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Control of periodic ferroelastic domains in ferroelectric $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films for nano-scaled memory devices

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

2015

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Citation for published version (APA):

Nesterov, O. (2015). *Control of periodic ferroelastic domains in ferroelectric $\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$ thin films for nano-scaled memory devices*. [Thesis fully internal (DIV), University of Groningen]. [S.n.].

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Chapter 1

Introduction

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1.1 Scope

The scope of this thesis is to study the fundamental properties of ferroelectric and piezoelectric thin films with a view into the future development of new devices based on these materials. Nowadays piezoelectrics are widely used in sensors such as in airbags and in all kind of electromechanical transducers. They are even used in small, low power, non-volatile memory devices for wireless technology, which keep the information when power is off. An example is the eZ430-Chronos from Texas Instrument - a highly integrated and wireless system that provides a complete reference design for developers creating wireless smart watch applications. The future of piezo-ferroelectrics is seen in the very urgent problem of energy consumption. Environmental energy that is overall wasted can be utilized for low-power applications, such as sensors and wifi transmission networks. In particular, energy of vibrations from different sources can be collected and recycled [1, 2]. Car traffic results in deformation of the road pavement and electromechanical transducers built into the highway could recycle part of this energy. People commuting on a daily basis in crowded cities also produce sufficient energy to power Light Emitting Diodes (LEDs) or to help recharging your mobile phone on the go. For this prospect to become a reality there is a need for developing efficient and less toxic piezoelectrics by reducing the amount of lead, an element present in most piezoelectric materials. In this work we present progress towards this goal. Non-toxic piezo- and pyro-electric devices may in the future allow developing small low-power plants which can be implanted into the human body. They will harvest energy from our own body moves or heat and power devices such as hearing implants or pacemakers that will not need battery replacement, RFID sensors and so on. For all this integrated application, ferroelectrics in thin film form are required.

Firstly, let's briefly describe the material we are going to discuss. The best piezoelectric materials at the moment are solid solutions containing the classical ferroelectric perovskite PbTiO_3 . An example is the well-known $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT) that is used in all electromechanical transducers in most piezoelectric applications. Thus, it is important to first understand the behavior of PbTiO_3 in thin film form and then try to modify the chemistry to reduce the amount of lead while keeping or improving the performance. The advantage of this thin film approach is that we can modify the misfit strain induced in the material and in this way introduce more control levers to tune the properties of PbTiO_3 . Moreover,

in this way we can create features such as domains, domain walls and vortices with nanoscale sizes. Reducing the size of materials while keeping the functionality is another desired approach towards the sustainable use of resources and towards low-power devices.

1.2 Ferroelectric materials

1.2.a Symmetry requirements

Solid-state crystalline materials are widely used in modern technology. The electronics market is full of components made of crystalline materials, such as transistors, capacitors, diodes, etc. The focus in this thesis is on *ferroelectrics* - crystals which exhibit spontaneous and reversible electrical dipoles below a critical temperature T_c . Ferroelectrics are also the best piezoelectrics. Looking at the symmetry of the crystal lattice we can define piezoelectrics as materials without a center of symmetry. There are 32 crystallographic classes or point groups and 21 have no centre of symmetry. However, non-centrosymmetric group 432 could not exhibit piezoelectricity due to other symmetry elements excluding that. Out of the 20 piezoelectric point groups, 10 can allow a dipole moment in the unit cell, and are, therefore called polar groups. These are 1, 2, m, 3, 4, mm2, 3m, 6, 4mm and 6mm.

Crystals with those polar groups can have a polarization (dipole moment per unit volume) in the absence of an electric field and are known as *pyroelectrics* because such spontaneous polarization is temperature dependent. Changing temperature induces a flow of charge to and from the surfaces of the polar crystal, inducing a current through an external circuit. This is the pyroelectric effect. Therefore, the 10 polar crystal classes are sometimes referred to as the pyroelectric classes. If such a spontaneous polarization can be switched by an electric field, then the crystal is also ferroelectric. In other words, ferroelectrics are materials which possess an electric polarization in the absence of an externally applied electric field that can be reversed if an electric field is applied. Since all ferroelectric materials exhibit a spontaneous polarization, all ferroelectric materials are also pyroelectric. In conclusion, ferroelectrics are a small group of pyroelectrics, which, in turn, are a subclass of piezoelectrics. As stated above, in these materials, symmetry allows for the reversibility of the dipoles in the crystal lattice - a very useful feature for applications such as memory devices.

It is also necessary to define a ferroelastic material as a mechanical equivalent to the ferroelectrics. Ferroelasticity is a structure-dependent property. A crystal is ferroelastic if it has two or more stable orientational states in the absence of mechanical stress or electric field, and if it can be reproducibly transformed from one to another of these states by the application of mechanical stress.

1.2.b Ferroelectric perovskites

The center of attention in this thesis is a specific class of ferroelectrics - the perovskite class with general chemical formula ABO_3 . The perovskite crystal structure was first found in $CaTiO_3$ mineral by Gustav Rose, a German mineralogist. In this structure, the A-site ions are located on the corners of a cubic lattice; the B-site ions are in the centre of the lattice and the oxygen anions are in the centre of the cubic faces, forming corner-shared octahedra throughout the lattice. In Figure 1.1 an ideal cubic unit cell of such a compound is sketched. A classic example of a cubic perovskite is $PbTiO_3$ in the high-temperature paraelectric state.

