heating per unit volume \( \dot{q}_J \) of the ferroelectric can be written as

\[
\dot{q}_J = \sigma(E, \omega)E^2
\]

where \( E \) is the applied electric field during the cycle and \( \sigma(E, \omega) \) is the ac conductivity of the ferroelectric. For the PZT films investigated here, the ac conductivity at typical operating frequencies (0.1-1 kHz) is
\[ \sim 10^{-6} \ (\Omega m)^{-1} \] at room temperature.

For an energy conversion device, the ferroelectric switching and joule heating effects discussed above result in a reduction of the output energy densities and a rise of the background temperature of the ferroelectric thin film due to self-heating. The temperature of the ferroelectric is also affected by the reversible electrocaloric effects will cause an additional cooling / heating of the ferroelectric depending on the electric field profile.

### 7.3.3 Effect on Electrical Losses on Power Outputs and Device Temperatures

From the above discussion, for a realistic energy conversion cycle with \( E_c \sim 250 \text{ kV/cm} \), mean electric fields of \( \sim 50 \text{ kV/cm} \), \( P_r \sim 50 \mu \text{C/cm}^2 \) and consisting of a minor loop that is \( \sim 10\% \) of the total hysteresis loop area, we expect a loss from hysteresis in the material of \( \sim 5 \times 10^6 \text{ J/m}^3 \) and from joule heating of \( \sim 2.5 \times 10^7 \text{ J/m}^3 \).

Based on the measured power production densities in the previous section, which correspond to an energy production density of \( \sim 1 \times 10^8 \text{ J/m}^3 \) at an operating frequency of 1 kHz, we expect the hysteretic losses and joule heating to correspond to 5\% and 25\% of the total energy density of the pyroelectric energy conversion device, respectively. The large fraction of losses from joule heating can be reduced by utilizing materials with lower conductivities such as La doped PZT and BaTiO\(_3\).

The total heat generated within a ferroelectric per unit volume during the electric field cycling which results in heating of the ferroelectric can be written as

\[ \dot{q} = \frac{H\omega}{2\pi} + \sigma(E,\omega)E^2 \]

i.e., a sum of energy dissipated due to ferroelectric hysteresis and joule heating. In order to estimate the actual temperature rise as a result of these losses, we assume that the thermal conduction through the substrate is the primary heat transport mechanism and model the substrate as a semi-infinite solid with a thermal conductivity \( k \). The temperature rise of the ferroelectric-substrate interface as a result of the electrical losses with time \( t \) can be modeled as [158]

\[ T(t) = \frac{2h\dot{q}}{k} \left( \frac{\alpha t}{\pi} \right)^{1/2} \]

where \( h \) is the thickness of the ferroelectric layer and estimated here for a device on SrTiO\(_3\) substrates with a thermal conductivity \( (k) = 11 \text{ W/mK} \) and thermal diffusivity \( (\alpha) = 3.7 \times 10^{-6} \text{ m}^2/\text{s} \). The temperature at the ferroelectric-substrate interface was estimated at three frequencies [Fig. 7.6] and shows that the self-heating due to electrical losses is \(< 1 \text{ K} \) for up to 100 seconds and increases quadratically with time. As a result, long term characterization of the pyroelectric conversion cycles (longer than a few hours), particularly at
Figure 7.6: Calculated temperature rise at the ferroelectric-substrate interface due to hysteretic losses and joule heating at three operating frequencies for a typical pyroelectric energy conversion device with a PZT thin film on a SrTiO$_3$ substrate.

high operating frequencies (> 1 kHz) should take electrical losses into consideration or provide an adequate thermal sink to prevent overall heating of the device.

These estimates provide evidence for a potentially unexpected challenge that will need to be addressed in the design of these devices due to electrical losses associated with ferroelectric hysteresis and joule heating. These will have to be addressed to maximize the output energy densities, maximize the device efficiency, and reduce the effects of dissipation induced degradation of the energy harvesting device due to heating.

