Control of periodic ferroelastic domains in ferroelectric Pb1-xSrTiO3 thin films for nano-scaled memory devices  
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Chapter 1

Introduction

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1.5 Outline of the thesis
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 PbZr$_x$Ti$_{1-x}$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 vortexes 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 $\text{ABO}_3$. The perovskite crystal structure was first found in $\text{CaTiO}_3$ 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 $\text{PbTiO}_3$ 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).](image)

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, mono-
clinic or triclinic. Which distortions are favored in the perovskite com-
pound 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 lat-
tice (lowering its symmetry from cubic parental phase) like tilting of BO\(_6\)
octahedra or shifting of B-ions from their centre position inside the octa-
hedra. 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 Pm\(_{3m}\) (e.g. SrTiO\(_3\), \(t = 1.002\)). Three different distortion
mechanisms are of interest for perovskites: octahedral distortion, octahed-
ral 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 PbZr\(_{1-x}\)Ti\(_x\)O\(_3\)). Sleight and Ward (1962) have
modified the Goldschmidt tolerance factor to include complex perovskites
such as \(A(B_{0.5}^1B_{0.5}^2)O_3\):

\[
t = \frac{r_A + r_O}{\sqrt{2}(r_{B_1}^1 + r_{B_2}^2 + r_O)}
\]

As analogous equation could be derived for other general compositions,
like \(AB_{1/2}B_{1/2}^2O_3\), 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 \( P \) 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 \( \epsilon_{ij} \) 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 \( d_{ijk} = \left( \frac{\partial P_i}{\partial \sigma_{jk}} \right)_T \), where \( \sigma_{jk} \) 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 \( \epsilon \), 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 $\epsilon$ (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 $\epsilon$ 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 $\text{ABO}_3$ 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 $\text{PbTi}_x\text{Zr}_{1-x}\text{O}_3$ (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 (MBP), 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 $\text{PbTiO}_3$). 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 $R3m$) 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 piezoresponses [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].
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. Homoeptaxy 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 discreet 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 $25 \times 25\, \text{nm}^2$) 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 \(180^\circ\) 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:

\[
Nb = N_a a + N_c c
\]

\( N_a \) 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 \( \alpha \) in order to share the common (101) planes. In other words, in

\[
\alpha = \arctan\left(\frac{N_c}{N_a}\right)
\]
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 $a = 3.90\text{Å}$ and $c = 4.15\text{Å}$ (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, $w_a^{\text{min}} = c/\sin(\alpha)$. 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 $a/c$ ($90^\circ$ domains) is typically larger than that for the formation of $c+/c-$ ($180^\circ$ domains). Thus, first a $180^\circ$ domain pattern is favourable and then, at larger thicknesses, a ferroelastic $a/c$ or $90^\circ$ 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 $\gamma$ 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 $90^\circ$ 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 $90^\circ$ domains ($a/c$ twins) in the thickness
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$_x$Sr$_{1-x}$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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Chapter 2

Experimental techniques

Outline

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2.1 Abstract

This chapter presents a detailed description of the experimental techniques used in the work associated with this thesis. We first describe the preparation of thin films of ferroelectric PbTiO$_3$ (PTO) as well as Pb$_x$Sr$_{1-x}$TiO$_3$ (PST) on SrRuO$_3$ (SRO) buffered (110)-DyScO$_3$ (DSO) substrates. We then introduce the techniques used for the characterization of the films.

2.2 Introduction

In order to achieve a high quality epitaxy during the deposition of thin film layers, first, the crystalline substrates should be prepared such that they display atomically flat surfaces. The chemistry involved in the substrate treatment process is explained in the following section. Then, we discuss the Pulsed Laser Deposition (PLD) technique for thin film growth, which is an advanced method that includes a vacuum chamber, pressure gauges and a laser of high power. Moreover, Reflective High Electron Energy Diffraction (RHEED) is used to observe the thin film state during the growth process in-situ in real time. Next, we explain the basic techniques and methods used for the characterization of the thin films. In order to check the topography and the state of the surface of an epitaxial thin film, we utilize Atomic Force Microscopy (AFM). This gives a first idea about the quality of the grown sample, its microstructure, and the quality of the interfaces. In order to check the piezoelectric characteristics of the thin film, AFM is used in piezoresponse mode, what is known as Piezo Force Microscopy (PFM). This allows us to observe ferroelectric domains and to measure ferroelectric polarization-field (P-E) loops and deformation-field loops for qualitative measurements of the piezoelectric coefficients.

The crystallographic structure, thickness and epitaxial quality of the thin films were then studied by X-ray Diffraction (XRD) and X-ray reflectometry. In this work, for this thesis two types of X-ray setups were used. The first setup used a lab diffractometer with a relatively weak X-ray source, which is good enough for measurements such as reflectivity to control the film thickness, longitudinal scans to check for spurious phases and, for relatively thick films, to determine the unit cell size perpendicular to the surface and even for some reciprocal space maps in order to check the strain state of the film. The second type of XRD setups used, which brings most accurate measurements, was an 8-axes diffractometer at a syn-
As described above, we work with PTO and PST thin films deposited on top of SRO-buffered DyScO$_3$ (DSO) substrates. In order to have good initial conditions for the growth and preferred crystal orientation of the thin films, the substrate has to be prepared to achieve an atomically flat surface. In this work we used the single crystal orthorhombic perovskite DyScO$_3$ (DSO) with (110) faces, for reasons that will become clear in the following chapters. The substrates were purchased from CrysTec GmbH.

To describe the crystal of DSO, standard #62, Pnma space group is used [1–4] and the lattice parameters were: $a_o = 5.717\, \text{Å}$, $b_o = 7.903\, \text{Å}$, $c_o = 5.440\, \text{Å}$ [1]. As it can be seen from the Figure 2.1, in the orthorhombic structure of DSO, the plane (101) determines a pseudocubic lattice with Sc or Dy cations surrounded by oxygen anions. The lattice parameters of such a pseudocubic lattice are then given by $a_{pc} \approx c_{pc} = \sqrt{a_o^2 + c_o^2}/2$, $b_{pc} = b_o/2$, which are respectively equal to 3.943Å and 3.944Å (data is taken from [1, 5, 6]). Room temperature PTO has long and short lattice parameters respectively equal to 4.143Å and 3.892Å [7]. Thus (101)-DSO makes a very attractive substrate for growth of PTO epitaxial thin films under tensile strain with rather low mismatch of 1.3% at room temperature. As usual, the substrate faces cannot be made perfectly parallel to the (101) atomic planes and the substrates have a small degree of miscut, in our case usually less than 0.1 degrees. This miscut is the reason for which the surfaces form terraces - one unit-cell high steps along the direction of the miscut, see Figure 2.2. In our case, it is also important to control the stoichiometry of the surface layer, that is if the surface is an AO or an BO$_2$ sublayer, since that will determine the SRO growth. A chemical and thermal treatment method was developed for the DSO substrates, which
Figure 2.1: DyScO$_3$ pseudocubic lattice (red coordinates) inside an orthorhombic unit cell (black coordinates). Note tilted octahedral build with oxygen (red) atoms.

is also applicable to other scandates [8].

First, we thermally treated the DSO substrate at 1000°C, in a tube furnace, with a 150 CC/min oxygen flow, for approximately 4 hours. At this temperature, surface diffusion is very active. Atoms on a surface terrace tend to move towards the edge, thus lowering its energy. Such diffusion process resulted in nice and straight terraces on the surface of the substrate (see Figure 2.2 (b)). These well-ordered steps help with the film growth later. The exact annealing time depends on the terrace length, longer terraces require more time for the diffusion to be complete.
Secondly, we have to make sure that the termination sublayer of the substrate is homogeneous and the right one. For the growth of the electrode SRO layer, it is important that the substrate is ScO\(_2\) - terminated, because SrO grows better on this surface than RuO\(_2\) on the DyO-terminated surfaces [9]. A selective wet etching process using water has been developed at the University of Twente in order to achieve this for scandate substrates [8]. The structure of the perovskite electrostatic bond strength (e.b.s.) for Dy and Sc cations differs, pointing to an increased reactivity of Dy versus Sc. Therefore, the following reaction dominates the etching process:

\[
\text{Dy}_2\text{O}_3 + 3\text{H}_2\text{O}(l) \rightarrow \text{Dy(OH)}_3(aq) \tag{2.1}
\]

Where OH acts as a catalyst. This should result in ScO\(_2\)-terminated surfaces, but it is often irreproducible and time consuming. In order to improve the process the following steps were introduced:

1) 30 minutes rinse in water
2) 30 seconds buffered-HF etching
3) 1 hour in 12 Molar NaOH-deionized water (DI) \( \text{(2.2)} \)
4) 30 minutes in 1 Molar NaOH solution rinsing
5) Cleaning with ethanol

The most crucial steps were 2 and 3. The short HF wet etching (step 2), used to etch small pits on the surface of the substrate to increase \( \text{H}_2\text{O} \) active reaction surface. The high-concentrated NaOH-DI solution (step 3) served as a donor of OH groups for hydratetization of Dy atoms, according to reaction (2.1). The result is as seen in Figure 2.2. It is not easy to distinguish between double and single termination with AFM (Figs. 2.2 b-c) but the growth of the subsequent SrRuO\(_3\) layer clearly reveals the substrate termination [8], as it will be shown in Chapter 3. It is useful to add that thermal treatment should not be performed after the chemical etching as at 1000\(^o\)C major bulk diffusion will result in mixed surface termination again.

### 2.4 Pulsed Laser Deposition (PLD)

Interest in thin film devices makes it important to have a controllable way to make them. Pulsed Laser Deposition (PLD) is only one of the
existing thin film deposition techniques that allow high quality epitaxy. Other methods include Molecular Beam Epitaxy (MBE), Chemical Vapor Deposition (CVD) and Sputter Deposition. In the 1990s, the development of new laser technology, such as lasers with high repetition rate and short pulse durations, made PLD a very competitive tool for the growth of well defined thin films with complex stoichiometry. The main disadvantage of PLD is its scalability - the homogeneous area of the film is around a few \( \text{mm}^2 \), which is quite small compared to other techniques (however progress is being attained on that front as well and there are now systems allowing PLD growth on 8 inch Si wafers [10]). On the other hand, PLD gives the advantage of a very controllable ultra-thin (starting from a single atomic layer) film growth with exceptional quality and very good stoichiometry transfer between the original bulk target and the final grown film.