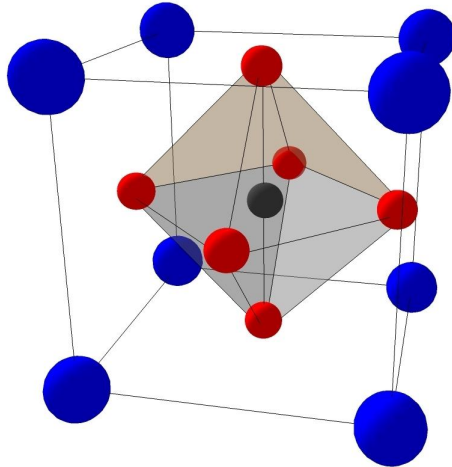


Figure 1.1: *In the perovskite structure, the A cations (blue) sit at the cube corner positions $(0, 0, 0)$, the B cations (black) sit at the body centre position $(0.5, 0.5, 0.5)$ and the oxygen anions (red) sit at face centred positions $(0.5, 0.5, 0)$.*

But the most interesting features of the ferroelectric perovskites, like

spontaneous polarization, appear in non-cubic states. Small distortions of the lattice (small shifts in the cation and oxygen positions) can lower the symmetry to tetragonal, rhombohedral, hexagonal, orthorhombic, monoclinic or triclinic. Which distortions are favored in the perovskite compound depends on the relative size of the A and B ions. The difference in ionic size of the A and B ions gives rise to a slight distortion of the lattice (lowering its symmetry from cubic parental phase) like tilting of BO_6 octahedra or shifting of B -ions from their centre position inside the octahedra. The latter results in a permanent electric dipole per unit-cell, and thus in ferroelectric behaviour, as found in perovskites such as BaTiO_3 . A shift of the A -cations with respect to the oxygen octahedra also produces ferroelectricity, as found in PbTiO_3 and BiFeO_3 .

The tolerance factor [3] was introduced by Goldschmidt to describe the stability and distortions in the perovskite structure. The general formula for the tolerance factor is:

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

where r_A , r_B and r_O are the ionic radius of A , B and oxygen ions, respectively. Only compounds for which t is close to unity adopt the cubic space group $\text{Pm}\bar{3}\text{m}$ (e.g. SrTiO_3 , $t = 1.002$). Three different distortion mechanisms are of interest for perovskites: octahedral distortion, octahedral tilting and cation displacement. The tetragonal phase is adopted by perovskites with the tolerance factor being larger than 1. For t in the range $0.9 < t < 1$, the most common phases are cubic and rhombohedral; for $0.75 < t < 0.9$ the structure tends to be orthorhombic.

There are also examples where either the A or B site is occupied by two different species (such as $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$). Sleight and Ward (1962) have modified the Goldschmidt tolerance factor to include complex perovskites such as $A(B_{0.5}^1 B_{0.5}^2)O_3$:

$$t = \frac{r_A + r_O}{\sqrt{2}\left(\frac{r_B^1 + r_B^2}{2} + r_O\right)}$$

As analogous equation could be derived for other general compositions, like $AB_x^1 B_{1-x}^2 O_3$, in order to predict their structure and properties. This is of great interest, since, by gradually replacing one cation with another, we can tune interesting properties in a continuous manner.

Ferroelectrics, as stated above, are a type of dielectrics which display electrical polarization that can be switched with an external electric field. But they also possess polarization in zero field condition - the so-called remanent polarization P_r . The polarization remains in the material up to the ferroelectric Curie temperature (T_c) - the temperature above which a material becomes paraelectric. T_c typically coincides with the transition to the cubic phase. Due to the switchable nature of ferroelectrics, the polarization versus the applied external field shows hysteretic behaviour (a hysteresis loop), as seen in Figure 1.2. The bistable remanent polarization in this case, plays the role of a binary state for a memory device.

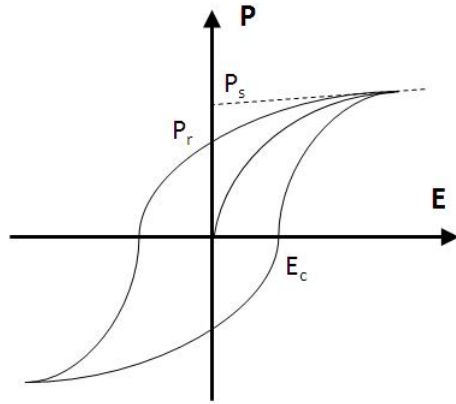


Figure 1.2: Typical hysteresis loop when measuring polarization P versus applied external field E . P_r is the remanent polarization in the absence of E .

1.2.c Ferroelectric phase transitions

As described above, the Curie temperature determines the temperature below which the material becomes ferroelectric. So what happens when we cool a material through the Curie temperature? The material changes from the paraelectric state to the ferroelectric state by changing the symmetry of the crystal from centrosymmetric to non-centrosymmetric. During heating through the phase transition, the remanent polarization of the ferroelectric disappears. Such a variable that is non-zero below T_c and becomes zero above T_c is known as an "order parameter" of the phase transition and reflects the symmetry elements that have been lost at the phase transition. This change may occur abruptly or continuously.

An abrupt or discontinuous disappearance of the order parameter gives rise to a first-order phase transition. The first-order phase transitions are characterized by a nucleation process, during which the new phase appears in the old phase via nucleation and subsequent growth. Thus, it is possible to observe two phases simultaneously, one of them being the stable phase and the other one being the metastable phase, depending on the direction of the change of the external parameter (in this case, temperature). Because of that, a first order transition is also recognized by the existence of latent heat and hysteresis.