7.4 Conclusions

In this Chapter, we have investigated thermal energy harvesting using the pyroelectric effect in ferroelectric thin films. A microfabricated platform utilizing epitaxial ferroelectric thin films and microfabricated Pt line heaters was developed to investigate energy harvesting in an Ericsson cycle with simultaneous control of electric fields and temperature across the ferroelectric. Preliminary results show that fast temperature ramp rates (> $10^4$ K/s) and high power densities (> 100 kW/cm$^3$) could be obtained in such pyroelectric energy conversion cycles and indicate that thin film energy scavenging devices could pave the way for efficient
harvesting of waste heat. A detailed study of the device response is currently underway to understand the device performance and optimize the cycle operation parameters to obtain optimal efficiency for a given ferroelectric material.
8.1 Summary of Findings

In this thesis, we have systematically identified important contributions to ferroelectric susceptibilities of epitaxial thin films using PZT as a model system. Even though the dielectric and piezoelectric properties of ferroelectric thin films have been investigated using a variety of experimental and theoretical techniques previously, the understanding of pyroelectricity in thin films is vastly underdeveloped. At the same time, systematic design rules for the optimization of these susceptibilities, even though being very important from a device standpoint, is still unavailable. In the present work, we have identified large contributions to dielectric and pyroelectric susceptibilities in tetragonal PZT thin films from extrinsic (i.e., domain wall driven) and secondary (i.e., film-substrate thermal expansion mismatch driven) effects. Using a combination of theoretical and experimental techniques, we have demonstrated systematic enhancement of dielectric and pyroelectric susceptibilities in PZT thin films. We have then proceeded to identify new functionalities beyond epitaxial strain via strain gradients in compositionally graded PZT thin films to obtain exotic ferroelectric properties and enhanced susceptibilities. The present work has developed new theoretical tools and experimental techniques thereby overcoming major hurdles that have stymied earlier work in this area.

These advances include

- The development of a comprehensive GLD theory to predict the ferroelectric susceptibilities of polydomain thin films as a function of epitaxial strain, composition, temperature, electric field, and film thickness.
• The development of an MgO based hard-mask process that enables the fabrication of epitaxial metal-ferroelectric-metal capacitor structures.

• The implementation of a phase-sensitive technique to characterize the pyroelectric properties of ferroelectric thin films

The GLD models described in Chapter 2 predict that the 90° domain walls in tetragonal ferroelectrics provide a large extrinsic contribution to the intrinsic dielectric (or pyroelectric) susceptibility due to an electric field (or temperature) induced motion of the 90° domain walls. The density of 90° domain walls increases with increasing tensile strain and as a result, the extrinsic contribution was found to increase both dielectric and pyroelectric responses with increasing tensile strain. The nature of the extrinsic effect, however, was qualitatively different between the two susceptibilities. While the extrinsic effects were always positive (or increased the intrinsic property) for the dielectric susceptibility, it was dependent on the sign of epitaxial strain for the pyroelectric susceptibility. In this case, the extrinsic effects increased the intrinsic pyroelectric response for tensile strains, but reduced the same for compressive strains. Overall, tensile strained Ti-rich PZT thin films were found to possess the highest dielectric and pyroelectric susceptibilities near room temperature. Furthermore, the effect of thermal expansion mismatch between the film and substrate was also found to impact the pyroelectric susceptibility due to a temperature induced thermal strain between the film and the substrate. This effect was particularly significant in polydomain thin films and is observed to increase the pyroelectric properties on tensile strained films on substrates with larger thermal expansion coefficients.

The predictions of the GLD model were confirmed on model thin films of PZT grown via PLD in a range of epitaxial strain from -0.8% to 0.9%. The growth and characterization of these films including the MgO hard-mask process are detailed in Chapters 3, 4 and in Appendix A. Characterization of the domain structure by XRD and PFM confirmed an increasing density of 90° domain walls and electrical characterization showed an increasing dielectric and pyroelectric coefficient in good agreement with predictions of the GLD model including the extrinsic and secondary effects. The insight gained from this study represents a significant step forward in our understanding of the electric field and temperature dependent properties of ferroelectrics and enables the design of high-performance dielectric and pyroelectric materials for a variety of practical applications.