Smith and Turner [11] first introduced the Pulsed Laser Deposition technique for thin film growth. Pulsed laser deposition (PLD) is a physical vapor deposition technique where a high-power pulsed laser beam is focused inside a vacuum chamber to strike a target of the material that is to be deposited. This material is vaporized from the target (in a plasma plume) which deposits it as a thin film on a substrate (such as a DyScO\(_3\) substrate). A suitable gas has been used to direct the material efficiently from the target to the substrate. Oxygen is commonly used when depositing perovskites to help oxygenate the deposited films. This makes PLD a broadly used method to grow thin films of oxide materials such as per-
ovskites. In addition, in the last decades, the technique has been developed such that it is possible to use electron diffraction to monitor the growth in-situ, similar to what it was commonly done during MBE growth. This has increased the control of the PLD-grown films, making it possible to use this technique to grow films of complex oxides atomic layer by atomic layer [12–17].

There is a complex physics behind the pulsed laser deposition technique, but the basic setup is quite simple in comparison to the other deposition methods. Figure 2.3 shows the sketch of a PLD setup, used for making thin film samples. The main components of the set-up are 1) a powerful laser, 2) a vacuum chamber, with a typical vacuum pressure is $\approx 10^{-7} - 10^{-8} mbar$, 3) a heater with glued substrate - silver paste was used as glue to ensure good heat transfer from heater, 4) a target holder, and 5) an electron gun with the fluorescent screen for real time monitoring of the growth process.

![Figure 2.3: Scheme of the PLD setup with the main components.](image)

In order to prepare for the deposition of the oxide film, a target (polycrystalline or single-crystalline) was prepared with the stoichiometry of the desired films and placed inside the vacuum chamber. A single crystal substrate was placed in front of the target on a heater. The substrate was then heated to the growth temperature and an oxygen atmosphere was created in the previously evacuated chamber. Then a Lambda PhysiK COMplex Pro 205 KrF excimer laser ($\lambda = 248 \text{ nm}$) with 25ns pulses was focused
at the target with a well-controlled fluence. The laser energy absorbed by
the target resulted in the ablation of the material. The fluence has chosen
such that the ablation takes place homogeneously. A typical laser energy
density on the PTO target was $\approx 2.1 J/cm^2$.

The ablated material contains highly energetic ionized species (plasma)
in the form of a plume. The plume expands in the direction perpendicular
to the target surface and reaches the substrate surface. The laser fluence,
the laser pulse frequency, the image area of the laser in the target, the dis-
tance between the target, and the substrate and the oxygen pressure in the
chamber, all determine the density of species in the plume and their energy
when reaching the substrate surface. The background oxygen pressure has
a large influence as it slows down the highly energetic species in the ex-
panding plasma plume. Too energetic species arriving to the substrate can
cause re-evaporation, give rise to lack of stoichiometry and defects, while
too low energy species lack diffusive power to form an atomically flat film.
A typical background oxygen pressure for PTO growth was 0.06 mbar for
a distance between the substrate and the target of 55 mm and a laser rate
of 10 Hz.

The nucleation process and growth kinetics of the film depends on
the density of species arriving at the surface and on the energy of those
species. The important parameters determining the film growth are, thus,
all those mentioned above plus the substrate temperature. The substrate
surface temperature has a large influence on the nucleation density. Surface
diffusion acts as a distribution mechanism for the deposited ions. This
results in less nucleation centers and more mobility of the species with
increasing the temperature. To determine the diffusion process, the surface
roughness, substrate miscut, surface quality and surface chemistry are also
important factors to consider.

Each pulse of the laser lasts around 25 nanoseconds. During this time,
a lot of material is being deposited on the surface. This gives rise to a large
supersaturation. This supersaturation causes a large nucleation density on
the surface. Under certain circumstances, this high nucleation density in-
creases the smoothness of the deposited film. PLD growth is, thus, ruled
by kinetics rather than thermodynamics of the surfaces involved. Gener-
ally, the nucleation density determines the growth mode. In particular, it
will determine if the film growth is atomic layer by atomic layer or, on the
contrary in step-flow mode (give rise also to flat surfaces but without the
in-situ thickness control) or in island growth mode which results in rough
films.

### 2.4.a Reflective High Energy Electron Diffraction (RHEED)

Reflective High Energy Electron Diffraction (RHEED) was used in order to have a real-time and in-situ control over the process of growth inside the PLD chamber [18]. This is a very accurate surface sensitive technique, as the incident and probing angles of the electrons on the growing surface are very small.

A simple sketch of such a RHEED set-up, as a part of a PLD system, depicted in Figure 2.3 (a). It consists of a directed electron source (gun), fluorescent detector screen and a sample with atomically flat surface. The electron gun generates a beam of electrons, accelerated to 10-30 keV, which strike the sample at a very small angle (within 1.5 degree relative to the sample surface). Incident electrons reflect from atoms at the surface of the sample, and a small fraction of the electrons diffract at specific angles and form regular patterns on the detector. The image that is then recorded by a CCD sensor. An example of such an image is depicted in Figure 2.4 (b). So the diffraction pattern at the detector tells about the structure of the sample surface. Electrons are heavily scattered by the gas molecules used during growth, which made the technique useless for PLD growth for a long time. Nowadays, a differentially pumped path is created (the pressure is a few orders of magnitude lower than in the rest of the chamber) using a guiding tube connected to a separate pump. In addition, the chambers are designed as small as possible to minimize the length of the diffracted path [13].

The diffracted electrons interfere at specific angles according to the crystal structure and spacing of the atoms at the sample surface and the wavelength (energy) of the incident electrons. The diffraction pattern created on the detector, in principle, can be analyzed and used to characterize the crystallography of the sample surface, although the accuracy is less than that offer by XRD. Figure 2.4 (b) shows a RHEED pattern obtained from electron diffraction for a clean atomically flat 6 nm SrRuO₃ thin film grown on top of the DyScO₃ substrate. The bright spots indicate high intensity of electrons reaching the detector.

Two types of mechanisms contribute to the RHEED patterns. Some incident electrons undergo an elastic scattering at the sample surface, so-called kinematic scattering. Dynamic scattering occurs when electrons undergo multiple diffraction events in the crystal and lose some of their
energy due to interactions with the sample. We constructed the so-called Ewald’s sphere to find out the structure of the sample surface. Ewald’s spheres easily show where to expect the diffraction spots for kinematically scattered electrons, see Figure 2.4 (d). The Ewald’s sphere analysis for surfaces is similar to that for bulk crystals. Due to the surface sensitivity of the RHEED technique, there are no diffraction conditions in the dimension perpendicular to the sample surface; in other words due to the very shallow angle of the incident electron beam, the scattering wave vector has very small component perpendicular to the sample surface. The observed reciprocal lattice of the sample differs from that of a bulk material, which typically consists of a set of points in 3D space. The reciprocal lattice of a crystal surface is a series of infinite rods extending in the direction perpendicular to the sample surface, see Figure 2.4 (c-d).

The Ewald’s sphere has its center on the sample surface and its radius is equal to the magnitude of the electron wave vector $k_0 = 2\pi/\lambda$, where $\lambda$ is the wavelength of incident electrons. The diffraction condition, so-called Laue condition, are satisfied where the rods of the reciprocal lattice intersect the Ewald’s sphere. The elastic nature of the scattering process takes care that the magnitude of any vector $k_i$, going from the center of the Ewald’s sphere to the intersection with any reciprocal lattice rods is equal in magnitude to $k_0$, see Figure 2.4 (c). Formally this could be written as $|k_0| = |k_i|$. The vectors $G$, defined as $G = k_0 - k_i$, are the reciprocal lattice vectors, which satisfy Laue condition and, thus, define the crystal structure of the sample by means of the relation $G_{hkl} = 2\pi/d_{hkl}$, where $d_{hkl}$ is the distance between (hkl) crystal planes. The $G$ vectors can then be used for finding the distance between arbitrary planes in the crystal. In particular, in our case of surface diffraction, it was used to extract the in-plane lattice parameters. Since electrons do not provide as high sensitivity as X-rays, the RHEED characterization is considered as a qualitative measure of the sample crystallinity.

Next to the elastic process just described, some electrons penetrate the bulk crystal and fulfill Bragg diffraction conditions, being able to scatter more than once. These inelastically scattered electrons can reach the detector to yield the so-called Kikuchi diffraction patterns. Kikuchi patterns are characterized by lines connecting the intense diffraction points on a RHEED pattern.

Another important piece of information about thin film growth is ex-
2.4 PULSED LASER DEPOSITION (PLD)

Figure 2.4: a) Sketch of the RHEED set-up. b) Screen view of a RHEED pattern after the growth of a clean atomically flat 6 nm thick SrRuO$_3$ thin film, deposited on the surface of a (110)-DyScO$_3$ substrate. c) Side view of the sample with the Ewald’s sphere and the rods of the reciprocal lattice. d) Top view of the sample with Ewald’s sphere and the rods (look as dots from the top) of the reciprocal lattice. Figures c) and d) adapted from [19, 20].

Extracted from an intensity analysis of diffraction points on a RHEED pattern. The intensities of individual spots on the RHEED pattern fluctuates in a periodic manner as a result of the relative surface coverage of a thin film growing in a layer-by-layer fashion. Figure 2.5 (c) shows an example of the intensity oscillating at a single RHEED point during PLD growth of epitaxial Pb$_x$Sr$_{1-x}$TiO$_3$ thin films on a SrRuO$_3$-buffered (110)-DyScO$_3$ substrate.