On the other hand, in a continuous phase change, so-called second-order phase transition, there is no latent heat involved or hysteresis, since the phase transition does not take place by nucleation and growth but rather by critical fluctuations. While increasing temperature, the order parameter (P_r) decreases continuously and goes to zero at T_c . However, the first derivative of the order parameter, that is the dielectric susceptibility in case of ferroelectrics under electric field, diverges at the phase transition. The dielectric susceptibility is directly related to the correlations between dipolar units and to the fluctuations of the order parameter, both of which also diverge at the Curie temperature. Such dramatic enhancement of the dielectric susceptibility, or dielectric permittivity, which measures the response of the material to the electric field, is of great interest in applications. This critical behaviour is actually responsible for the increased values of dielectric permittivities found in ferroelectrics, with respect to other dielectrics, even at temperatures far from T_c . Because of that, ferroelectrics are used in the electronic industry as supercapacitors.

This is also relevant for piezoelectric applications since at the phase transition not only the dielectric constant ϵ_{ij} ($\epsilon_{ij} = 1 + \chi_{ij}$; $\epsilon_{ij} = (\frac{\partial P_i}{\partial E_j})_T$) shows a very pronounced peak (a divergence, according to the statistical mechanics and thermodynamic theories) but also the piezoelectric coefficients, commonly known as d_{ij} (which are components of a third rank tensor $d_{ijk} = (\frac{\partial P_i}{\partial \sigma_{jk}})_T$, where σ_{jk} is the stress tensor) [4], peak at T_c . The high values and the tunability of these responses are the reasons why piezoelectric ceramics are widely used in applications.

Examples of first and second order phase transition are sketched in Figure 1.3 (a) and (b) respectively, where the order parameter (polarization, P) changes differently as the material goes through the Curie temperature while cooling and heating. A first order transition is also associated with an anomaly in the dielectric permittivity ϵ , which also makes these

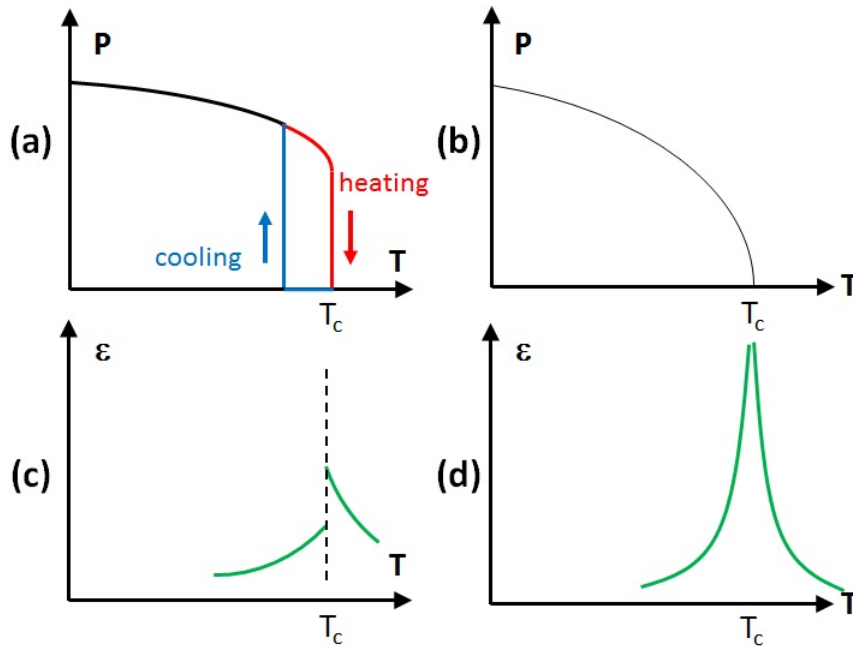


Figure 1.3: (a) In a first order-transition the polarisation becomes zero discontinuously at the Curie temperature. With an associated thermal hysteresis. (b) In a second-order transition, the order parameter itself is a continuous function of temperature, but there is divergence in its first derivative at T_c . This leads to a large anomaly in dielectric permittivity ϵ (d), which is much more pronounced than in the case of first-order phase transitions (c).

materials very responsive to the external field (Figure 1.3 (c)), although not as much as in the case of a second-order phase transitions, for which ϵ is theoretically infinite, see Figure 1.3 (d). It is worth mentioning that for the first-order transition, when heating, the low temperature phase can exist at temperatures above T_c as a metastable phase. This also applies to the high temperature phase, which can persist below the transition point. This effect, related to the nucleation and growth phenomena mentioned earlier, is called thermal hysteresis and it is inherent to first-order phase transitions.

1.3 Novel ferroelectrics by design

As explained above, ferroelectrics are very popular in a number of applications due to their unique properties. But in order to compete with modern market demands we have to take an extra effort to further improve the materials performance. In addition to their large permittivity values, the nonlinear nature and electric-field dependent permittivity of ferroelectric materials can be used to make capacitors with tunable capacitance. Typically, a ferroelectric capacitor simply consists of a pair of electrodes sandwiching a layer of ferroelectric material. The permittivity of ferroelectrics is not only tunable but commonly also very high in absolute value (see previous section). Because of this, ferroelectric capacitors can be made smaller in physical size than dielectric (non-tunable) capacitors.