We then proceed to investigate composition gradients as a potential route to control the ferroelectric properties of PZT thin film. Compositionally graded ferroelectrics have shown a variety of novel functionalities in prior studies and strain gradients (which are naturally present in compositionally graded heterostructures) have been recently identified to significantly impact the properties of ferroelectric thin films. However, the
origin of the novel properties and the routes to controlling them are unclear in spite of extensive theoretical and experimental research. In Chapters 5 and 6, we present a systematic investigation of compositionally graded ferroelectric thin films using a combination of novel phenomenological models to describe compositionally graded heterostructures and the experimental tools described previously.

Extensive studies of a variety of gradient profiles included in Chapter 5 indicate that the structure of compositionally graded thin films is governed by the structural compatibility at the substrate interface. By minimizing the misfit strain at this interface, we show that the tendency to form misfit dislocations is reduced and as a result, large strains (of up to 4%) can be retained within the graded films. The large retained strains result in novel structural and ferroelectric properties that are not found in single layer variants of PZT including tetragonal structure in Zr-rich PZT, large built-in electric fields, and low dielectric susceptibilities. The results of the experiments are in agreement with a phenomenological model which includes the effect of strain relaxation and flexoelectric effects. The theoretical models described in Chapter 6 indicate that the origin of the novel ferroelectric properties of the graded heterostructures is the generation of a built-in field due to a flexoelectric coupling between the in-plane strain gradient and the out-of-plane polarization. Due to the large strain gradients ($> 10^5$ m$^{-1}$) possible within compositionally graded heterostructures, their ferroelectric properties are drastically altered as compared to single layer thin films with a homogeneous composition. These studies firmly establish composition gradients and flexoelectricity as a powerful and unique functionality in ferroelectric thin films and pave the way for further studies on such compositionally graded heterostructures.

Finally, we consider an example of a device application employing the concepts developed in the thesis thus far. In Chapter 7, we study the performance of pyroelectric energy harvesting in a microfabricated device architecture employing ferroelectric thin films and integrated Pt-line heaters. Reversible Ericsson-like cycles of the thin film ferroelectrics employing electric field sweeps and fast temperature ramps ($> 10^5$ K/s) show that large power densities can be obtained in such thin film devices. These studies provide preliminary evidence for an efficient solid state waste heat harvesting system using pyroelectric thin film devices.

### 8.2 Suggestions for Future Work


The ferroelectric susceptibilities discussed in the present work could also be enhanced, from a materials standpoint, by various ways such as the field induced ferroelectricity in anti-ferroelectrics, coupling to other degrees of freedom (such as ferromagnetism) in composite ferroelectric-ferromagnet multiferroic...
materials, or due to finite size effects in nanostructures / ultrathin films. There is very little theoretical or experiment work, however, on any of these systems. A modification of the GLD model to predict the ferroelectric susceptibilities could be an excellent starting point to improve the susceptibilities using these novel mechanisms in systems such as PZT.

2. Effect of a magnetoelectric coupling on electrocaloric effects and pyroelectric energy conversion.

The coupling of a ferroelectric to structural and magnetic degrees of freedom in a multiferroic material could provide improved energy conversion efficiencies due to additional entropy contributions under the application of an electric field or a change in temperature. A systematic theoretical and experimental study would provide fundamental scientific insights leading to improved device design and energy conversion efficiencies.

3. Effect of an electrode metal-insulator transition on the dielectric and pyroelectric properties of ferroelectric capacitors.