Each full period in the oscillations corresponds to the formation of a single atomic layer. Thus, intensity oscillations are used to control the thickness of the film. The oscillation period is highly dependent on the material grown, electron energy and incident angle. The RHEED intensity can also be used to determine the growth mode: if a 2D-like diffraction pattern is observed, like in Figure 2.5 (a) and (b), but no oscillations are seen in the RHEED intensity, then the growth more is step-flow, while
island growth would result in a regular 3D diffraction pattern, see example on Figure 2.5 (d).

### 2.4.b Synthesis of polycrystalline targets

In this work we study the ferroelectric properties of PbTiO$_3$ (PTO) and Pb$_x$Sr$_{1-x}$TiO$_3$ (PST) thin films, where $x = 0.55 - 1.00$. There is no commercially available single crystal or ceramic targets for PLD growth of such material. The targets used in this work were therefore made in-house. In the following paragraph we describe this process.

Due to the volatile nature of Pb, in order to avoid unplanned Pb vacancies, the targets should be prepared with an excess of Pb. A 4% Pb-excess
has been shown to work in our case (the Pb excess in the target, as well as the target density, will strongly influence the growth conditions and the final quality). A so-called solid state reaction is used to prepare such solid solutions from metal oxides, according to the formula:

$$xPbO + (1 - x)SrCO_3 + TiO_2 \rightarrow Pb_xSr_{1-x}TiO_3 + (1 - x)CO_2 \quad (2.3)$$

The solid-state reaction is the most used method for the preparation of polycrystalline solid solutions from a mixture of solid materials. Solids do not react together at room temperature and it is necessary to heat them to much higher temperatures in order for the reaction to occur at a reasonable rate. The factors that influence the rate and efficiency of a solid state reaction include the reaction conditions, structural properties of the reacting materials, surface area of the solids and their reactivity.

The reagents in powder form were dried thoroughly prior to weighing. The reactants were weighed in the required amounts according to the chemical reaction (2.3) and then mixed. First manual mixing, with mortar and pestle, and then mechanical mixing, using a ball mill (Fritsch pulverisette 6), were used, for a total time of 2 hours. If necessary, the process of milling was repeated or prolonged. Before heat treatment, the prepared powder was pressed and shaped into the form of a cylindrical pellet suitable to use as target in the PLD chamber. This also increases the area of contact between the powder grains facilitating the sintering. Powders were first placed into a DIY (a cylinder with corresponding piston made of a hard steel), which consist of a metal cylinder with a piston 20 mm in diameter, and the DIY was then positioned in a hydraulic press. After 5 to 15 minutes under $\approx 30 MPa$ of pressure, a pellet was formed. Then, chemically inert alumina crucibles and boats were used to bring the pellet to the high temperatures required for the reaction. In order to preserve volatile Pb during heating, extra PbO$_2$ powder was supplied in the alumina boat to create a Pb rich atmosphere around the pellet, which was then covered with an alumina crucible. The next crucial step was the heat treatment. A different heating program was used depending on the composition of the target. On Figure 2.6 the heating program for PST with $x = 0.9$ is shown. A Nabertherm P 320 furnace was used.

The stoichiometry of the sintered pellet was checked by means of powder X-ray diffraction, as explained later.
2.5 Atomic Force Microscopy (AFM)

In this work the properties of thin films as thin as 6 nm are investigated. The minimum thickness is around 15 atomic layers (from now on called monolayers) of material. Such thin films usually have roughness around 1 or 2 monolayers. Atomic force microscopy (AFM) has been used to characterize the topographical features of the film, in the nanoscale regime.

Firstly, this type of local probing technique was developed as a particular type of Scanning Probe Microscopy (SPM). SPMs are suitable for local measurements and imaging of mechanical and electronic properties of materials. The images of the surface are formed using a physical probe (cantilever) that scans the sample. Such technique has the advantage of about 6 orders of magnitude higher magnification compared to optical imaging, which only has a maximum magnification of 2000x. In short, advantages of probing techniques are: 1) the resolution of the microscopes is not limited by diffraction, but only by the size of the tip-to-sample contact/interaction patch, which can be as small as a fraction of an angstrom (in the tunneling regime), resulting in atomic resolution in the case of the Scanning Tunneling Microscope (STM) and it is around 10-50 nm in the case of AFM; 2) the interaction between tip and sample can be used to locally modify the sample with mechanical pressure and electromagnetic field; 3) different ambient conditions can be used during the measurements; it is not necessary to have a vacuum (although this is of course necessary to observed a surface free of contaminant or at low temperatures) or particular pressure conditions.

Scanning probe imaging started with the invention of the Scanning
Tunneling Microscope (STM) by Binnig, Gerber and Weibel in 1982 [21]. STM is based on the concept of quantum tunneling of electrons. A conductive tip is brought very close to the surface of the sample (which must be of metallic nature). A bias applied between the sample and the tip allows electrons to tunnel through the vacuum between the two. The resulting tunneling current is a well-known exponential function of effective tip-to-sample distance, applied voltage and the local density of states (LDOS) of the sample. The current is monitored as the tip scans across the surface such that slight changes in the roughness (thus the tip-to-sample distance) produce quantifiable changes in the current, providing information of the sample topography, which is displayed in image form, as the probe scans the surface. A crucial aspect in the technique is the possibility to follow accurate cantilever movements using a reflection of a laser on the cantilever. Next to this, Binnig et al. found a way to measure the forces involved in the of tip-to-sample interaction. This sets the start for Atomic Force Microscopy (AFM) [22]. Although the resolution is clearly lower than STM, a major advantage of AFM over STM is that it needs no conductive sample. We can categorize different AFM modes with respect to the force it measures. It could be induced mechanically, magnetically, by the electric field, the surface potential or by the Van-der-Waals and chemical bonding forces. Unlike the previous techniques that work with very small and well controlled tip-to-sample distances, there is also a relatively new technique called Conductive-AFM (CAFM), which uses full contact mode and measures the current through the sample (between a bottom electrode and a conducting tip) in order to probe local conductivity. By means of an amplifier (commercialized as TUNA\textsuperscript{TM} module in the case of our Dimension V, VEECO-Bruker microscope), currents as small as \textit{pA} can be detected and, therefore, this is very appropriate to observe hot spots and local conduction in insulators and semiconductors. The most interesting and useful mode for the work presented in this thesis is Piezoresponse Force Microscopy (PFM), used to measure qualitative and (under some conditions) quantitative piezoresponse in ferroelectric thin films. In this regime, the set-up measures the coupling between the AC electric field applied to the material across its thickness (applying a bias voltage between the bottom electrode and the metallic tip touching the surface), and the deformation (strain) of the sample induced by the same field. This technique also allows to measure and, under the application of a sufficiently large field, to manipulate the orientation of the ferroelectric polarization.
2.5.a AFM microscope description

The main components of an AFM microscope are: 1) a cantilever with sharp tip (probe) at the end; 2) a photosensitive detector; 3) an AC voltage generator; 4) a feedback mechanism and 5) a lock-in amplifier for signal detection.

The cantilever with a sharp tip at its end is used to probe the sample surface. The cantilever is typically made of silicon (or silicon nitride) with a tip radius in the order of nanometers. For specific applications, other materials such as diamond, carbon nanotubes or fullerenes has been used. The tip's sharpness/size determines the lateral resolution of the microscope. In contact mode (as used in CAFM and PFM), we also should account for a normal wear of the tip such that it becomes less sharp during scanning process. To reduce the tip wear, a proper amount of force, which depends on the mode of scanning, the material of the sample and the tip, should be applied to the tip. For the two measurements modes mentioned above (CAFM and PFM), the tip is covered with a thin conductive layer, which increases the tip size and decreases the resolution. Typical cantilevers used in this work for PFM measurements are made of silicon coated with conductive Co-Cr. The elastic constant for the tip is $5 \text{ N/m}$. When the tip is in contact with or in the proximity of a sample surface, the force between the tip and the sample leads to a deflection of the cantilever according to the tip's elastic parameters (Hooke's law). The deflection of the tip is then measured using a narrow laser beam reflected from the top reflective surface of the cantilever into an array of photosensitive diodes, see Figure 2.7. The laser spot position is then fed to the lock-in amplifier.

Subsequently, this information is transferred to the feedback mechanism. To provide precise tracking of the sample surface or sample deformation under the applied field, the feedback mechanism adjusts the position of the tip holder over the sample surface to maintain a constant force experienced by the tip. The tip is controlled by the piezoelectric tube scanner. The tube scanner can move the sample in the $x$, $y$, and $z$ directions using a single tube piezo actuator. The AC generator is used to provide an alternating voltage, hence electric field, to the sample. This is required during piezoresponse measurements. In this work the range of frequencies used for the piezoresponse is from $5 \text{ kHz}$ to $2.5 \text{ MHz}$, which is the limitation of the optical detector.

Working with ultra-thin films (6 nm thick) sets great demands on the AFM set up, while working in PFM mode, as it works at its sensitivity
limits, where the noise signal is comparable with the piezoresponse of the sample. In order to overcome this problem the measurements were done at a frequency close to the resonance frequency of sample-tip mechanical system. This method vastly improves the signal to noise ratio [23].

2.5.b Topology and tapping mode

This is the mode used to image the topography of the top surface of the samples. Probing with an AFM tip is based on short-range forces. Thus the cantilever is in close contact with the sample and consequently this results in tip wear and contamination (especially while working in ambient conditions), hence reducing probing resolution and causing artifacts appear on the image. In order to overcome this problem, the so-called tapping mode was invented.

In tapping mode, a voltage generator provides signal to the small piezoelectric element mounted on the AFM cantilever holder, which drives the tip to oscillate up-down at frequencies near the mechanical resonance frequency of the cantilever. The amplitude of these oscillations is in the range from 100 to 200 nanometers. The oscillating system starts approaching the surface of the sample. As the tip comes close enough to the surface, forces like the Van-der-Waals force or electrostatic forces change the amplitude of the oscillations. The feedback loop of the AFM will then modify the position of the tip in order to keep amplitude of the oscillations constant. The changes in tip position as the tip scans the surface are a direct reflection of the height of the sample surface at each location, allowing to image the topology of the sample without physical contact between tip and surface. Nevertheless, the lateral resolution of the method is limited by the radius of the tip’s end, which is in the range from 5 to 30 nm. On the other hand, the vertical resolution could be as small as a few angstroms as it is only limited by thermal and electrical noise. This is a very gentle mode and it is usually used to map not only solid state materials, but also soft polymer molecules and samples under liquid atmosphere.

