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### Structure and domain formation in ferroelectric thin films

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*Document Version*

Publisher's PDF, also known as Version of record

*Publication date:*  
2009

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Vlooswijk, A. H. G. (2009). *Structure and domain formation in ferroelectric thin films*. [Thesis fully internal (DIV), University of Groningen]. [s.n.].

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# Chapter 1

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## General introduction

### 1.1 Introduction

This chapter serves as an introduction for a general audience to the basic concepts concerning thin films and ferroelectrics. For the sake of simplicity, several aspects in this chapter are simplified, generalized or described in an intuitive way and not always according to strict definitions. Therefore, advanced readers are advised to skip this chapter.

In modern electronics, many important devices are very slim. Their main active elements are very thin layers of material with a specific response to an electrical signal. While in many applications these layers are still micrometers thick (we call them “thick films”), we will deal with thinner films (“thin films”) that are only 10 to 250 unit cells thick (4-100 nanometer). Besides their low weight and the fact that they require very low power for operation as a memory element, the main breakthrough of thin films is their integration into integrated circuits as active elements. The limited size of such thin films provides another, more academic, advantage: it allows to model sometimes even the whole film by theoretical atomistic calculations; something unthinkable for bulk materials. This allows a great deal of feedback between theorists and experimentalists and has allowed the field to progress very rapidly in the last few years. And last but not least, these thin films can have properties that are different, and sometimes better than those of the same material in bulk form.

We will start by explaining some aspects and definitions related to thin films, in general, and crystalline thin films, in particular. “Crystalline” means that a material consists of *crystals*: a homogeneous solid of regularly ordered atoms with fixed distances between them. The focus in this thesis is on a specific kind of these materials: *ferroelectric* and *piezoelectric* materials. Piezoelectric or ferroelectric materials are used in devices like ferroelectric computer memory or airbag sensors. Understanding what a ferroelectric material is,

why a material is ferroelectric and how we can modify and use the properties of ferroelectrics to our advantage will help to understand the relevance of this thesis. And even more important: it can help to gain more insight into the importance of these types of materials for the operation of memory elements or airbags.

Ferroelectrics are surprising materials in itself. They display a spontaneous electric polarization. Above a certain temperature,  $T_c$ , this spontaneous polarization disappears. When the temperature approaches  $T_c$ , many materials' properties, which determine its response to external stimuli (temperature, electric field or pressure), reach enormous values. This means below  $T_c$  ferroelectrics are useful, but close to  $T_c$  their behavior and response is enormously interesting! The  $T_c$  of the material we have used,  $PbTiO_3$ , is  $490^\circ\text{C}$ , not such a convenient temperature for many applications. This is one of the reasons to make thin films of the material, because it is a way to modify the material in a controlled way and change this  $T_c$ . The modification is due to pressure: when a thin crystalline film is grown on a crystal substrate, the film is forced to adopt the crystal structure of the substrate and this is equivalent to constantly applying pressure to a material in two dimensions.

## 1.2 Thin films

Ferroelectrics are used in many shapes and sizes. In the previous section we have explained the main advantages of thin films of ferroelectrics. One of them is that a certain *misfit* between substrate crystal lattice and film crystal lattice is likely to exist when a thin film is deposited on a substrate (the two lattices in Figure 1.1b and c are good illustrations of a misfit). Due to the limited thickness of the thin film compared to the substrate, the film will tend to strain to fit the substrate. The influence of the substrate on the thin film results in so-called misfit strain in the thin film. This method of using a crystal misfit to achieve strain in a thin film and modify its properties is often called "strain engineering".

### 1.2.1 Stress and (misfit) strain

For "strain engineering", it is important to distinguish stress from strain. Stress is defined as the external force applied to a system per unit area, in

units of  $Pa = N/m^2$ . This is different from strain, which is usually the result of an externally applied force and it is defined as the relative (lattice) deformation due to an applied stress. This means that strain has no units. In a substrate/thin film system, the misfit strain is defined as the difference between in-plane lattice dimensions of substrate ( $b$ ) and film ( $a$ ), normalized by that of the substrate:

$$u_m = \frac{b - a}{b} \quad (1.1)$$

### 1.2.2 Lattice relations

Thus, unlike amorphous or polycrystalline thin films, single crystalline thin films have a strong relation with their substrate. Terms defining this single crystal substrate-thin film relationship, are often used in a sloppy manner. Therefore, we emphasize here what is meant in this work by

- \* epitaxy and monotaxy, which refer to the growth process;
- \* coherency and incoherency, which refer to the substrate-film interface;
- \* strained and relaxed thin films, which refer to the grown thin film.