Ferroelectric capacitors typically have metallic electrodes to compensate for the bound charges and stabilize the out-of-plane polarization. As mentioned in Chapter 2, the lack of metallic electrodes or the presence of an insulator surrounding the ferroelectric could significantly destabilize ferroelectricity. This is due to an additional depolarization energy and has been observed to result in 180° domain structures and reduced remnant polarization. Therefore, if one could tune a metal to insulator transition in the metallic electrode with temperature or electric field, this could significantly affect the ferroelectric domain structures and result in large susceptibilities. A temperature induced metal-insulator transition in nickelates such as NdNiO₃ or SmNiO₃ on a highly insulating ferroelectric such as La-doped PZT would provide an ideal system for such a study. Furthermore, this would provide the first demonstration of electrode control of bulk ferroelectric properties and a novel route to high susceptibilities in any ferroelectric material.

4. Ferroelectric domain structures in epitaxial nanostructures fabricated via the MgO process.

The effect of boundaries and a finite lateral size on ferroelectric domain structure is another exciting avenue for future study. There is limited work on enhanced piezoelectric properties in micron sized pillars PZT due to reduced substrate clamping and enhanced domain wall mobility. Even though the translational symmetry breaking due to edges could be very significant in determining ferroelectric domains structure - in particular, for low-symmetry materials such as BiFeO₃, no work exists on this topic. This is predominantly due to a difficulty in fabricating epitaxial nanostructures of complex oxide materials. AAO template based techniques result in poor edge definition and crystallinity while
focussed ion beam induced milling of ferroelectrics causes significant edge contamination due to Ga implantation. The MgO-based hard mask described in this work process provides a minimally invasive technique to the fabrication of complex oxide nanostructures. Preliminary work indicates that feature sizes down to 1 µm can be fabricated with MgO process and in conjunction with non-invasive ion-milling steps can be used down to 100 nm sized features. Further optimization of the nanofabrication process has an immense potential for scientific discovery in a variety of functional complex oxide materials including ferroelectrics, multiferroics, colossal magnetoresistive, and superconductors.

5. Pyroelectric properties of free-standing ferroelectric thin films.

The ferroelectric thin films described in this work relied extensively on substrate induced epitaxial strain to tune the domain structure and ferroelectric susceptibilities. For many practical applications such as infra-red imaging, thermal / vibrational energy harvesting, and pressure sensing, however, the substrate could be detrimental due to its large heat capacity and stiffness. In this regard, free-standing ferroelectric thin films would provide an ideal platform for high performance devices. Back side etching of the substrate or wet-etching undercut techniques have been attempted to fabricate such a device using selective etching of substrates and bottom electrodes. Further work, however, is necessary to optimize the fabrication process and characterize free-standing single crystalline ferroelectric films in the form of piezoelectric cantilevers, pressure sensing membranes, or ultrasensitive infrared sensors.


The built-in electric field observed in up-graded ferroelectric thin films could be very useful in photovoltaic application as it naturally serves to separate the electron-hole pairs generated in response to incident photons. However, the high bandgap of PZT based ferroelectrics (> 3 eV) is a significant hurdle towards improving the overall performance. The graded ferroelectric thin films, however, provide an exciting opportunity for utilizing the built-in field for carrier separation and in conjunction with cation doping could be used to synthesize high-efficiency solar cells based on ferroelectric materials.
Appendix A

Pulsed-Laser Deposition of Complex Oxide Thin Films

In this thesis, we have relied extensively on pulsed-laser deposition (PLD) for the synthesis of epitaxial complex oxide thin films. In this appendix, we will provide a basic overview of PLD as a growth technique and introduce the fundamentals of plume formation and growth kinetics as related to thin film epitaxy. Complex oxide materials, particularly in thin film form, have become a playground of condensed matter physics and modern electronic devices in the past decade. The development of advanced synthesis techniques of these materials has enabled the exploration new properties, development of exotic functionalities, and have enabled researchers to address fundamental scientific issues in a wide variety of such materials. Among the various growth techniques for the synthesis of such thin films, PLD has arguably developed into the technique of choice ever since the growth of epitaxial high temperature superconductors via PLD at Bellcore in 1987 [159]. In the last two decades, PLD has developed into a sophisticated thin film growth technique with the addition of ultra-high vaccum and in situ growth monitoring capabilities such as RHEED (reflection high energy electron diffraction) and scanning probe micrsocopy. Now, PLD routinely enables unit-cell control of thickness, excellent crystallalinity, stoichiometry control, and even the growth non-equilibrium materials such as superlattices and nanostructures [17,19].