2.5.c Contact mode and piezo-force microscopy (PFM)

As mentioned before, contact mode provides the ability for AFM to measure local properties such as piezoresponse or conductivity. In this mode, the tip is engaged to the surface of the sample at some predefined force and then the tip is dragged over the scan area. The feedback mechanism
is responsible to keep this force constant. In this way it is possible to map
the topology of the sample, although with less resolution than in tapping
mode. Here we will focus on the contact mode technique of most relevance
to the present thesis: PFM. In order to reveal intrinsic electric dipoles in
the bulk of ferroelectric thin films, an AC field is applied between the tip
touching the surface of the film and a bottom electrode onto which the
film has been grown (a conductive thin layer under the measured film).

Imaging and manipulating the local response of piezo and ferroelectric
films has been achieved with success by Piezo Force Microscopy (PFM)
[23]. This has been done in contact mode with a ferroelectric (or piezo-
electric) thin film and applying an AC bias to the tip in order to excite
local deformations of the sample, whose magnitude is proportional to the
piezoelectric coefficients of the film. As explained above, the resulting de-
flexion of the cantilever is detected by a photodiode detector and then
amplified and decoded by the lock-in amplifier. In this way we have two
images simultaneously: topography and ferroelectric response. It is also
possible to switch regions of ferroelectric domains with the application of a
voltage bias to the tip that is larger than the coercive field (the switching
field) of the material. The sensitivity and the resolution of the method
greatly depend on tip sharpness, contamination of the sample surface, and
other cantilever properties like stiffness and resonance frequency.

The piezoelectric effect can be mathematically written as:

\[ D_i = P_i + \varepsilon_0 E_i = d_{ijk}\sigma_{jk} \]

(2.4)

where \( \sigma_{jk} \) is the component of the stress tensor, \( d_{ijk} \) is the component
of the piezoelectric tensor, \( D_i, P_i \) and \( E_i \) are electric displacement, po-
larization and electric field, respectively. \( \sigma_{jk} \) is a second order symmetric
tensor and thus it has only 6 different components. For simplicity this
tensor is often expressed with a single index only:

\[
\begin{align*}
\sigma_1 &= \sigma_{xx} \\
\sigma_2 &= \sigma_{yy} \\
\sigma_3 &= \sigma_{zz} \\
\sigma_4 &= \sigma_{yz} = \sigma_{zy} \\
\sigma_5 &= \sigma_{xz} = \sigma_{zx} \\
\sigma_6 &= \sigma_{xy} = \sigma_{yx}
\end{align*}
\]

(2.5)

Thus, the piezoelectric tensor \( d_{ijk} \) has in total maximum (for the com-
plex case of triclinic symmetry) 18 different components. That is why a
6x3 matrix is used instead of a 3x3x3 tensor for convenience. Therefore, the $d$ coefficients are often described by two indexes [24]:

$$
D = \begin{pmatrix}
D_1 \\
D_2 \\
D_3
\end{pmatrix} = 
\begin{pmatrix}
d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\
d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\
d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36}
\end{pmatrix}
$$

(2.6)

From what has said above, it is possible to apply a constant voltage across a piezoelectric film, which leads to physical deformation of the film. The deformation will be very small due to the piezoelectric coefficients being quite small, even for the best bulk materials like PbTiO$_3$ (PTO) (longitudinal coefficient $d_{33} \approx 50$ pm/V [25, 26]), Pb$_{x}$Zr$_{1-x}$TiO$_3$ (PZT) ($d_{33} \approx 290-450$ pm/V [27–29]) or BaTiO$_3$ ($d_{33} \approx 185-260$ pm/V [30, 31]). For film thicknesses of a few tens to a few hundreds of nanometers, this deformation is below the level of AFM sensitivity. In order to overcome this problem and increase the signal-to-noise ratio, the voltage applied to the sample is modulated as:

$$
V(\omega) = V_0 \cos(\omega t)
$$

(2.7)

Where $\omega$ is the modulation frequency and $V_0$ is the amplitude of the modulation. This leads to an oscillatory deformation of the sample with the same frequency:

$$
d(t) = d_0 + A \cos(\omega t + \phi)
$$

(2.8)

Where $d_0$ is equilibrium position of the sample surface and $A$ is an amplitude of the sample oscillations with associated phase difference $\phi$ with respect to the driving field. These parameters are extracted by a lock-in amplifier. The lock-in amplifier takes the reference signal applied to the tip (2.7) as well as the signal recorded from the photo detector (2.8) and applies a demodulation technique, from which the amplitude $A$ and phase shift $\phi$ can be derived. The amplitude $A$ then can be used to extract the corresponding components of the piezoelectric tensor via formula (2.4).

There are two possible modes while doing PFM: vertical and lateral. Vertical PFM (or VPFM) records the piezoelectric response of the sample in the direction of the applied field. In the easiest configuration, for which the polar axis is normal to the surface of the sample (see Figure 2.7 (a)),
this method allows to measure the longitudinal $d_{33}$ coefficient of single crystal samples. If the polar axis lies in the plane of the film, the transversal $d_{31}$ or $d_{32}$ coefficients were being measured.

The PFM set-up, as depicted in Figure 2.7 (b), also allows to record the shear piezoelectric response of the sample through the torsion motion of the tip. The limitation of such a set-up is that lateral PFM (LPFM) senses only in one of the in-plane directions, as depicted in Figure 2.7 (b). Therefore the polarization component in the direction normal to the scan direction will not be measured at all. In order to overcome this, we rotate the sample and perform measurements for different lateral directions. To construct the full picture of the sample polarization (build full piezoelectric tensor) we check all possible directions of polarization.

The shear components of the stress $\sigma_{13}$ and $\sigma_{23}$ ($\sigma_5$ and $\sigma_4$ in matrix notation) can be detected in this mode. Having an electric field $E_3$ applied (bias between the tip and the bottom electrode), the piezoelectric coefficients $d_{34}$ and $d_{35}$ can be measured.

Theory predicts the intrinsic behavior of the piezoelectrics and ferroelectrics very well. On the other hand, it occurs frequently that, during experiments, extrinsic factors encountered are greatly influence the imaging of the domain and domain walls in the thin film. Firstly, adsorbents from the atmosphere condense on the sample surface, making measurements
difficult. In order to overcome this problem, in this work the sample was cleaned in two stages: by chemical treatment in acetone and alcohol followed by heat treatment in the oven at 200°C with a small flow of pure oxygen, for about 2-3 hours. In this way we remove the surface contaminants, which would act as a barrier between the tip and the sample. This barrier would serve as a dielectric layer in the capacitor sample-contamination-tip system. As we apply a potential between the tip and the sample, the capacitor would accumulate charges, which would result in huge electrostatic forces and distort piezo signal of the sample. After the cleaning procedure, immediate PFM measurements showed particle free surfaces and a much improved signal to noise ratio, with only few artifacts.

2.6 X-ray diffraction

X-ray diffraction has been used to determine the atomic structure of a single crystal of the grown film or the polycrystalline material of a PLD target, in which the perfect ordering of the atoms of a crystal lattice over sufficiently long length scales causes a beam of X-rays to diffract (similar to the RHEED technique described before). By measuring these diffracted beams at specific angles we can produce a three-dimensional image of the localized density of electron clouds in the crystal lattice. From this electron density, the mean positions of the atoms in the crystal, distance between atomic planes and several other features (which change electron density of the structure) can be determined. In this work we used two different sources of X-rays, namely synchrotron and lab sources, which provided X-ray wavelengths of 1.2398 Å and 1.5402 Å, respectively. Thus the wavelength is small enough to resolve the distances between atomic planes (about 4 Å) of the studied material.

To perform an X-ray diffraction experiment, a crystalline/polycrystalline material is mounted on a goniometer and it was gradually rotated while being bombarded with X-rays, thus producing a diffraction pattern of regularly spaced spots, called Bragg reflections. A Fourier transformation is used to convert the two-dimensional diffraction image into three-dimensional structure of the density of electrons, which reveals the position of atomic planes or other periodic features. Since X-ray diffraction was used in this work to determine the structural features of the sample, the main interest was the elastic scattering of the X-rays. In other words, the scattered X-rays have the same wavelength as the incident X-rays.
Bragg’s law provides a good visual description of diffraction as the interference between X-ray beams that reflected by different crystal planes. Bragg’s law provides the conditions for constructive interference and, thus, for the angular positions of the diffraction intensities as:

\[ n\lambda = 2d_{hkl} \sin \Theta_{hkl} \]

Where \( n \) is the order of diffraction, \( \lambda \) is the wave length, \( d_{hkl} \) is the distance between (hkl) atomic planes (perpendicular to the [hkl] direction) and \( \Theta_{hkl} \) is the X-ray incident (and reflected) angles. This law is visualized in Figure 2.8. The vector \( G \), defined as \( G = k_d - k_0 \), is the difference between the scattered and the incident wave vector. These vectors determine the reciprocal space, whose periodicity is inversely related to that of the real space. Dealing with reciprocal space vectors facilitates the solution of the crystal structure. Once the reciprocal space vectors (the position of the Bragg reflections) are known, the real space (distance between atomic planes) can be extracted using the simple relation: \( e^{iKR} = 1 \), where \( K \) are the vectors of the reciprocal lattice and \( R \) are those of the real lattice.

**Figure 2.8**: Bragg’s law visualization. a) Real space lattice of a crystal bombarded by the X-rays. Constructive interference between the reflected beams occurs only when Bragg’s condition is fulfilled. b) In reciprocal space, Bragg’s law fulfill when the Ewald’s sphere of radius \( k_0 = 2\pi/\lambda \) intersect with the reciprocal lattice points of the crystal.