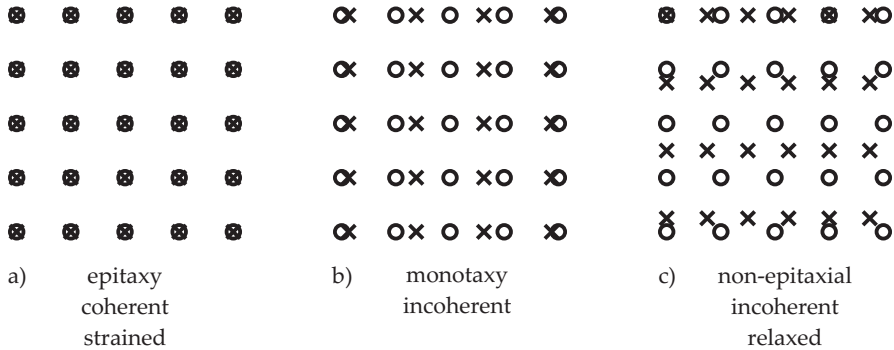
We use the definitions found in some well-known literature [6, 7, 8]. The general definitions are followed by some comments relating them to this work.

**Epitaxy:** *Mutual orientation of two crystals of different species, with two-dimensional lattice control, usually, though not necessarily, resulting in an overgrowth (Figure 1.1a).*

Although the definitions of epitaxy (from Greek; “*epi*”= above and “*taxis*”= in ordered manner) found in literature differ considerably, we use the definition of the International Union of Crystallography [8]. Substrate-film combinations with a coherent interface and no relaxation within the thin film, meet this requirement. Epitaxy is only possible for low misfit film-substrate systems. Layer-by-layer grown films which do not relax after growth (due to differences in thermal expansion coefficient between film and substrate) are very likely to be epitaxial.

**Monotaxy:** *Mutual orientation of two crystals of different species, with one-dimensional lattice control (line of atoms in common), (Figure 1.1b).*

The Greek etymology, (“*mono*” meaning one) clarifies the meaning of this



**Figure 1.1:** Top view of the lattice relations between a substrate of circles ( $A$ ) and a thin film of crosses ( $B$ ). a) represents  $A/B$  epitaxy with a coherent interface and a strained  $B$  lattice. b) shows the uncommon  $A/B$  monotaxy with an incoherent interface and a  $B$  lattice which is strained in one in-plane direction and relaxed in the other. c) is a relaxed thin film  $B$  with an incoherent  $A/B$  interface.

rarely used term. When this term was defined by the International Union of Crystallography [8], no examples of monotaxy were known to the committee defining it. Introducing slightly rectangular substrates makes this term valuable. Lattice matching in one of both in-plane directions seems unlikely, but is surely not impossible.

**Coherency** (Figure 1.1a) means that the corresponding atom planes and lines are continuous across an interface. There is an atom-by-atom matching across the interface, meaning that there are no atoms missing (dislocations) at the interface.

**Incoherency** (Figure 1.1b+c) means that there is no continuity of atomic planes and lines at the interface. If the atom-by-atom matching across the interface does exist, but only locally, we speak of a locally coherent interface.

**Strained thin films** (Figure 1.1a) refer to thin films that adjust their in-plane lattice parameters to fit to the substrate. In other words, all or most of the film-substrate misfit is accommodated by lattice deformation. Very little or no defects, dislocations or other stress accommodating mechanisms, like domain formation, are present in a strained thin film. The term “strain engineering”

is applied to strained thin films. This term is adopted from semiconductor industry, where misfit was first used to enhance the properties of functional layers. For this, only small lattice misfits and small thicknesses are used. For increased thicknesses, the imposed stress can generally be accommodated more easily by dislocations and domain formation (growth of differently oriented crystals), thus limiting the applicability of strain engineering.