The technique of PLD is quite simple to understand and implement. A pulsed laser source is used to create a plasma plume from a sintered ceramic target of the desired film composition and the plume is directed towards a hot substrate on which the material condenses to form a thin film. The growth occurs in a vacuum chamber (in a background pressure of oxygen for oxide materials) which contains the target holder and substrate heater but the energy source is a laser housed external to the chamber. As a result, the
technique is relatively easy to set-up, offers a great amount of flexibility in choice of materials, provides a high-throughput, and enables the growth of epitaxial thin films of complex chemistries. Due to the small size of the plume, however, it is difficult to scale to an industrial scale deposition over large areas. At the same time, the process of ablation, plume formation and propagation, plasma chemistry, as well as the nucleation and growth of the film are quite complex [17,160,161]. As a result, a wide variety of experimental knobs are available to carefully tune the morphology, crystallinity, and chemistry of materials and provides the user a great deal of freedom in the control of the growth process.

In the process of ablation, the energy from the laser is converted to thermal, chemical, and mechanical energy in the target resulting in temperature of upto 5000 K at heating rates $10^{11}$ K/s [17,19,161]. Most of the incident energy from the laser is absorbed in small $(<0.1\text{cm}^2)$ and a very shallow region near the target surface. As a result, all the material in the incident volume is vaporized to form a plasma within $\sim 10-100\text{ps}$ due to the high incident energy. The control of laser penetration depth is crucial since sub-surface heating of the target results in splashing and deposition of particulates on the substrate [17]. Typically a pulse duration of $\sim 10-100\text{ns}$ with a wavelength of 248 nm or 193 nm fluence of $\sim 0.5-2\text{J/cm}^2$ is utilized for the deposition of stoichiometric complex oxide materials such as those used in the present work. For such long pulses, the incident pulse causes additional heating and expansion of the plasma as it moves towards the target. As the plasma propagates, the atoms, ions, and electrons in the plume thermalize before reaching the target and condense to form a film. The typical growth rate that allows for the thermalization of the plume and deposition of a stoichiometric film is $\sim 0.1-1\text{Å per pulse}$ resulting in tens of pulses per unit cell. As a result, the thickness of the film can be tightly controlled with in situ monitoring techniques such as RHEED.

The transfer of stoichiometry from the target to the films is one of the most important factors governing the success of the PLD process. For most complex oxide materials, the conditions described above preserves the stoichiometry from the target to the film. If one of the materials is more volatile than the others or if the plume is not thermalized, however, there will be an off-stoichiometry corresponding to an enrichment of the less volatile element in the film. Similar, off-stoichiometry can also occur if the elements do not have the same sticking coefficient or has a tendency to re-sputter. In such cases, a non-stoichiometric target rich in the volatile element (such as Pb in PZT) is utilized to promote the stoichiometric transfer from the target to the film. For the PZT films grown in this work, the targets had 10% excess Pb to compensate for its increased volatility from the film. Other growth parameters such as background oxygen pressure, incident laser fluence, temperature, and even target-substrate geometry can also be used to control the film chemistry and morphology. Such a wide variety of control knobs is one of the main reasons PLD often achieves better
functional properties in complex materials such as ferroelectrics and high-temperature superconductors in-spite of the complex high-energy processes that control the deposition.