To tune the ferroelectric properties, one can vary the external parameters in order to move closer to or further away from a ferroelectric phase transition. Although we have previously discussed the most obvious case of temperature-driven phase transitions, this is not the best parameter to use for applications, as it is discussed later, and for tuning of ferroelectric properties a few other methods exist: first, we will discuss composition tuning, applicable both to bulk and to thin films. Then we will introduce the strain engineering method for thin films. A combination of both mentioned methods gives rise to a more advantageous approach that allows finely controlling the strain in a continuous manner by tuning the composition of thin films epitaxially grown on a properly chosen substrate. This thesis exploits this combined approach, which will be described in detail in Chapter 5.

1.3.a Composition tuning

Earlier we discussed and described phase transitions, in particular ferroelectric phase transitions, which are very useful to make small and effective capacitors or responsive ferroelectrics. Temperature is the easiest parameter at our hands to manipulate the phase or state of the material. However most modern devices are used at room temperature, while Curie temperatures (the temperature at which the phase transition takes place) are usually higher, for example T_c is around 490°C for the famous perovskite ferroelectric PbTiO_3 . Moreover, temperature stability is always a requirement in devices and physical properties that change too rapidly with temperature variations are not desirable. This results in the inability

to use temperature for tuning properties of a ferroelectric capacitor. Luckily not only temperature can trigger a phase transition: there are other intensive variables, such as pressure and electric field, that have been used to induce a change of phase or to shift the transition temperature T_c .

In bulk ferroelectrics, the expression "chemical pressure" is often used. In particular in ABO_3 perovskites, the chemical substitution of one of the A - or B -cations with a C -cation of different size affects the structure in similar way as the application of pressure. In this way it is possible to create different crystal phases of the material at a fixed temperature. By carefully choosing the ratio between the ionic radii of C - and A - or B - cations, it may be possible to shift the boundary where two different phases meet such that it takes place at room temperature.

It is, indeed, in such solid solution of the most popular piezoelectric $PbTi_xZr_{1-x}O_3$ (PZT) where, close to the boundary between different phases a large increase in the room temperature dielectric and piezoelectric response was discovered [4]. Moreover, in PZT, the boundary between two phases, a so-called Morphotropic Phase Boundary (MPB), does not depend, or depends very slightly, on the temperature. These two features - a very large piezoelectric response and a very slight temperature variation, in addition to the easy synthesis of this ceramic solid solution - make of PZT the preferred material for most applications for the past four decades. In Figure 1.4 (a), the original phase diagram of PZT, as reported by Jaffe et al. in 1971, is shown, where the temperature is plotted against the composition (mole percentage of $PbTiO_3$). PZT has a MPB between a tetragonal and a rhombohedral phase at $x=0.52$ [4]. Later on, this phase diagram has been revised using higher resolution diffraction techniques, more recently available, and new features have been discovered, especially at low temperatures (a region that was not investigated by Jaffe et al.). According to these new studies [5] there is a new monoclinic phase in a narrow composition triangle around the MPB. This monoclinic phase is the symmetry bridge between the rhombohedral (space group $R\bar{3}m$) and tetragonal (space group $P4mm$) phases, and its space group (Cm) does not contain a polar axis, but only a polar (mirror) plane. Therefore, in this monoclinic phase, the polarization is free to rotate within the mirror plane (in gray in Figure 1.5 c), which further improves the dielectric and piezo-responses [6,7]. Later, neutron diffraction and theoretical calculations have helped to get a complete picture of PZT's phase diagram, shown in Figure 1.4b [8].

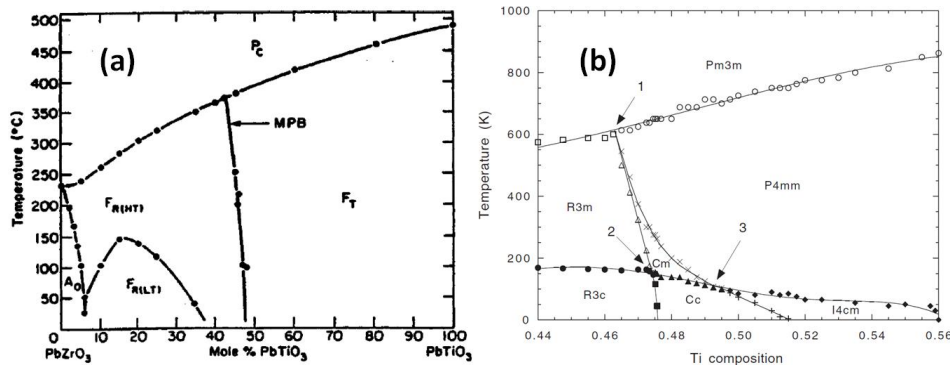


Figure 1.4: PZT phase diagram after Jaffe (1971) [4] (a) and the most recent one [8] at the MPB (b).

1.3.b Thin films and strain engineering

The industry uses ferroelectrics in the shape of bulk pieces and thin films on a substrate. In this section we will discuss the particular properties of very thin layers of ferroelectrics. They present clear advantages because they require little power to operate, offer minimum size of the device and can be easily integrated into modern semiconductor electronics, i.e. as memory devices. With modern synthesis techniques, thin films can be grown with atomic control. This not only makes a better and more reproducible material, but also one that is closer to the model systems used by the theorists, making the feedback between theory and experiment meaningful and extremely useful.