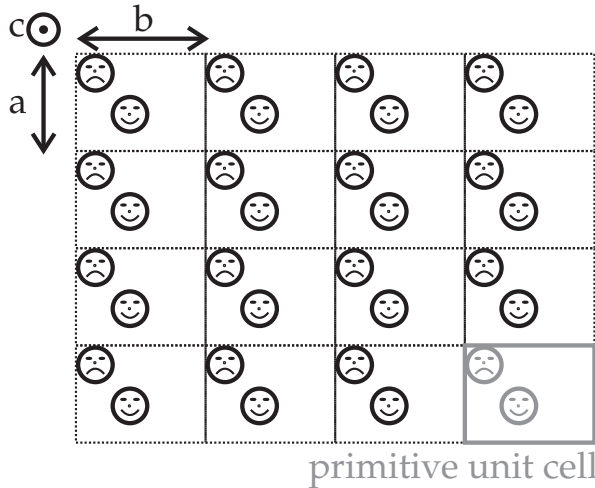
**Relaxed thin films** (Figure 1.1c) are thin films in which the misfit stress is too large to be accommodated by lattice strain. Therefore, the stress is accommodated by dislocations, domain formation or other stress-relieving mechanisms other than elastic deformation.

These lattice relations are important because they determine to a large extent the properties of thin films. In thin films of ferroelectrics there is a direct coupling between the strain state and the properties of the material, which makes thin films of ferroelectrics the ideal playground for “strain engineering”. To understand the possible effects of strain, we will continue by describing some fundamental aspects of ferroelectrics.

## 1.3 Ferroelectricity and related concepts

### 1.3.1 Crystals and symmetry in ferroelectrics

Crystals and crystalline materials are not only used for jewelry, but also for many technologically important applications, like transistors, solar cells and diamond saws. By looking more carefully at the structure of crystals, we see that a certain arrangement of atoms is repeated over and over again. The smallest arrangement of atoms is called the *primitive unit cell* and the sizes of the smallest box one can draw around this in three dimensions are what we call the *lattice parameters*  $a, b, c$  (Figure 1.2). The unit cell is repeated in three dimensions periodically to form the crystal lattice. Besides, specific (combinations of) symmetry operations can be performed on the crystal without changing its ordering. These symmetry operations are translation, reflection, rotation and inversion. The absence of an inversion center is one require-



**Figure 1.2:** Representation of a two-dimensional crystal lattice with a non-centrosymmetric primitive unit cell. Besides the lattice parameters  $a$  and  $b$ , a single primitive unit cell is indicated.

ment for a material to be piezoelectric<sup>1</sup>. Materials which lack an inversion center are called non-centrosymmetric. In addition to this requirement of non-centrosymmetry, a material should not be a conductor and preferably, an insulator, to develop a dielectric polarization when it is subjected to an electric field. In this case, we call a material piezoelectric: it displays a change in electric polarization with a change in applied stress. Piezoelectric materials also display the reverse effect: they deform upon the application of an electric field. If a piezoelectric crystal has a unique polar axis even in the absence of stress, it is called polar or pyroelectric. Materials from the

<sup>1</sup>All possible combinations of translation, reflection, rotation and inversion, give rise to 230 different *space groups*. The space group is determined by the *crystallographic point group* and the translational symmetry. The point group is formed by all symmetry operations other than translation; these being reflections, rotations, inversion, and combinations of these, that leave at least one point unmoved and the crystal unchanged. There are 32 possible point groups and many crystals' properties can be deduced by looking at the point group. Looking at the 32 possible point groups, 11 are centrosymmetric and 21 are non-centrosymmetric. This last category lacks an inversion center and crystals from these groups display piezoelectricity - except point group 432 which is non-centrosymmetric but has other symmetry elements that combine to exclude piezoelectricity.

subgroup of pyroelectrics that have a reversible or switchable polarization, are called ferroelectrics. A schematic of this classification is shown in Figure 1.3. Note that all ferroelectrics are also pyroelectric and piezoelectric. The name ferroelectric is somewhat confusing: Although iron is not necessarily involved, they are called *ferro*electrics because they are the electric analogue of *ferro*magnets. These permanent magnets that we know from kitchen magnets, hard disks etc., have taken their name from their most popular example: iron (ferrum). A ferroelectric is therefore defined as a material which has a switchable permanent polarization, also in the absence of an electric field. A typical property of a ferroelectric (and experimental proof of ferroelectricity) is a polarization-electric field hysteresis loop: the direction of the spontaneous polarization can be reversed by an applied electric field, with a typical switching behavior and dissipation as shown in Figure 1.3. A material is only ferroelectric below a certain critical temperature  $T_c$  and above  $T_c$  the crystal is said to be paraelectric, exhibiting a linear and non-hysteretic polarization-electric field dependence.