A typical X-ray diffractometer consists of a source of radiation, a number of slits to adjust the shape and size of the beam, a sample holder
mounted on the goniometer and a detector. The set-up can also have other equipment and parts in order to provide necessary functionality to the user. One of the most important elements is the monochromator, which typically consists of one or two pairs of parallel Si or Ge crystals that select a particular wavelength, see Figure 2.9. In relation to the diffracted path, there are different types of the detectors: 1) point detectors, which sense the X-ray beam only at one point in space; 2) linear detectors, that consist of a linear array of point detectors (pixels) to sense x-ray intensity from a line in space; and 3) area detectors that consist of a two-dimensional array of point detectors to sense a diffracted beam in some area in the space and provide the information of its angular deflection with respect to the incident beam. The fastest way of getting information is, of course, from the two-dimensional area detector as it scans the space more efficiently.

![Sketch of the thin film diffractometer at the P08 beamline at PETRA III-HASYLAB, DESY (Hamburg, Germany), where some of the X-ray experiments of this work have been performed. The names correspond to the relevant motors (as named by the beamline software) or, in other words, the degrees of freedom that need to be controlled during the experiment.](image)

### 2.6.a X-ray powder diffraction

As described in section 3.2, all polycrystalline pellets used as PLD targets were home-sintered via solid state reaction process. The final target characterization has been performed by power X-ray diffraction, which allows
to determine the purity of the target and its structure.

Figure 2.10 shows the powder diffractogram of a PbTiO$_3$ target with a PbO excess, which is needed to compensate for the Pb loss that takes place during the PLD process, together with the results of the simulation pattern as obtained by using the PowderCell refinement software. From the results of the refinement the PbO/PbTiO$_3$ ratio of the final target was extracted, which was composed of $\approx 94\%$ pure tetragonal PbTiO$_3$ and about $6\%$ PbO ($1.4\%$ - tetragonal phase plus $4.7\%$ orthorhombic phase). No other phase was detected. The same procedure was followed for all the other targets used in this thesis.

**Figure 2.10:** The diffraction pattern of a PbTiO$_3$ polycrystalline target (black line). The gray line is the overall fit for PbTiO$_3$, tetragonal PbO and orthorhombic PbO. The green curve below zero intensity is the difference between the overall fit and the experimental data.

### 2.6.b Thin films reciprocal space maps (RSM)

In this work our main diffraction focus will be on the Reciprocal Space Map (RSM). RSM is a scan of the reciprocal space around a diffraction peak of the structure. Since the structures of the film and the substrate are similar to each other, in epitaxial thin films RSMs provide information
about the lattice parameters of the film (or films in case of multi-layered sample) and the substrate as well as the relationship between the two. From this information we extract the strain state of the film, induced by the substrate. Also, RSMs are used to determine the deformation of the unit cell (crystal phase), polarization orientation and (if periodic) domain structure of the ferroelectric thin films.

An RSM is a two-dimensional scan around a particular (hkl) Bragg peak. The main axes of the scan are $2\Theta - \omega$ (longitudinal scan perpendicular to the corresponding (hkl) atomic planes and $\omega$ (the transversal - rocking curve direction)); where $2\Theta$ is the angle between the detector and the incident beam, and $\omega$ is the angle between the sample surface and the incident beam. For specular reflections, $2\Theta = 2\omega$. First, we rotate the sample and detector (X-ray source are fixed in all diffractometers) to fulfill the Bragg condition, see Figure 2.11.

![Figure 2.11: Sketch explaining the Reciprocal Space Mapping (RSM).](image)

At the Bragg condition, the incident and the diffracted wave vectors, respectively $k_0$ and $k_d$, end up on the surface of the Ewald’s sphere and their difference - the scattering wave vector - geometrically coincides with the reciprocal lattice vector $G$ of the thin film. From Figure 2.11 we can state that, while changing axes $2\Theta - \omega$, we change the length of the scattering vector. This gives us information about the periodicities along the
direction of the scattering vector. On the other hand, when we vary only $\omega$, the direction of the scattering vector changes, keeping its magnitude constant. In reciprocal $k-$space, the distances are measured in units of the radius of Ewald’s sphere, so called reciprocal lattice units (rlu), being $1 \text{ rlu}=2\pi/\lambda$. This allows for easy comparison between measurements taken with different wave lengths. From Figure 2.11, it can be seen that an RSM map is a two-dimensional image with axes:

$$q_{||} = 2k \sin \Theta \sin \delta$$

$$q_{\perp} = 2k \sin \Theta \cos \delta$$

Where $q_{||}$ and $q_{\perp}$ are the components of the scattering wave-vector parallel and perpendicular to the sample surface, and $2k \sin \Theta$ is the magnitude of the scattering vector. By measuring extended RSMs, we can extract other features around the main Bragg peaks which can provide information of the lattice relaxation mechanisms such as periodic arrays of dislocations, periodic ferroelectric domains, gradual lattice relaxation, etc. We can also measure out- and in-plane lattice parameters of multi-layered films.

### 2.6.6 Reflectivity

We have discussed that the RHEED technique is quite effective in observing the growth of thin films in-situ. Thus, in experiments where the growth takes place atomic layer by atomic layer, it is possible to determine the thickness of the grown film in such a way. Since this is not always possible and, in particular for thicker films, the amplitude of the oscillations may decrease to become unobservable (and due to the fact that the growth conditions may change during the deposition, extrapolation of the growth rate may result in misleading information on number layers that has been grown), in order to check the actual thickness of the film we use X-ray reflectivity. It is based on the interference of the X-rays reflected from the surface and the film-substrate interface. When they interfere in the detector, they form an interference pattern that consists of periodic dark and bright fringes, called Kiessig fringes. The periodicity of the resulting pattern depends on the phase difference between the two beams. In this way, we can extract some valuable information like the thickness of the
film, roughness of both interfaces and difference in electronic densities. Since the reflectivity of a surface decays abruptly with increasing incident angle, above the critical angle of total reflection, typically it is only possible to obtain clear Kiessig fringes for incident angles up to $5^\circ$. The reflectivity spectra are, thus, $2\Theta - \omega$ linear longitudinal scans spanning approximately the range of $0.3^\circ - 8.0^\circ$. The requirements for observing Kiessig fringes are relatively flat and parallel interfaces as well as thicknesses in the range of $6\ nm - 100\ nm$ (otherwise the periodicities are either too small or too large to be observed).

2.6.d Grazing incidence X-ray diffraction

![Grazing Incident Diffraction (GID) geometry. a) From the side. Incident beam comes at angle $\alpha_i$, which is just below critical angle (condition for full reflection). b) Top view of the geometry; Bragg condition fulfilled for (hk0) planes.](image)

From X-ray RSMs we can extract lots of different information about the thin film structure in what we call Bragg-Brentano or reflection geometry in which the scattering vector always has a component perpendicular to the sample surface. This means that the signal detected in the case of very thin films epitaxially grown on a bulky single crystal substrate is dominated by the substrate signal. Since substrate and films can have very similar structures, this makes it difficult to investigate the film structure. It is thus very useful in the case of thin films, to be able to perform purely...
in-plane measurements. This is only possible in grazing incidence geometry. Grazing incidence diffraction (GID) is performed at incident angles below the critical angle of total reflection of the material, which is typically $0.1^\circ-0.5^\circ$. The result of this geometry is that there is no component of the incident wave vector normal to the sample surface, thus no X-ray intensity penetrating in the sample, except for the weak and exponentially decreasing evanescent wave. This evanescent wave is used as the incident beam for pure in-plane X-ray diffraction (that to measure distances between $(hk0)$ planes). Thus the scattering vector in this geometry lies fully in-plane of the studied film. Unlike in the out-of-plane geometry, incident, diffracted and scattered vectors do not belong to the same plane (see Figure 2.12). The advantage of GID for thin films is double: on the one hand the $(hk0)$ reflections are free from size effects (broadening), offering sharp and intense Bragg peaks and more accurate values of the lattice parameters; on the other hand, under proper conditions, the evanescence wave does not reach the substrate, giving rise to cleaner thin film signals. Because of the weak intensity of the evanescence wave and because of the need of accurately defining the incidence angle, the brilliance and high collimation of synchrotron sources are often required for GID.
Bibliography


Chapter 3

Thickness scaling of ferroelastic domains in PbTiO$_3$ films on DyScO$_3$

3.1 Abstract

In this chapter we investigated the thickness dependence of the ferroelastic domains of PbTiO$_3$ films grown on (110)-DyScO$_3$ with low thicknesses (up to 240 nm), which fall outside the validity range of the square root law proposed by Roytburd [1]. For slow-grown films, the data revealed the linear thickness dependence predicted by Pertsev & Zembilgotov (using a complete elastic description) [2]; while a 2/3 scaling exponent found for fast-grown films. Extremely long domains running all through the samples was observed in the latter case, compared to the short domains observed in slow-grown films. These differences were ascribed to the in-plane anisotropy for domain wall nucleation, which was likely caused by the anisotropic elastic modulus of the substrate.

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3.2 Introduction

The response of domains and domain walls crucially affects (and often determines) the dielectric properties and switching behavior of ferroelectrics. This is particularly important in thin films where the ferroelectric (180°) and ferroelastic (non-180°) domains walls are formed in order to comply with the stringent electrical (large depolarizing field) and mechanical (substrate mismatch strain and clamping) boundary conditions.

The size of the domains increases with increasing film thickness as a result of the balance between the depolarizing field energy (for 180° domains) [3], or elastic strain energy (for non-180° domains) [1], 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 [4]. It is therefore most relevant to have good control of the domain formation and the density of domain walls [5].

Domain formation in ferroelectrics has been largely studied [1, 2, 4, 6–15]. 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 [7,8]. It is known that there is a quadratic dependence, $W \propto d^{1/2}$, of the domain width ($W$) with the crystal thickness ($d$). In ferroelastic domains (typically 90° domains), this $d^{1/2}$ dependence is an approximation in the regime of $d \gg W$ [1]. For smaller thicknesses, a linear dependence has been predicted by Pertsev and Zembilgotov (P&Z) [2] but, to the best of our knowledge, it has not been experimentally confirmed yet.