Once the plume is expunged from the target, it expands normal to the target surface towards the substrate due to coulomb repulsion and recoil from the target surface. The spatial distribution of the plume is dependent on the background pressure of oxygen inside the PLD chamber. The density of the adatoms in the plume can be described by a lobe with a shape of $\sim \cos^n(\theta)$ with $n \sim 5 - 10$ \[17\]. Under ideal conditions, the lobe is stoichiometric in composition and has adatoms with large kinetic energies greater than $1 - 100$ eV. Once the adatoms reach the surface of the substrate, they condense and form the thin film. The exact growth process is controlled by a variety of parameters such as incoming adatom energy, substrate temperature, and substrate crystal miscut. Due to the large kinetic energy of the adatoms and the high substrate temperature, they are very mobile on the substrate surface at the high growth temperature. In the absence of any nucleation sites, they reach a step edge to increase the coordination and reduce their energy. If the time between the laser pulses is large as compared to the thermalization time of the atoms on the surface, they diffuse to the step edge before they can agglomerate. As a result, the material grows in a smooth fashion and this growth mode is called step flow \[19,161\]. Step flow growth maintains a perfect interface and an atomically smooth surface morphology. A large incoming flux, lower growth temperature, or small substrate miscut can prevent step flow growth and result in island or layer-by-layer growth modes. Under these conditions, the incoming adatoms can nucleate for form islands (before reaching a step edge) which grow and run into each other. At low growth rates, the pits between the islands are filled with incoming atoms to complete one monolayer at a time of growth. As a result, smooth films are obtained even under conditions of low adatom mobility on the surface. If sufficient time or energy is not provided for the layer-by-layer growth, however, new islands will nucleate before the completion of the previous layer resulting in significant roughening with continued growth. This is called 3D island growth mode \[19,161\] and results in rough thin films with poor interfaces and is not a preferred growth mode for the heteroepitaxial growth of complex oxide materials. Apart from growth conditions, the compatibility of the film with the substrate can also impact the wetting of the adatoms on the surface. Under conditions of large lattice mismatch, 3D island growth mode is typically preferred due to the large interfacial energy associated with the elastic strains in a perfectly interface. As a result, epitaxial thin films cannot be grown beyond a few percent lattice mismatch between the film and the substrate.

The thin-film growth of all the ferroelectric heterostructures in this dissertation was done using a KrF excimer laser (Lambda Physik LPX205i) with $\lambda = 248$ nm. Depositions were completed at repetition rates between $1 - 20$ Hz with energy densities ranging from $0.75 - 1.5$ J/cm$^2$ depending upon target material
and density. Laser energies were measured using a Gentec pyroelectric detector and spot sizes were taken using thermal paper to calculate the energy densities. The substrates were ultrasonicated in acetone and isopropanol prior to insertion in the deposition chamber. The substrates were adhered to the heater using silver paint (Leitsilber 200 silver paint from Ted Pella, Inc.). Deposition temperatures ranged from as low as 500°C to 750°C and deposition pressures from 20 – 200 mTorr partial pressure of oxygen. Samples were typically cooled in 760 Torr pressure of oxygen to room temperature at 5 K/min.
Appendix B

A Modified Look Ahead Minimizer for Graded Heterostructures

Including strain relaxation by misfit dislocation formation, the total strain energy per unit area \( U \) in a compositionally graded thin film is given as \([51,117,119]\)

\[
U = \int_{0}^{t} \left[ Y \left( u_m \pm \int_{0}^{x_3} \rho \cos \lambda \right)^2 + G \frac{\rho |b|^2}{2\pi} \ln \left( \frac{t - x_3}{|b|} \right) \right] dx_3
\]

where the first term represents the reduction in energy due to misfit dislocation formation and the second term represents the energy cost of forming dislocations. The total strain \( u \) at the position \( x_3 \) is

\[
u = u_m \pm \int_{0}^{x_3} \rho \cos \lambda
\]

\( u \) is a combination of substrate induced misfit \( (u_m) \) at that location and dislocation density \( (\rho) \) induced screening of the substrate in the underlying thickness. In this equation \( Y \) is the biaxial modulus, \( G \) is the shear modulus, \( t \) is the thickness of the film, \( \rho \) is the dislocation density, and \( b \) is the Burgers vector for the lowest energy dislocations (i.e., \( \langle 110 \rangle \) dislocations inclined at \( \lambda = 45^\circ \) to the substrate). The sign of \( b \) in the first term is chosen to reduce the misfit strain at that location with \( |b| = \sqrt{2}a \) and the sign in the first term is chosen appropriately at every location. Due to the presence of composition gradients, all coefficients except \( \lambda \) are position dependent in the above equation.