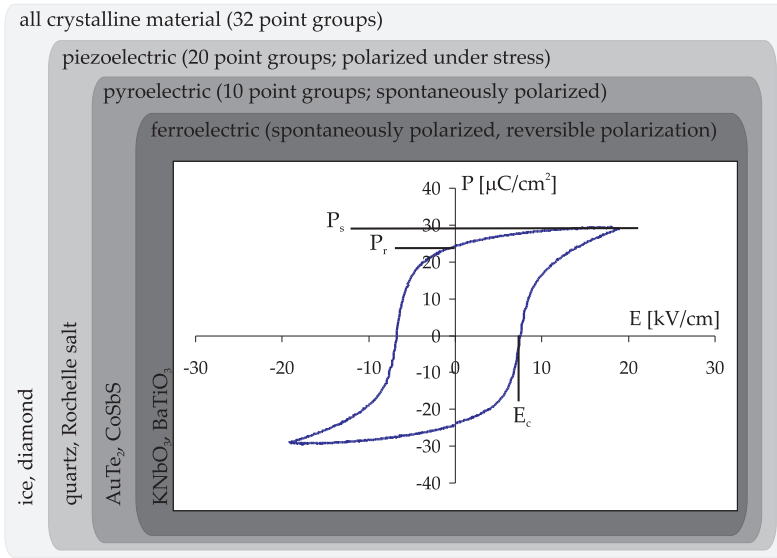
### 1.3.2 The mechanism of ferroelectricity

Different types of ferroelectrics exist, but we will only treat the class of displacive ferroelectric oxides with a perovskite structure. These materials have a permanent polarization density, which is often simply called 'polarization'. In electromagnetism, the polarization is the dipole moment per unit volume (the amount of charge multiplied by it's displacement, per unit volume). The total polarization can consist of an electronic polarization (due to the displacement of the electronic shells) and the ionic polarization (due to the displacement of ions). The total polarization  $P$  of a ferroelectric in an electric field consists of a spontaneous polarization  $P_s$  and the polarization due to the external electric field  $P_E$ . This total polarization modifies the electric field inside the ferroelectric, therefore the electric displacement field  $D$  that accounts for the effect of bound charges, should be considered as:

$$D \equiv \epsilon_0 E + P = \epsilon_0 \epsilon_r E + P_s \quad (1.2)$$

Where  $\epsilon_r = 1 + \chi$  is the dielectric constant and  $\chi$  is the dielectric susceptibility. In addition to a spontaneous polarization, ferroelectrics have the largest dielectric constants of all known materials. Ferroelectrics with the largest po-





**Figure 1.3:** Diagram of the crystal groups and subgroups defining piezoelectrics, pyroelectrics and ferroelectrics. Vertically, some examples of the concerning materials' class are given. On top of that, a typical ferroelectric P-E hysteresis loop is shown, measured on a  $790\mu\text{m}$  thick PZT sample supplied by Joost van Bennekom (University of Twente). The measurement has been taken with a ferroelectric tester from Radiant Technologies, using a maximum applied voltage of  $1500\text{V}$  and a hysteresis period of  $4\text{ sec}$ . Indicated are the coercive field,  $E_c \approx 7.2\text{kV}/\text{cm}$ , the saturation polarization,  $P_s \approx 29.3\mu\text{C}/\text{cm}^2$  and the remanent polarization,  $P_r \approx 24.3\mu\text{C}/\text{cm}^2$ .