In this chapter we investigated the thickness dependence of the width of ferroelastic 90° domains (a/c twins) in the lower thickness regime using PbTiO$_3$ films grown on DyScO$_3$ substrates. This combination has chosen because there is a very small lattice mismatch between film and substrate at the growth temperature. This minimizes the formation of defects during growth. As the films are cooled down strain develops and can be relaxed by forming a/c domain walls. The absence of defects allows these domains to form in a very periodic fashion [13,16]. Interestingly, when the films are grown by pulsed laser deposition at high laser frequencies (10Hz), extremely long domains are formed along one of the in-plane crystallographic directions, despite the very small difference in lattice parameters and thermal expansion coefficient of both in-plane lattice parameters of (110)-DyScO$_3$. 
3.3 Experimental

The thin films were grown on (110)-oriented DyScO$_3$ substrates [17] by Pulsed Laser Deposition (PLD) from PbTiO$_3$ targets with 4 atomic % excess lead. Orthorhombic (110)-DyScO$_3$ substrates were obtained from CrysTec GmbH. The two in-plane lattice directions were then [1-10] and [001], named as a-axis and b-axis, respectively. The substrates exhibit double-terminated surfaces (with both DyO and ScO$_2$ surface layers) and they were chemically and thermally treated to get a single ScO$_2$ termination [18]. This allows growing high quality SrRuO$_3$ layers, since SrRuO$_3$ preferentially nucleates in that surface [19]. An 8 nm-thick SrRuO$_3$ layer was grown between the film and the substrate. The SrRuO$_3$ layer is fully strained and acquires the lattice parameters of the substrate. The growth was monitored by Reflection High-Energy Electron Diffraction (RHEED). The RHEED intensity oscillations, together with X-ray reflectivity, were used to determine the thickness of the films. Two series of films were grown at two different growth rates, using laser frequencies of 1 Hz and 10 Hz. The rest of the growth parameters were tuned to minimize the film roughness and maximize the RHEED intensity oscillations: the laser fluence, spot size at the target, substrate temperature, substrate-target distance and O$_2$ pressure in the chamber were 1.5 J/cm$^2$, 0.8 mm$^2$, 570°C, 48 mm and 0.13 mbar, respectively, for the 1 Hz series, and 2.0 J/cm$^2$, 0.8 mm$^2$, 580°C, 50 mm and 0.06 mbar, respectively, for the 10 Hz series. These have resulted in deposition rates of about 1 unit cell per 55 sec and 7 sec. We will refer to these series as slow-grown and fast-grown, respectively. Scanning Transmission Electron Microscopy (STEM) experiments in High Angle Annular Dark Field (HAADF) were carried out in a probe-corrected FEI Titan 60-300 microscope operated at 300 kV with a probe size of 1 Å. Atomic Force Microscopy (AFM) was performed using a VEECO (now Bruker) Dimension V microscope. AFM images of sample preparation are shown on Figure 3.1.

3.4 Results and Discussion

(110)-DyScO$_3$ does not have a totally squared in-plane lattice, however, the difference between the two in-plane parameters is typically considered too small to give rise to anisotropic domain formation. In agreement with this, for the slow-grown samples, we found domain walls along both in-plane dir-
The domains organize in bundles with perpendicular domain walls forming four-fold symmetric patterns [13, 20](see Figure 3.2a). However, for the fast-grown samples, extremely long domain walls were observed along the a-axis of the substrate, as shown in Figure 3.2b; while shorter, less straight and less periodic domain walls were observed perpendicularly, along the b-axis. The length of the long domain walls (||a) seems to mainly be limited by the length of the sample and only in rare cases a domain wall starts or ends at one of the perpendicular (||b) walls. STEM revealed that, despite the apparent differences between the sets of perpendicular walls in the AFM images of the fast-grown samples, both cross-sections consist of a/c twins (Figures 3.2c-3.2d).

In order to clarify the origin of the observed anisotropy, we have looked
at the effect of the substrates terraces on the domain formation. PbTiO$_3$ thin films were grown on DyScO$_3$ substrates with different direction of miscut, that is different orientation of the substrate steps: forming 0°, 45° and 90° with respect to the in-plane crystallographic directions. The domain structures created on two substrates with differently-oriented terraces are shown in Figure 3.3. It is observed that the a/c domain walls form along the a-axis of (110)-DyScO$_3$, independent on the orientation of the substrate terraces.

Therefore, the long domain walls $\parallel a$ must form in response to the lattice strain experienced along the b-axis. At the growth temperature the
Figure 3.3: AFM images of PbTiO$_3$ films on DyScO$_3$ substrates with different miscut angle: the atomically flat terraces of the substrate propagate along the [001] a), [1-10] b) and [1-11] c) crystallographic axes, as indicated in the insets. The long and straight domain walls run along [1-10] (a-axis); while the curved and shorter walls run perpendicularly, independently of the orientation of the substrate terraces. The differences in morphology and contrast between the two images have to do with the differences in film thickness: 200 nm for a) and 180 nm for b) and c), respectively.

misfit strain along the a-axis is close to zero (well below 0.1%); while the misfit strain along the b-axis is slightly tensile (0.12%). Lattice parameters were taken from [27] and [17] and are shown in Figure 3.4. The difference between the fast-grown and slow-grown samples can be explained if we
assume that the bulk phase transition is shifted upwards, already under such relative small strain values, such that the material grows in the ferroelectric phase [21, 22]. Then, differences in nucleation of the domain walls along both in-plane directions could explain the observed differences in domain formation. Because during fast growth the sample is far from thermodynamic equilibrium (higher supersaturation), if the energy barrier for nucleation of domain walls ||b was larger than that of the walls ||a, the formation of the former walls would be hampered. Different energy barriers for domain wall nucleation can originate in the anisotropic elastic properties of DyScO$_3$ substrates, recently reported [23]. Slow-growth conditions will better reflect the equilibrium phase diagram of the system and its quite small misfit strain anisotropy.

That also implies that, during fast growth, the critical thickness for nucleation of domain walls would depend largely on the in-plane direction. This is, indeed, consistent with our observations: AFM pictures of PbTiO$_3$
films with different thicknesses are reproduced in Figure 3.5. It shows that for a given film, the density of walls $|b|$ is smaller than the density of walls $|a|$. In addition, while the walls $|a|$ are visible for thicknesses above 15 nm, the walls $|b|$ are only observed above 50 nm.

We now look at the thickness dependence of the domain width. For too thin films, $a/c$ domains are not expected, however, at these very small thicknesses the increased depolarizing field induces $180^\circ$ domains [24, 25]. A crossover from $180^\circ$ to $90^\circ$ domains was thus expected at a particular thickness. In this case the crossover between $180^\circ$ and $90^\circ$ domains is found at $d \sim 10$ nm but only for $d > 15$ nm, we were able to observe well-defined, ordered $a/c$ domains [22, 26]. Figure 3.5 shows the high degree of ordering of the $a/c$ domains (with walls $|a−axis|$ in PbTiO$_3$ on DyScO$_3$ and the robustness of the domain size across the film, allowed us to monitor their size not only by local probe techniques, such as AFM and piezo-AFM, but also by x-ray diffraction (XRD) [13, 20]. Typically, the best sensitivity was obtained using XRD for the relatively thinner films (Figure 3.5a) and using AFM for the thicker films (Figure 3.5 b-c).

The data collected for all the samples, including slow-grown and fast-grown samples, are summarized in Figure 3.6, showing the domain size ($W$) as a function of the film thickness ($d$) in a double logarithmic scale. The slow-grown films follow the trend predicted by P&Z [2]: a minimum introducing a change of trend at the lowest thicknesses and a linear $W(d)$ dependence for thickness $30 \text{ nm} < d < 100 \text{ nm}$. A quantitative fit was not successful and the best possible fit (using $T = 440^\circ\text{C}$ and $\sigma = 19 \text{ mJ/m}^2$) was off by 41 nm (better seen in linear scale on Figure 3.7).

In Figure 3.7, the domain periodicity is plotted versus film thickness using the P&Z model applied to our slow-grown PbTiO$_3$ films on (110)-DyScO$_3$. The actual fitting parameters in the model are the domain wall energy density ($\sigma$) and the so-called relative coherency strain ($S_r$), which depends on the lattice mismatches of the two tetragonal axes ($S_a$ and $S_c$) with the substrate. $S_r$ is temperature dependent, as the thermal expansions of the film and substrate differ and, thus, we used the temperature of formation of the final domain configuration as the experimental input parameter, calling it freezing temperature ($T_{fr}$). A relatively high temperature ($440^\circ\text{C}$) has been chosen for the fits, based on experimental observations. For experimental temperature values please read Chapter 4.