In order to minimize this free energy \( U \) numerically to obtain the equilibrium dislocation densities and total strains, we utilize a modified look ahead minimizing scheme as described below. The thin film with
an arbitrary composition profile is approximated by \( N \) constant composition layers each having a thickness \( t/N \). The composition corresponding to each of the layers is obtained by linear interpolation of the end members of the graded profile. \( N \) is chosen such that \( t/N > |b| \) to obtain physically meaningful solutions (since otherwise the energy cost of a dislocation can be less than zero). For a film thickness of 100 nm such as those investigated in the present work, \( N = 100 \) was typically chosen.

Initially, the lattice constants, misfit strain, and elastic constants of all the \( N \) layers are calculated from the bulk values of the PZT system. The dislocation density is set to zero and the burgers vectors are initialized assuming no strain relaxation at every location. The minimization is accomplished with a modified two step look ahead minimization scheme. In the original look ahead minimizer [119], the energy is iteratively reduced in \( N - 1 \) steps two adjacent layers at a time starting from the substrate interface. Starting from \( i = 1 \), the current energy is compared against eight new configurations - \( U_{++}, U_{+-}, U_{-+}, U_{-0}, U_{0+}, U_{0-}, U_{-0}, \) and \( U_{0-} \), where the first and second subscript indices correspond to modified dislocation densities at layers \( i, \) and \( i + 1 \) by \( \Delta, -\Delta, \) and 0 for \( +, -, 0 \) respectively. The configuration of dislocations among the nine which has the lowest strain energy is taken as the new minimum and the process repeated until \( i = N - 1 \) is reached. After one such sweep, the value of \( \Delta \) is modified to lower value = \( f\Delta \) (with \( f = 0.999, \) say) and the sweep is performed repeatedly until the \( \Delta \) reaches a low threshold value (= 1000, say). The starting value of \( \Delta \) is taken to be a large dislocation density, corresponding the maximum local misfit strain for the heterostructure. However, this procedure suffered from poor convergence and sometimes unphysical minima for the up-graded and down-graded films discussed in this thesis. This could possibly be due to the capture in local minima and insufficient sampling of the dislocation density space at each layer. As a result, the algorithm was modified as follows to ensure robust convergence and better sampling. In the modified technique, instead of assuming a constant \( \Delta \) for all layers that monotonically reduced by a factor \( f, \) a separate value of \( \Delta[j] \) was chosen for each layer which was initialized to the maximum possible dislocation density at that layer which reduces the local strain to zero. As a result, the maximum possible iterations at every layer was also different corresponding to the low limit dislocation density cutoff. As a result of the modification, after a given step of the two step look-ahead minimizer at \( i = j, j + 1 \) with dislocation density modified by \( \Delta[j] f^{n_j} \) and \( \Delta[j + 1] f^{n_{j+1}}, \) where \( n_j \) and \( n_{j+1} \) corresponds to the local increment index at that location. If a new configuration is accepted, the values of strains, burgers vectors, and \( \Delta[j] \) are re-initialized and \( n_i \) is set equal to 0 for all \( i = j + 2 \) to \( N \) and the next two layers are considered. If no new configuration is accepted after a full sweep from \( i = 1 \) to \( N - 1, n_i \) is increased by 1 for all layers and a new sweep is performed. The sweeps are repeated until the values of \( n_i \) at all locations from \( i \) to \( N \) has reached the maximum values at that location. This process was found to result in robust convergence and increased

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effectiveness for arbitrary composition profiles such as those considered in this thesis.
References