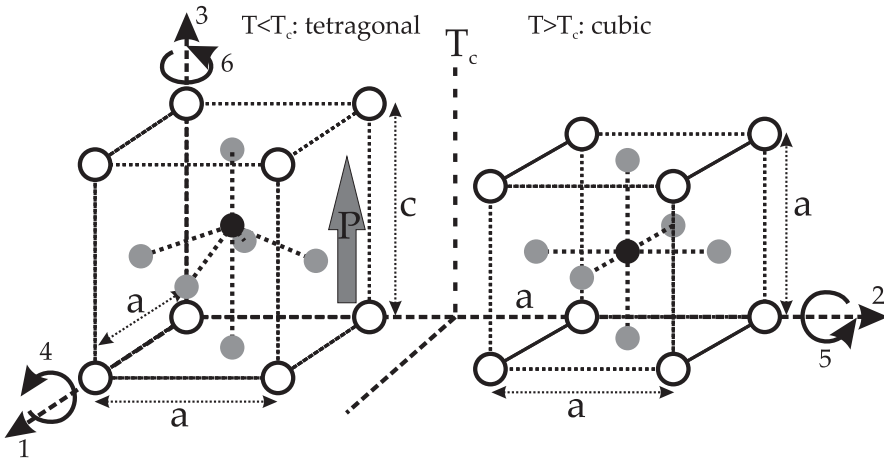
larizations are often  $ABO_3$  perovskites ( $A$  and  $B$  stand for metal ions).

Figure 1.4 shows the tetragonal (ferroelectric) and cubic (paraelectric) unit cell of the material mainly used in this thesis,  $PbTiO_3$ . Although every  $ABO_3$  ferroelectric perovskite has its own specific properties due to different  $A$  and  $B$ -site atoms, several mechanisms are general. From here on, we will treat  $PbTiO_3$ , which has a ferroelectric (cubic-to-tetragonal) phase transition at  $T_c = 490^\circ\text{C}$ . Above  $T_c$ ,  $PbTiO_3$  is cubic and non-polar (paraelectric), below  $T_c$  it is tetragonal ferroelectric. Figure 1.4 also shows that in the ferroelectric tetragonal phase, the ions are displaced from their highly symmetric positions.

One might wonder why the ions in a ferroelectric are displaced in the first place and, more generally, why a material is ferroelectric. The general answer

will be given here, while the details will be dealt with in chapter 2. The atoms, treated as particles, interact via two main mechanisms on two different length scales: long-range attractive Coulomb interactions and short-range repulsive interatomic interactions (Rydberg-like potential). Whereas the long-range Coulomb interactions in the perovskite structure favor the ferroelectric state, the short-range repulsive interactions favor the non-polar cubic state [9].

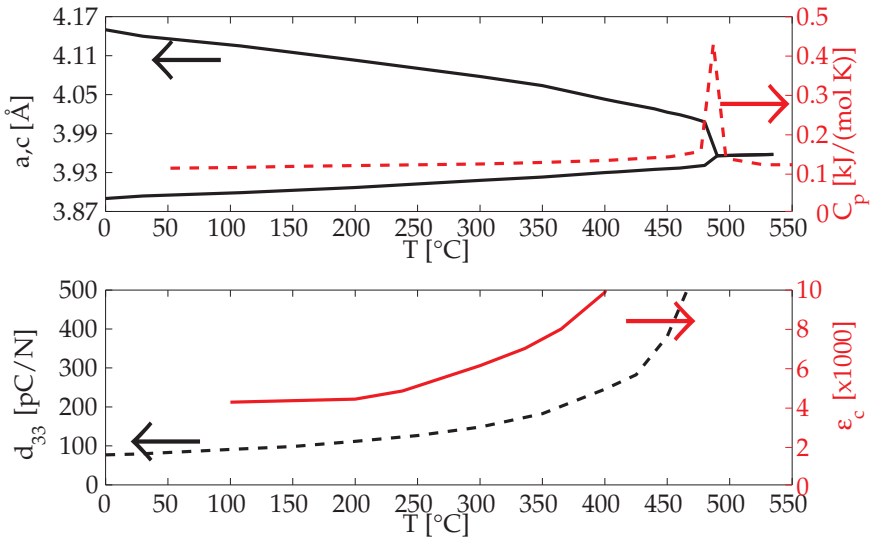
In  $PbTiO_3$ , the structural phase transition from the cubic to the tetragonal



**Figure 1.4:** Schematic representation of the tetragonal (left) and the cubic (right) unit cell of the ferroelectric material lead titanate ( $PbTiO_3$ ). Bulk  $PbTiO_3$  is tetragonal below  $T_c$  and cubic above  $T_c$ . Indicated are the cubic lattice parameter  $a$ , the tetragonal  $a$  and  $c$  lattice parameters, the polarization vector,  $P$ , and the definitions of directions (1,2,3) and rotations (4,5,6), useful for the definition of the piezoelectric tensors. Lead atoms are depicted in white, titanium in black and oxygen in gray. The atomic displacements are not to scale.