The main subject of this thesis relates to epitaxially grown coherent thin films. Epitaxial films are those that have a crystallographic relation with the underlying single-crystal substrate. If the film either orients randomly with respect to the substrate or does not form a crystalline layer, the growth is non-epitaxial. If an epitaxial film is deposited on a substrate of the same composition, the process is called homoepitaxy; otherwise it is called heteroepitaxy. Homoepitaxy is used to grow materials that are more pure than the substrate or to grow material with different doping levels. Epitaxial growth is often used to grow crystalline films of materials for which crystals cannot otherwise be obtained, to fabricate integrated crystalline layers of different materials (as in devices), or to modify the properties of known materials by inducing epitaxial strain. So-called co-

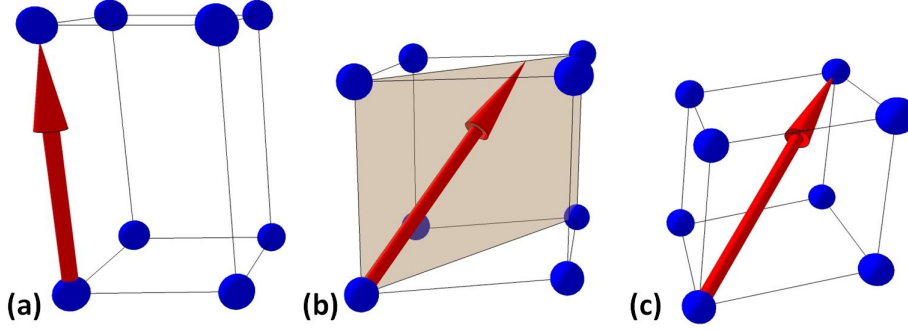


Figure 1.5: *PZT unit cell sketch in different phases, where the red arrow shows polarization direction: a) tetragonal; b) monoclinic with plane of rotation; c) rhombohedral phase.*

herent thin films are those for which the ground state crystal lattice of the material used to grow the film has the same type of structure and a very small lattice mismatch with that of the substrate. In this way the film atoms can exactly follow those of the substrate [9] and the material is deformed with respect to the free bulk state, that is, it grows under epitaxial strain.

As discussed in the case of bulk materials, it is interesting to tune the properties of the ferroelectric by using a control parameter that, unlike temperature, is robust during the device working life. Epitaxial stress/strain can be used as such variable. This is so-called "strain engineering". The film grown on top of a substrate with a small lattice mismatch will try to accommodate to the lattice of the substrate, assuming that the thickness of the substrate is larger than that of the film. Such accommodation produces lattice deformations (strain) in the film. Mathematically, strain is expressed as a dimensionless parameter:

$$u_m = \frac{b - a}{a}$$

Where b and a are in-plane lattice parameters of the substrate and the film, respectively. The strain can be tensile (positive) or compressive (negative) depending on the relative values of a and b . It is to be noticed that this picture is only valid for ultra-thin films of the order of a few nanometers to a couple of tens of nanometers. Only in exceptional cases,

films of a few hundreds of nanometers thick can be grown under strain. Most thin film and devices used in modern technology are thicker than that (of the order of a few micrometers).

It is important to understand that keeping a film under the strain costs energy and that there is a linear dependence between the total elastic energy accumulated in the film and its thickness. So the thicker the film, the more difficult to keep the strain state. The elastic energy stored in the films competes with the energy needed to relax the film by means of formation of dislocations, disclinations, vacancies or other defects and, in the case of low symmetry and ferroelastic materials, also by means of crystallographic or ferroelastic domains, also called twins [10–12]. The mechanism of relaxation very much depends on the material type, mismatch and kinetics of the growth, but for ferroelectric/ferroelastic thin films it is more favorable to relax forming twins than forming dislocations. In particular, dislocations can be totally avoided if the film and substrate materials are chosen such that they present a quasi-perfect lattice match at the growth temperature and similar thermal expansion coefficients. In this way, the epitaxial stress only appears upon cooling down the sample through the paraelectric-ferroelectric/elastic phase transition.

Previously, we described the phase diagram of PZT, where the presence of the MPB makes this material very attractive for applications. In this thesis, we follow the strategy of using strain as a tool to create similar boundaries for the design of improved materials. A phase diagram calculated for single domain thin films of PTO under the epitaxial strain was reported [13], as seen in Figure 1.6 (a). Interestingly, it shows another MPB predicted at room temperature for pure PTO. Later, experiments proved that in PTO films of only 5 nm in thickness, grown on (110)-DSO substrates ($u_m = 0.12\%$), there are regularly spaced polar domains in which polarization appears rotated away from the substrate normal [14], which would be expected for the r -phase predicted in [13]. It has to be noted though that first principles calculations on the same material at 0 K did not predict an intermediate r phase [14]. Using a similar theoretical approach as that in [13] a Landau-Ginsburg-Devonshire-type nonlinear phenomenological theory, only this time taking into account formation of domains in epitaxial ferroelectric thin films of PTO, a new phase diagram was calculated (see Figure 1.6 (b)) [15].