We used $\sigma$ as a second adjustable parameter to try to fit our slow-grown data (grey symbols) with the P&Z model [2] since this is the data set that
Figure 3.5: The top panels show AFM images (5µm × 5µm) of PbTiO$_3$ layers on DyScO$_3$ with different thicknesses, d, and average domain periods, W: a) d=50 nm, W=80 nm; b) d= 80 nm, W=105 nm; c) d=180 nm, W=197 nm. The substrate b-axis is horizontal in all three images. The method used to determine the domain size is shown for each sample in the bottom panels: d) X-ray reciprocal space mapping around the (002)$_c$ reflection shows the intensity oscillations due to periodic domains. Axes are in units of $k_o = 2\pi/\lambda$, being $\lambda$ the x-ray wavelength. The color scale represents log(I). A linear scan along the dashed line (rocking curve) is plotted as a solid curve showing the intensity maxima from whose $k_||$ values the domain periodicity is obtained; e)-f) AFM auto-correlation images of b)-c), respectively, and their Fast Fourier Transforms (in the insets).
Figure 3.6: Log-log plot of the observed domain period, $W$, as a function of film thickness, $d$, for $90^\circ$ domains in PbTiO$_3$ thin films grown on SrRuO$_3$-buffered DyScO$_3$ substrates. The data for the slow-grown and fast-grown samples are plotted as open and closed circles, respectively. The red line is a linear fit for the fast-grown films with $d \geq 20$ nm. The dashed blue line corresponds to the $n=1/2$ exponent [1], and uses the materials parameters at $T=480^\circ$C and a domain wall energy of 21 mJ/m$^2$. The dashed green line is obtained subtracting 41 nm from the domain period produced with the P&Z model [2] using the lattice parameters at $440^\circ$C and a domain wall energy $\sigma=19$ mJ/m$^2$ (see Fig. 3.7 and description to it).

should show a better agreement with equilibrium models. We found that no set of realistic input parameters ($T$, $\sigma$) reproduces the experimental data, however we find a similar linear slope and a similar position for the curve minimum for $T_{fr} = 440^\circ$C and $\sigma = 19$ mJ/m$^2$, a value that is in agreement with the literature values for $90^\circ$ domain wall formation energies. Quantitatively, the experimental domain periodicities for slow-grown samples were 41 nm smaller than those predicted by P&Z, as it can be seen in Figure 3.7 (the thin solid line curve is exactly the thick solid line curve shifted down by 41nm).
Figure 3.7: Linear $W$ vs. $d$ plot showing the best qualitative P&Z fit to the slow-grown data (same slope and same minimum position) obtained for $T_f = 440^\circ C$ and $\sigma = 19 \text{ mJ/m}^2$ (thick line). The experimental data can only be reproduced by an overall down-shift of the curve of $41 \text{ nm}$ (thin line).

The lack of quantitative agreement between the data and the P&Z model is not surprising. Firstly, the data do not correspond to the equilibrium domain configuration and, secondly, several elements are missing in the P&Z model. This model comprises a rigorous calculation of the elastic energy of the system, considering a fictitious array of dislocations and disclinations that mimic the same strain fields as those present in domain formation. It is thus a purely mechanistic model. Important missing ingredients are the strain dependence of the order parameter and the depolarization field, which would induce ferroelectric $180^\circ$ domain formation at low thicknesses instead of a monodomain state. Moreover, it is assumed in the model that the strain is fully released by formation of dislocations/disclinations (or domain walls), while the films are often not fully relaxed after domain formation.
For the fast-grown samples, the experimental domain size does not follow the predicted evolution, since it does scale neither as $d^{1/2}$ [1] nor linearly with $d$ [2]. Instead, fitting the data in Figure 3.6 for the fast-grown samples resulted in an exponent $n = 0.68 \pm 0.03$ ($n \approx 2/3$), thus experimental results exhibit a behavior in between the classic Roytburd’s square-root law and Pertsev’s linear law. One possible explanation is that we were probing the crossover between these two regimes. One can argue that, indeed, for the lowest thicknesses ($d < 40 \text{ nm}$) the data are not inconsistent with a $n = 1$ exponent; however, for the large thickness regime, there is no indication of approaching $n = 1/2$. Intermediate scaling exponents $1/2 < n < 1$ have been reported before for fractal domains [28] but clearly the wall roughening mechanism cannot be invoked here, since our domains are perfectly smooth. Fractional scaling exponents have also been extracted from switching dynamics [29], and thus it may be the case that our exponent reflects the dynamics of domain nucleation. Indeed, it rather looks like we are seeing a law that differs from that predicted by equilibrium models, something unsurprising for such fast-grown films.

According to the usual description of the energy balance between domains and domain walls [12], the domain size is found by minimizing the sum of the elastic energy stored within the domains plus the energy of the domain walls. This minimization leads to the well-known Kittel formula, $W = \sqrt{\frac{\sigma U}{d}}$, where $U$ is the volume energy density of the domains and $\sigma$ the energy per unit area of the walls. In the standard derivation of Kittel’s law it is assumed that $U$ and $\sigma$ are independent of the thickness $d$, but this is not a realistic assumption for very thin films where strain is only partially relaxed or when structural and compositional gradients [30], and competing relaxation mechanisms with different critical thicknesses (such as dislocations and twinning) introduce a thickness dependence on the energy densities. Within the thickness range of this study, the domain size scales as a power law, which implies that the energy densities can also be expressed as power laws: $U = ud^K$ and $\sigma = \eta d^L$ and Kittel’s law thus becomes $W = \sqrt{\eta/ud^{(-K+L+1)/2}}$. Comparing with the experimental result, $W \propto d^{2/3}$, we get that $L-K=1/3$.

The exponent $K$ that determines the volume energy density as a function of thickness has been amply studied by the semiconductor thin film community. The equilibrium models for strain relaxation and formation of dislocations [31–33] give rise to a residual strain that is inversely proportional to the layer thickness ($e \propto d^{-1}$), which, given that elastic energy is
proportional to the square of the strain (Hooke’s law), implies that $K=-2$. On the other hand, it has also been shown that during epitaxial growth, the non-equilibrium kinetics of dislocation formation can lead to $\varepsilon \propto d^{-1/2}$ (or $U \propto d^{-1}$) [34]. In contrast, much less is known about the value of $L$ that determines the thickness dependence of the domain wall energy. Since the energy cost of the walls is proportional to the spontaneous strain in the domains, a thickness dependence of the residual strain must also result in a thickness dependence of the domain wall energy. If we accept $-2 < K < -1$ as the two limiting cases for the volume energy density, then compliance with our empirical results requires $-5/3 < L < -2/3$ for the equilibrium and non-equilibrium growth scenarios, respectively.

### 3.5 Conclusion

We investigated the thickness scaling of the domain periodicity of slow-grown and fast-grown samples. We showed that, for films grown on (110)-DyScO$_3$, working out of equilibrium with well-defined conditions allows a large degree of control of the domain width and morphology, beyond the predictions of thermodynamical models. This is enabled by the differences in domain wall nucleation along different crystal in-plane directions, which is most likely caused by the anisotropy in the elastic modulus of the substrate.
THICKNESS SCALING OF FERROELASTIC DOMAINS IN PbTiO$_3$ FILMS ON DyScO$_3$


Chapter 4

Freezing of ferroelastic domains in ferroelectric PbTiO$_3$ films on DyScO$_3$

4.1 Summary

In the previous chapter we have studied the dependency of the size of the ferroelastic domains with the thickness of PbTiO$_3$ films grown on (110)-DyScO$_3$ substrates in the low thickness regime. In this case, the classical square root law is not valid and instead the validity of the Pertsev & Zembilgotov (P&Z) model in order to fit the domain scaling behavior was investigated with some success, in particular for the slow-grown samples. For the model, the so-called coherency strain experienced by the film due to the substrate, is calculated assuming lattice parameters of the substrate and the film at a fixed temperature, so called freezing temperature. In the model, this temperature is assumed to be constant for a particular film-substrate. In the previous chapter the freezing temperature, it was chosen such as to give the best fit for realistic domain wall formation energy density values. However, it was clear that the experimental behavior was not fully explained by the model, for the slow-grown films and not at all for fast-grown films. In this chapter we experimentally determine the freezing temperatures (temperature at which the domain size freezes) and investigate the dependency of freezing temperature with the film thickness. It is shown that the observed freezing temperatures depend on the film thickness in this low thickness regime, which also results in a variation of
strain values with film thickness. When introducing this dependence of the coherency strain with the film thickness in the P&Z model (what we call the modified P&Z model), consistent values for the domain wall formation energy density are obtained, as well as a very good fit to the experimental data. It is also been found that both Roytburds' and modified P&Z models are equivalent in the larger thickness regime giving rise to domain wall energy density being equal within error.
4.2 Introduction

In the previous chapter we used the P&Z [1] model to fit our experimental data [2,3]. We observed that, qualitatively, the P&Z [1] model fitted the domain size behavior of the slow-grown films reasonably well, but that, quantitatively, the domain size values were of the order of 40 nm smaller than the predicted ones and that, in that respect, the larger domain sizes of the fast-grown films were more realistic [2,3]. The thickness dependence of the fast-grown films, however, did not follow the expected scaling laws, which is not surprising since the growth took place out of equilibrium. The fitting parameters in the P&Z model are two: the domain wall formation energy density ($\sigma$) and the coherency strain ($S_r$), which is the strain experienced by the film. In our case, this is the strain induced in the PbTiO$_3$ film by the underlying (110)-oriented DyScO$_3$ substrate.

This strain contributes to the free energy and it increases with the film thickness. Above certain critical film thickness, the strain can be relaxed in the form of ferroelastic domains. In the case of defect-free thin films, this results in highly periodic domain structures [1,4,5]. The size and orientation of the domains are determined by magnitude of the lattice mismatch between the film and substrate, the electrical boundary conditions and mechanical boundary conditions. Since the experimental results have been shown to be robust and highly reproducible for given growth conditions, we propose that some of the assumptions of the model are too strict or ill-defined in this case. The first point of concern is the value of the coherency strain ($S_r$). Since, due to the differences in thermal expansion of the film and substrate, strain depends largely on temperature, it is not clear what are the relevant strain values: while experimental studies often consider the strain from the differences in lattice parameters at room temperature, theoretical models based on the Landau-Devonshire-Lifshits approach, often define the strain based on the extrapolation of the paraelectric lattice parameters of the film down room temperature (spontaneous strain). It should be, nevertheless, obvious that the relevant strain values to be considered are the ones existing at the temperature at which the current domain structure was frozen. In order to answer this question we study the domain formation and size as a function of temperature while cooling down from the paraelectric phase. In previous reports on the study of domain formation and its dependence with film thickness, the assumption is to consider the coherency strain of the grown films as constant with film thickness [1,6–8]. Here we show that this dependence clearly
exists in the low thickness regime. We, therefore, propose a modified P&Z model in which thickness dependence of $S_r$ is taken into account and shows that it provides a very good fit to the experimental data of the fast-grown samples.