phase is first order. This means that the transition is abrupt and coexistence of the two phases can be observed. In everyday life, freezing water ( $H_2O$ ) is a good example of a first order phase transition: The phase transition from water to ice (and vice versa) is accompanied by a large amount of energy (latent heat) and the heat put into the system is used to accomplish the phase change with no temperature variation (latent heat, see Figure 1.5). This also illustrates that phase transitions often lead to interesting effects: the phase transition from water to ice (and vice versa) is accompanied by an unusual

volume change. Besides first order phase transitions, also second order phase transitions exist, which are continuous phase transitions and have no associated latent heat. The main difference between the two types is that, while first-order phase transitions occur by nucleation and growth of one phase into the other, second order phase transitions occur due to fluctuations of the so-called “order parameter” (a property that is zero above  $T_c$ , such as the polarization). Although both transition types are associated with an anomaly of the dielectric susceptibility at  $T_c$  (i.e. an extreme response to an external electric field), this anomaly is much larger in the case of second order phase transitions (theoretically, infinity).

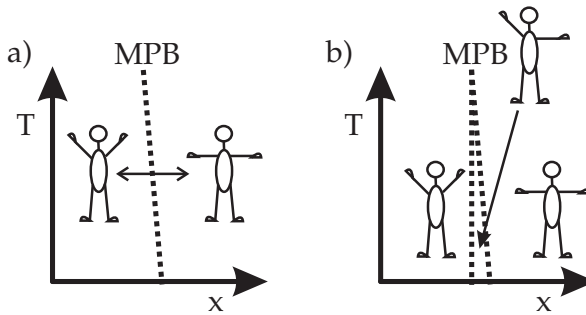


**Figure 1.5:** Characteristic temperature dependent properties of  $\text{PbTiO}_3$ , all showing an anomaly at the transition temperature  $T_c \approx 490^{\circ}\text{C}$ . (Top) The lattice parameters  $a$  and  $c$  (continuous line) [10] and the specific heat  $C_p$  (dashed line) [11]. (Bottom) The dielectric constant in the  $c$ -direction,  $\epsilon_c$ , (continuous line) [12] and the piezoelectric coefficient,  $d_{33}$ , (dashed line) [13] are shown.

### 1.3.3 Phase transitions

The phase transition in  $PbTiO_3$  is marked by a large change in lattice parameters, the release of latent heat and an increase in the dielectric constant and piezoelectric coefficients (Figure 1.5). In short: interesting changes in materials' properties occur at the phase transition. But the critical temperature of  $490^\circ C$  is not such a convenient temperature for many applications. It is therefore desirable to search for "knobs" to tune this transition temperature, or to induce other phase transitions. One may also want to modify the materials' response, that is the physical properties, such as the dielectric constant or piezoelectric coefficients. This requires variables which have a direct influence on the order parameter, the polarization. Besides temperature, the most important variables to influence the polarization are electric field and pressure. By changing the kind of substrate and/or the film thickness, the stress applied to the film can be tuned, making stress via epitaxial strain a suitable "tuning knob".

Ideally, the stress modifies the crystal structure in such a way that the



**Figure 1.6:**  $T - x$  phase diagrams of a ferroelectric, where  $T$  is the temperature and  $x$  a variable influencing the order parameter (e.g. chemical composition, pressure, electric field). The two phase diagrams describe two different models, in which the enhanced piezoelectric response close to the MPB is associated with a phase transition (a) or the existence of a low symmetry "bridging" phase (b).

$T_c$  and, thus, the phase boundary shifts to(wards) room temperature. This change of crystal structure also modifies the spontaneous polarization  $P_0$  and possibly the order of the phase transition. In bulk ferroelectrics, pressure-induced phase transitions have been shown by experiments in high-pressure cells, but also by the replacement of homovalent cations with different sizes,

which effectively gives rise to so-called “chemical pressure”. A giant piezoelectric effect<sup>2</sup> can be observed in ferroelectric perovskite solid solutions upon replacement of the B cation, at a composition at which a phase transition to another crystal phase takes place, corresponding to the so-called “Morphotropic Phase Boundary” (MPB; Figure 1.6). Originally, a MPB was a compositional phase boundary between two adjacent phases in the phase diagram with a weak (or no) temperature dependence [14], as happens in the well-known piezoelectric  $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$  (PZT). Nowadays, the more general concept is often used, and a MPB is any vertical, or nearly vertical, line in the temperature- $x$  phase diagrams,  $x$  being composition, pressure, electric field, etc. (Figure 1.6).