It is, however, difficult to be able to tune the material to be exactly at a predicted phase boundary, given the few commercially available substrates

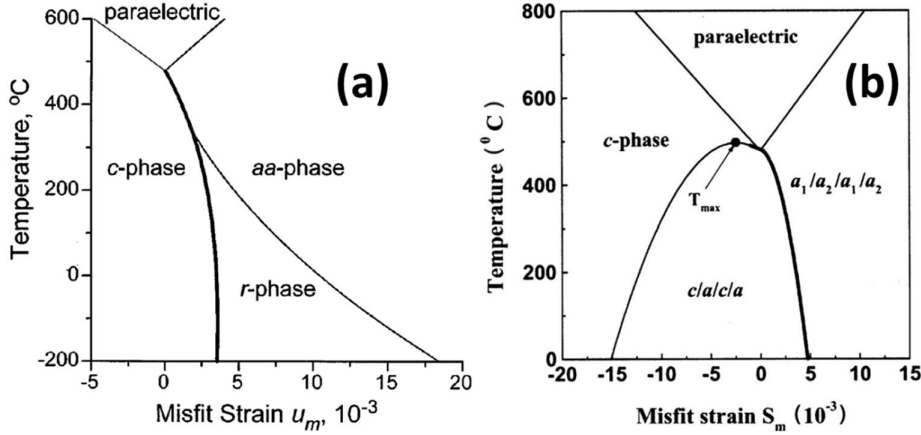


Figure 1.6: Phase diagram for single domain $PbTiO_3$ thin films under epitaxial strain [13] (a) and for polydomain strained $PbTiO_3$ films [15] (b).

(giving access to only a few discrete values of epitaxial stress). That is why in this work we use compositional substitution of the well-known ferroelectric $PbTiO_3$ epitaxially grown on the (110)-oriented $DyScO_3$ substrate. By partially substituting the toxic Pb cation by Sr we can experimentally access recently predicted phase boundaries [16] while we decrease Pb content at the same time.

1.4 Ferroelectric and ferroelastic domains

Building a better and smaller non-volatile memory device is one of the driving motivations for applied research on ferroelectrics. New market demands for memory devices, requesting memory densities of $1Tbit/in^2$ (that is 1 ferroelectric bit every $25 \times 25nm^2$) become difficult to satisfy with modern technology only. That is why natural, self-assembled patterns, such as highly periodic domain structures [10, 11] are seen as the key to move forward. Moreover, in the context of epitaxial strain, above a certain film thickness, domains cannot be avoided and thus understanding the mechanisms for the appearance of domains is of crucial importance.

Domain formation in ferroelectric/ferroelastic films has been largely studied already for many years [2, 10, 11, 17–26]. In order to adapt to the substrate and to locally minimize the mismatch strain or the depolarizing

field, the domains form in a periodic manner [10, 11, 20]. For devices, we typically use a slice of ferroelectric confined in between two electrodes, as a simple capacitor. If we assume a single phase ferroelectric having a spontaneous polarization pointing perpendicular to the electrode surface (in order to be able to later switch the polarization of the memory device), then this will result in a large surface charge. If the electrode is made of a very good metal, then the surface polar charges may be fully screened by the electrons in the metal, but typically with real metal layers, no complete compensation is achieved. These unscreened charges will result in a depolarizing field. For relatively thick capacitors this field is quite small, but it will increase as $1/d$ [27] and become very large when the thickness d of the ferroelectric slice decreases down to the nanoscale. Thus, this effect is a problem for rather thin ferroelectrics. Below some critical thickness this field can be large enough to totally suppress ferroelectricity.

In addition to electrode screening, a few other mechanisms exist to cancel the effect of the depolarizing field: polar adsorbates attracted to the surface of the ferroelectric or charged defects from within the ferroelectric itself. Another way to avoid huge depolarization fields is to divide ferroelectric area into energetically equivalent regions (domains) with alternating polarization vector. In this situation the net surface charge, hence the depolarization field, will be zero. Domains with polarization vectors alternating up and down are also called 180° domains and are equivalent to the stripe domains well known in ferromagnets [28]. In ferroelectric thin films, stripe domains are often referred to as $c+$ / $c-$ domains, where c is the long axis of the ferroelectric tetragonal unit cell, with the direction of this axis pointing out of the plane of the film surface either up ($c+$) or down ($c-$). Therefore, this type of domains appears to be driven by the electrical boundary conditions (that is, the presence of electrodes, the material of the electrode, the presence of adsorbates, charged defects, etc.).

There are also mechanical boundary conditions to consider. Thus, when the thickness of the film is large enough, such that the total elastic energy accumulated in the film is larger than the energy required to create domain walls, the film will start splitting into domains while it relaxes towards the bulk lattice. In this thesis we will work with (001)-oriented PbTiO_3 (PTO) thin films grown on pseudo-cubic (110)-oriented DyScO_3 (DSO) substrates [16]. In this system, b (in-plane lattice parameter of the substrate) lies between the long and short lattice parameters of PTO (c and a , respectively). Thus, $a < b < c$.

PTO epitaxially grown on DSO substrates exhibits a highly periodic a/c -domain pattern, where a -domain refers to a region of the film in which the polarization lies in the plane of the film (there are two perpendicular orientations or domains possible, called $a1$ and $a2$) and c -domain refers to a region with polarization out-of-plane. In Figure 1.7, a sketch of such a/c domain structure is shown. During the cooling stage, the lattice of the film experiences strain as the PTO a -lattice parameter becomes about 1.3% smaller than that of a pseudocubic (110)-DSO at room temperature. In order to compensate for the mismatch, in the absence of defects, the PTO crystal lattice alternates unit cells with their short and long axis in the plane of the film, such that, on average, the in-plane lattice parameter of PTO is equal to the pseudocubic unit cell of (110)-DSO substrate. Mathematically this can be explained as:

$$Nb = N_a a + N_c c$$

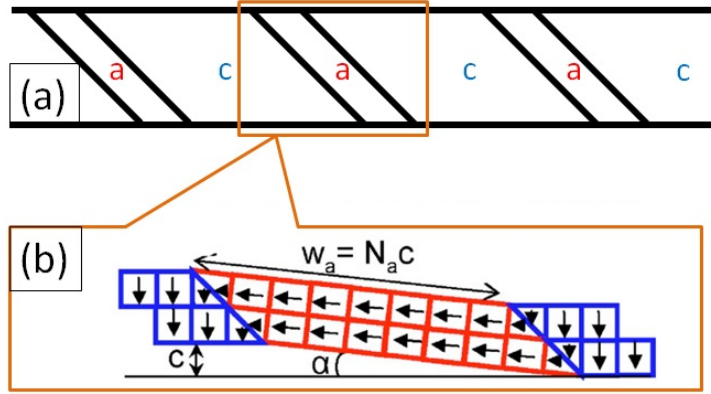


Figure 1.7: (a) Sketch of $a/c/a/c$ domain pattern. (b) The twin angle and the minimum size of an a -domain, determined by a/c ratio. The size of the a -domain needs to be such that it connects two adjacent c -domains with a vertical difference of one unit cell.

Where N_a and N_c are the number of unit cells in the a domain and c domain of the film respectively and N is the total number of unit cells in one period and b is the substrate lattice. Laterally, the lattice match between the c and the a domain requires the tilt of the domains by an angle α in order to share the common (101) planes. In other words, in

this configuration, for the two domains to form a coherent wall in between them, the domains need to slightly rotate (see Figure 1.7 (b)) in a process that is known as twinning. For the bulk situation this angle is expected to be equal to $90^\circ - 2 \arctan(a/c) = 3.55^\circ$, where $a = 3.90 \text{ \AA}$ and $c = 4.15 \text{ \AA}$ (for room temperature PTO). These assumptions allow estimating the size of the domain periodicity and the fraction of a -domain in the period. The number of unit cells of a -domain (N_a) necessary for mismatch compensation is given by $N/N_a = (b-a)/(c-a) \approx 0.20$. The width of the a -domain is such that the coherence between neighboring c -domains is preserved. There is, therefore, a minimum possible size of the a -domain in order to maintain lateral coherence (collinearity of the atomic planes in adjacent c -domains), that is, $w_a^{min} = c/\sin(\alpha)$. The conditions for a minimum size of the a -domains also implies that there is a minimum period size $\Lambda = Nb$, which depends also on the mismatch between substrate and the film.

Characteristic sizes for highly periodic domains can range from two hundred nanometers down to ten nanometers, which makes nanodomain formation attractive for a very high density ferroelectric memory.

1.4.a Domain formation models

The usefulness of the domain structures is nowadays seen to be very attractive as it allows to progress towards smaller devices based on conduction mechanisms of the domains walls [29]. It also allows to investigate the critical sizes for the observation of ferroelectricity and to study novel dipolar arrangements (vortices or closure domains) [1, 30] that may allow increasing storage densities. Thus it is important to have control and predictability of the domain structures when growing thin films. For ultra-thin films of the order of a few unit-cells to a few nanometers, no periodic structures are expected and the films are monodomain. These films are too thin to exhibit reliable ferroelectric switching, as often structural defects and other destructive features play significant roles. This, together with their large coercive fields, makes it very difficult to measure the electrical responses of such layers.

With increasing thickness, films tend to relax into domains, as explained before. The critical thickness for formation of a/c (90° domains) is typically larger than that for the formation of $c+/c-$ (180° domains). Thus, first a 180° domain pattern is favourable and then, at larger thicknesses, a ferroelastic a/c or 90° domain pattern forms. Of course, there is a

different critical thickness for every particular substrate/film combination. For the above-mentioned PTO/DSO combination [31], the crossover from 180° to 90° domains takes place at a thickness of about 18 *nm*. Films with thickness in the range from 10 nm to hundreds of nanometer are easier to work with as they have reliable ferroelectric response for qualitative and quantitative analysis.

The size of the domains increases with increasing thickness as a result of the balance between the depolarizing field energy (for 180° domains) [28], or elastic strain energy (for non- 180° domains) [17], and the domain wall formation energy. Thus, the thinner the films the larger the domain wall density and the greater the influence of the walls on the ferroelectric properties. Moreover, domain walls break spatial symmetry and could add new functionalities to the films when present in large amounts [18]. It is therefore most relevant to have good control of the domain formation and the density of domain walls [32].

Initially, a quadratic dependence between domain size W and film thickness d was proposed by Kittel [28] for stripe (180°) domains in ferromagnets. The same theoretical approach can be used to describe 180° domains in ferroelectrics [19]. The free energy associated with the film consists of at least two parts: one related to the energy of the domains themselves, which is proportional to the domain size W , and the other coming from the domain walls. The number of domain walls is inversely proportional to the domain size $1/W$ and the energy of a single domain is proportional to the domain wall area, which is a function of film thickness d . Mathematically, the total free energy of the film can be written as [24]:

$$F = UW + \gamma \frac{d}{W}$$

Where U and γ are the coefficients of proportionality. $dF/dW = 0$ under thermodynamic equilibrium, from which we derive the classical square root law for domain scaling as a function of thickness of the film/slab:

$$W = \frac{\gamma}{U} d^{1/2}$$

In ferroelastic domains (typically 90° domains), this $d^{1/2}$ dependence is an approximation in the regime of $d \gg W$ [17]. For smaller thicknesses, a linear dependence has been predicted by N. A. Pertsev and A. G. Zembilgotov (P & Z model) [12]. The P&Z method solves the full elastic problem

by mimicking a/c domain formation using arrays of fictitious dislocations distributed along domain boundaries and the film/substrate interface. The main distinction from the classical treatment [17] is that in this way the calculation properly takes into account the influence of the film free surface on the internal stress field. It also takes into account the effect of lattice matching, and Figure 1.8 depicts the sketch of such a model.