The nature of the MPBs and the associated abrupt increase in piezoelectric response is still a very lively research topic. Currently, two general views prevail to explain the enhanced intrinsic piezoelectric response. According to some, the sole presence of a phase boundary at the MPB is sufficient to produce large responses (Figure 1.6a) [15]. Based on the observation of a monoclinic phase at the MPB of PZT and related systems, other models stress the importance of an intermediate phase with lower symmetry (Figure 1.6b), which leads to enhanced piezoelectric response via polarization rotation [16]. Despite these differences, all models agree on one aspect: the importance of the change in direction of the polarization [17], either continuously or discontinuously due to a change of polar axis.

### 1.3.4 Ferroelectric and ferroelastic domains

In the previous sections, the intrinsic materials properties have been described. Now we move a step closer to consider a ferroelectric material applied in a macroscopic device. A logical first step is to make a device to store charge: A ferroelectric slab with electrodes on both sides (a capacitor). By doing so, some macroscopic effects will be incompatible with our ideal descriptions on the microscopic level. Up to now, we have assumed that a ferroelectric can be fully polarized in a single direction or strained to any state. But on the macroscopic level this gives rise to a charged surface and unrealistic lattice strain, respectively. Therefore, the macroscopic energetics and boundary conditions will interfere with the microscopic energetics and this gives rise to additional

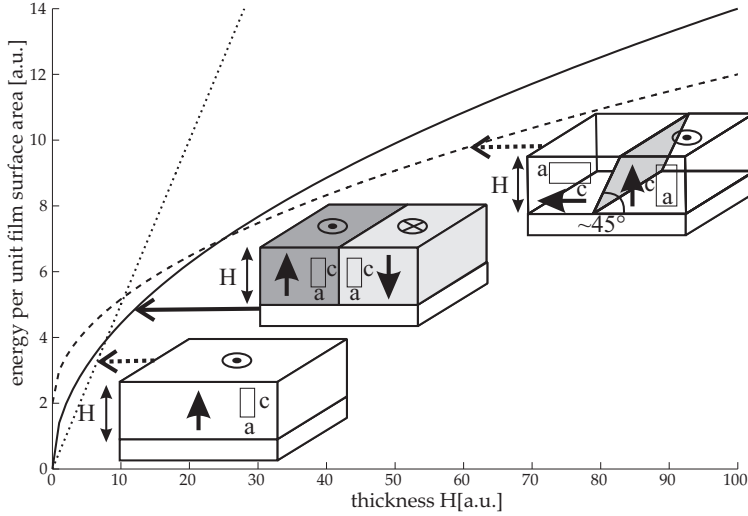
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<sup>2</sup>The surprisingly large increase in piezoelectric response of these materials close to the MPB is often called giant piezoelectric effect.

mechanisms to reduce the overall energy of the system.

Due to the imperfection of the electrodes, the macroscopic polarization in a capacitor is different from what one would expect based on the microscopic polarization. In the ideal case, the available charges totally screen the polarization and are located exactly at the electrode/ferroelectric interface. With realistic electrodes, the polarization may not be totally screened and the screening charges are distributed over a small region in the metal giving rise to finite dipoles at the interface with an associated voltage drop over the ferroelectric thin film, which in turn leads to a compensating depolarization field. For relatively thick capacitors, this field is relatively small, but with decreasing thickness of the ferroelectric, this field increases and ultimately suppresses the ferroelectricity. In the absence of one or any electrode, the situation becomes even worse: the free surface will attract any polar material (notably polar molecules, like  $H_2O$ ), with larger associated screening lengths to screen the charges. But there are other ways in which the existence of a macroscopic depolarization field is avoided above all. The most obvious way is by the formation of alternating up and down polarized domains. In this way, the existence of a macroscopic charged surface is prevented beforehand so no macroscopic depolarization field will be present. These domains are called up and down,  $180^\circ$  or  $c^+ / c^-$  domains and will form periodically (Figure 1.7).