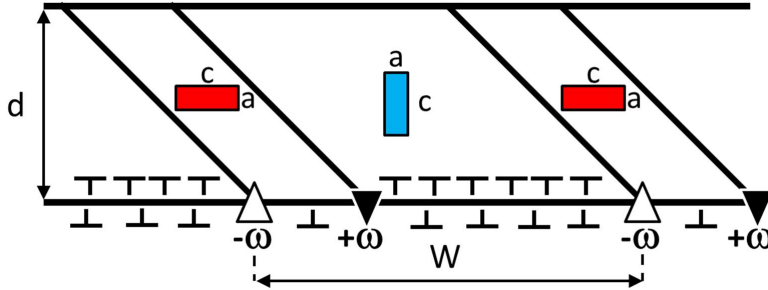


Figure 1.8: *The simplest case of the dislocation-disclination model, according to P&Z. Sketch of an $a/c/a/c$ domain structure in a tetragonal film matched to a cubic substrate [12]. The epitaxy is modelled using fictitious arrays of disclinations with strength $\pm\omega$ (denoted by triangles) and dislocations (T symbols).*

The approach leads to a complex analytical form that will be used for numerical calculations in this thesis. In Figure 1.9 there is the variation of the equilibrium period W versus film thickness calculated numerically in this way. The most interesting feature of this dependency is the presence of a linear part, a behavior that is quite unusual for laminar 90° domain structure in epitaxial thin films for ferroelectric/elastic ceramics, which normally obeys the square root law. This comes from the competition between the domain wall energy and the elastic energy of a disclination array located on the interface. In the regime where the film thickness $d \gg W$, the P&Z model recovers Roytburds' results and takes the simple square root law shape.

1.5 Outline of the thesis

Chapter 2 describes the experimental techniques used during the work that has led to this thesis. In Chapter 3, we investigate the thickness dependence of the period of ferroelastic 90° domains (a/c twins) in the thickness

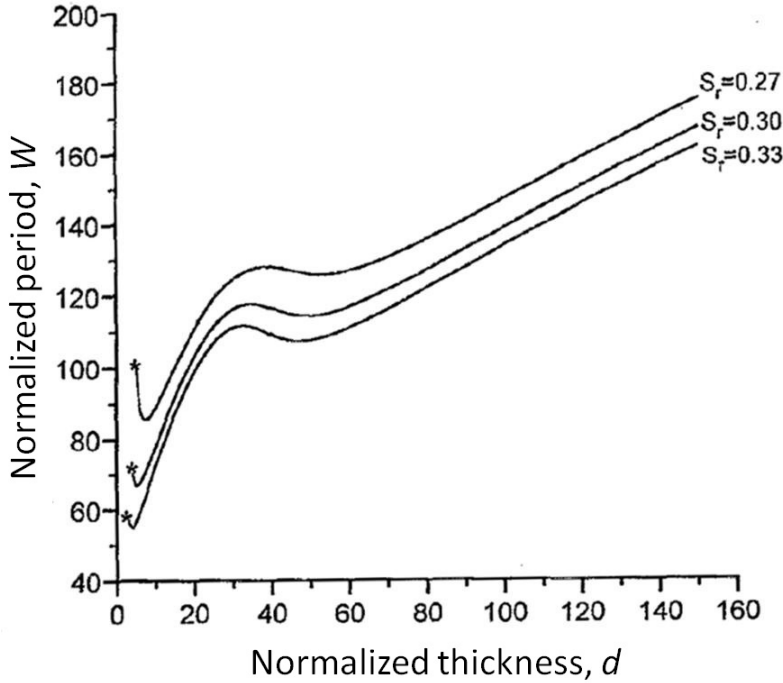


Figure 1.9: Normalized equilibrium domain period versus normalized thickness of the film for an $a/c/a/c$ domain pattern [12]. The normalization parameters will be discussed in Chapter 3.

regime from 10 nm to 240 nm using $PbTiO_3$ films grown on $DyScO_3$ substrates. We use the known domain formation models to interpret the observed behaviour. Because one of the main results is the importance of the kinetics in the domain formation, in Chapter 4, we investigated the freezing temperatures at which domains form. In that way we propose a modified Pertsev & Zembilgotov model that shows an excellent agreement with the experiments.

In Chapter 5, we perform strain engineering in $Pb_xSr_{1-x}TiO_3$ thin films, grown with very accurate control of the epitaxy. We are able to stabilize and control complex domain architectures at two different scales: periodic ferroelectric nanodomains with purely in-plane polarization organ-

ized in strain-equivalent superdomains (with micron size). We suggest the mechanism by which the two length scales coexist in the films. The presence of multiscale domains and strain neutral regions allows us to switch pure in-plane polarization by the in-plane external electric field available while applying a bias field to the tip of an AFM microscope.

In Chapter 6 we describe nanostructuring of 90° domains in PbTiO_3 thin films utilizing wet etching. Selective etching in combination with the high domain periodicity has led to a quasi-periodic mesh. Experiments proved that it is possible to utilize such mesh as memory bits, which can be manipulated independently by field applied to the top surface of the sample.

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