Similar to the electrical boundary conditions, the physical boundary conditions lead to a macroscopic strain state different from what one would expect based on the microscopic lattice strain. In (ultra)thin films the energy cost of lattice deformation is low, as it scales linearly with thickness. But with increasing thickness, the energy in these systems grows and above certain thicknesses it becomes energetically favorable to relax the strain on the unit cell level. In the case in which the lattice parameter of the substrate is in between those of the film ( $a_f < b < c_f$ ), the film will form regions with different crystal orientations, alternating the in-plane orientation between the short  $a$ -axis and the long  $c$ -axis. This so-called “ $a/c$ -domain” or  $90^\circ$  domain structure allows the lattice to relax when the energy cost of forming the domains, is more favorable than the lattice strain. Therefore, a critical thickness exists for every film/substrate combination, above which an  $a/c$ -domain structure will form. In the case of matched lattice parameters in the paraelectric phase with no defects present, the crystal will show periodic areas with different crystal



**Figure 1.7:** Thickness-energy (per unit surface area) plot. The corresponding domain structures are schematically represented. The dotted line corresponds to a monodomain film, the solid line to a  $180^\circ$  domain structure and the dashed line to a  $90^\circ$  domain structure. In all structures the polarization directions and crystallographic orientations are indicated.

orientations (Figure 1.7).

### 1.3.5 Materials for applications

The material used in this thesis work is  $PbTiO_3$ , a ferroelectric with well-known bulk properties. Although a classical ferroelectric, pure  $PbTiO_3$  is not amongst the most used ferroelectrics in commercial applications. Instead  $PbTiO_3$ -based solid solutions<sup>3</sup> are preferred in devices. The reason for this is their enhanced properties when they are tuned to be in the proximity of their so-called Morphotropic Phase Boundary (MPB), as explained

<sup>3</sup>Solid solutions are the solid state equivalent of solutions. This means that it is a solid state solute solved in a solid state solvent. The mixture remains in a single homogeneous phase and the solute is incorporated into the crystal structure of the solvent.

previously. Solid solutions based on  $PbTiO_3$ , like PZT<sup>4</sup>, PMN-PT and PZN-PT [18] are often used in applications, but also related, non-lead-containing, materials like SBT and BST<sup>4</sup> are found in devices. The coupling between polarization and stress in ferroelectrics, makes these materials ideal in situations where conversion between electrical and mechanical energy or vice-versa, is required (unfortunately, it also leads to fatigue issues in device operation). One can think, for example, of electromechanical actuators and sensors, production and detection of sound and ultrasound, generation of high voltages, memory devices, electronic frequency generation and ultra-fine positioning. In practice, this means that piezoelectrics are found in scientific instrumental techniques with atomic positional resolution, like STM, AFM and Scanning Near-Field Optical Microscopy (SNOM), and in everyday life in versatile applications as loudspeakers, inkjet printers, diesel engines, airbag actuators, sonar detectors, accelerometers, movement detectors, alarm buzzers, to name just a few.

All of the mentioned ferroelectric perovskites suffer from one problem (when undoped): they all are semiconductors in bulk [19]. This originates from the presence of impurities, the different possible oxidation states of metals, oxygen vacancies and, in some cases, like in  $PbTiO_3$ , cation vacancies. In bulk, the substitutional metal-ion impurities are mainly acceptors (due to abundances on earth) resulting in p-type semiconductivity. For this reason, lanthanum-doping on the lead-site is an effective means to suppress semiconductivity, which results for example in *La*-doped PZT (PLZT). Oxygen vacancies which is a specific problem in perovskites, and especially in thin films and surfaces, leads to n-type semiconductivity. Thin films of ferroelectrics are therefore often p-type semiconductors with n-type interface layers. This complicates electrical measurements and poling, since an applied electric field can give rise to a current instead of polarization switching.

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<sup>4</sup>The abbreviations are commonly used in the field of ferroelectrics and stand for  $PbZr_{1-x}Ti_xO_3$  (PZT),  $Pb(Mg_{1/3}Nb_{2/3})_xTi_{1-x}O_3$  (PMN-PT),  $Pb(Zn_{1/3}Nb_{2/3})_xTi_{1-x}O_3$  (PZN-PT),  $SrBi_2Ta_2O_9$  (SBT),  $Ba_xSr_{1-x}TiO_3$  (BST) and *La* :  $PbZr_{1-x}Ti_xO_3$  (PLZT).