4.3 Experimental

A series of PbTiO$_3$ thin films on SrRuO$_3$-buffered (110)-DyScO$_3$ substrates were grown by PLD with thicknesses from 30 nm to 240 nm, as discussed in 3.3. In order to get improved oxidation of the crystal lattice, the films were slowly cooled in the PLD chamber from the growth temperature (580°C) down to room temperature with a 3°C/minute cooling rate in reach (300 mbar) oxygen atmosphere. Such relatively slow rate results into a few things: first there is enough time for oxygen atoms to diffuse and fill vacancies in the perovskite lattice [9]; second, additional surface diffusion results in smoother and better quality films; and third, in this way the strain changes that the film experiences with decreasing temperatures can be better equilibrated giving rise to a more homogenous and reproducible domain formation [10, 11]. The latter occurs as a result of the difference in the lattice parameters of the film and the substrate during the cooling process [12, 13].

4.4 Results and Discussion

In this chapter we question the kinetics of domain formation and the strain of the films responsible for the final domain configuration. In order to get a proper answer we would have to follow the cooling process of the films in the PLD chamber in detail, but it is not possible to apply AFM or XRD techniques in-situ in our PLD. To overcome this problem and simulate the cooling process after growth, temperature-dependent x-ray diffractometry was used. The adequacy of this method is proven by showing that the size of the domains at room temperature after the temperature cycling in the x-ray diffractometer was the same as the size observed at room temperature immediately after growth. An "Anton Paar" heating stage was coupled to the goniometer of a laboratory thin film XRD diffractometer and used to heat the sample to high enough temperature so that the paraelectric phase was reached and no domains were observed. The heating stage is equipped with a closed dome that allows flushing with
Figure 4.1: a) AFM image (4 µm × 4 µm) with a close-up of 1 µm × 1 µm is included in the inset of a PbTiO₃ 40 nm thick film on SrRuO₃-buffered (110)-DyScO₃ substrate. b) X-ray Reciprocal Space Map (RSM) around the (001) Bragg reflection of the same film. White dashed lines point out the periodicity of the diffuse scattering due to the periodic domains. Black dot-dashed arrows point line-scan directions. RSM axes are in units of $2k_0 = 4\pi/\lambda$ ($\lambda = 1.2398$ Å). RSM presented was obtained at the HASYLAB P08 beamline (Petra III-DESY, DESY).
Figure 4.2: RSMs around the (001) Bragg reflection for PbTiO$_3$ thin films with thicknesses of 20 nm a), 50 nm b) and 200 nm c). Coupled black dashed lines point to the 1st order domains satellites in 20 nm thick film, blue - for 50 nm and red - for 200 nm. RSMs obtained with a Panalytical X Pert MRD Cradle (four axes) laboratory diffractometer.
oxygen gas during the XRD measurements. Then the temperature was controllably reduced in small steps and enough time was given at each step to equilibrate. During this process linear $2\theta$-$\omega$ scans and $\omega$-rocking curves were performed at each temperature point. These scans were used to determine the lattice parameter and domain period as a function of temperature and film thickness.

![Figure 4.3: $2\theta$-$\omega$ linear scans around (002) Bragg reflection of a PbTiO$_3$ thin films on a SrRuO$_3$-buffered DyScO$_3$ substrate (peak around 46°) with different thicknesses.](image)

The domain period was calculated with the help of AFM microscopy. Figure 4.1a shows an AFM image of a 40 nm-thick PbTiO$_3$ film on a SrRuO$_3$-buffered (110)-DyScO$_3$ substrate. In the inset of Figure 4.1a, the clear periodic nature of the ferroelectric/ferroelastic $a/c$ domain structure is visible. For our samples, 90° domains, as sketched in Figure 4.1 (c), have certain equilibrium period for a particular thickness. The domain pattern is well defined across the sample and, thus, produces characteristic
periodic features in the X-ray diffraction pattern as well [7,8,14,15]. The in-plane period of the 90° domains leads to diffuse satellite peaks around the Bragg peaks of the PbTiO$_3$. The domain structure is studied in detail from measured reciprocal space maps (RSM) around the $(110)_o$ and $(220)_o$ reciprocal lattice points of the DyScO$_3$ substrate, which correspond to the $(001)_c$ and $(002)_c$ Bragg peaks of the film and they will be addressed, for simplicity, as (001) and (002) in the following. In Figure 4.1b such an RSM around the (001) Bragg reflection point is presented for the same 40 nm-thick PbTiO$_3$ film of Figure 4.1(a). Diffuse satellites peaks appear on all reflections. As an examples, in Figure 4.2, RMSs for samples with thickness 20, 50 and 200 nm, for (001) Bragg reflection are depicted. The RMS spacing between satellite peaks, calculated from (001) and (103) maps of a particular sample, is equal to each other, which means that they originate from an additional periodicity in the film and not from symmetrically tilted domains. The out of plane lattice parameter of the grown film was extracted from linear $2\theta-\omega$ scan along the [00L] direction and the domain periodicity was obtained from linear $\omega$-scans (rocking curves) around the film peak (see dot-dashed arrows for scan directions in Figure 4.1b).

In order to describe accurately the formation of ferroelastic a/c domains in our thin films it is important to fully understand the strain state of the grown films as the coherency strain is a crucial structural parameter in both P&Z [1] and Royburds [5] models (see Chapter 3). In order to investigate this effect, linear $2\theta-\omega$ scans were first performed at room temperature for samples with varying thickness (see Figure 4.3).

The out-of-plane lattice parameter of the films was obtained from these measurements (from the film peak around 44° in Figure 4.3) are plotted in Figure 4.4. as a function of the film thickness. This graph reveals that domain formation has not fully relaxed the films to the bulk-like state and that thicker films were more relaxed, with their lattice parameters closer to the one of the bulk state. Therefore, these room temperature experiments show that the strain state varies with the thickness and this fact should be considered in mathematical models describing structural behavior of a/c domain patterns. As mentioned above, coherency strain is assumed to be constant even in the more advanced theoretical models such as the P&Z model [1].

Furthermore, at this point it is important to understand that after the film has been deposited in the PLD chamber, a crucial cooling down process to room temperature takes place. Simulation of this process is done
4.4 RESULTS AND DISCUSSION

Figure 4.4: Out-of-plane lattice parameter (red) of PbTiO$_3$ thin films vs. film thickness. The long-axis lattice parameter for bulk PbTiO$_3$ as represented by blue line. Data extracted from 2θ-ω scans (see Figure 4.3).

by heating of a sample above the ferroelectric/ferroelastic transition temperature and by subsequently cooling it down. XRD was used to observe the changes of film and substrate lattice parameters which takes place during this process. Figure 4.5 shows a summary of the measurements: while in the range from 530°C down to 30°C, the substrate out of plane lattice parameter moves to slightly larger angles (smaller lattice parameters), as expected from regular lattice expansion, the out of plane lattice parameter of the film strongly increases for decreasing temperatures, which is common in ferroelectric crystals due to the large, and strongly temperature-dependent, spontaneous deformation of the lattice. It was also observed that thickness fringes appear at the highest temperatures. This indicates the excellent quality of the films showing parallel interfaces and homogeneity once the ferroelectric distortion is removed and domains disappear.

During the cooling process, the lattice of the film has enough free energy to change its structure by elastic deformations. As explained previously, this deformations occur in order to match the difference between the in-plane lattice parameters of the film and the substrate while the
temperature is being decreased. In this case, forming elastic domains is preferential over other processes of lattice accommodation such as e.g. creation of dislocations. As temperature goes down and strain values change, domains can also change in size, provided that the domain wall formation energy is small enough and the walls are not clamped. Below certain temperature, the film does not have enough energy to change its domain structure and domain size. This is where the domain structure freezes and what we call the freezing temperature ($T_f$). In Figure 4.6 a set of $\omega$-scans (rocking curves) around the film peaks (see Figure 4.1b for scan direction) is presented at different temperatures during the cooling of the 40 nm-thick PbTiO$_3$ film. The lattice parameter changed during the cooling process and, thus, the film peak moved along the [00L] direction, as shown in

Figure 4.5: $2\theta$-$\omega$ linear scans of a 40 nm thick PbTiO$_3$ film during the cooling process. Vertical arrows point to the maximum of the film peak at each temperature of the measurement, which varies from 530°C (material in paraelectric state) to room temperature (\textasciitilde30°C). Scans are taken around the (002) Bragg reflection of DyScO$_3$ substrate (peak around 46°).
Figure 4.6: $\omega$-scans (rocking curves) of a 40 nm thick PbTiO$_3$ film (see dot-dashed line in Figure 4.1b) for different temperatures taken during cooling of the sample. The black arrow guides through the evolution of the peak position signaling domain periodicity. The red circle marks the temperature where domains freeze. $\omega_0$ is the $\omega$ value for the central peak (which varies with temperature).

Figure 4.5, and with it also the position of the peak in the omega scans. In Figure 4.6 all rocking curves are artificially shifted so that the film peak appear at the same position, marked by $\omega_0$ and in this way, we can more easily compare the peak position of the satellites that define the domain periodicity for the different temperatures. The black arrow in Figure 4.6 shows the evolution of the position of the satellite peaks for the 40 nm-thick PbTiO$_3$ film from a temperature at which no domains were observed (495°C, presumably in the paraelectric state) down to 380°C, with clear domains footprint. On the RSM made around the (002) Bragg reflection for room temperature and $T = 505^\circ$C (respectively depicted on Figure 4.7 (d) and (e)) for this sample, there is a clear absence of domain peaks for high temperature (only substrate and film peaks are present); while at
Figure 4.7: a)-c) $\omega$-scans (rocking curves) of a 80, 120 and 180 nm thick PbTiO$_3$ films, respectively, for different temperatures taken during cooling of each sample. $\omega_0$ is the $\omega$ value for the central peak (which varies with temperature). d) and e) are room temperature and $T = 505^\circ$C RSMs around the (002) Bragg reflection of a 40 nm thick PbTiO$_3$ film. RSMs taken with a Panalytical Xpert MRD Cradle (four axes) laboratory diffractometer.

room temperature conditions a and c domain peaks both are present. The red circle on Figure 4.6 points to the temperature where the position of the satellite peak stops changing. We consider this to be the temperature
at which the domain pattern freezes.

Figure 4.8: Domain freezing temperature ($T_{fr}$) versus thickness of PbTiO$_3$ thin films, extracted from the T-dependent ω-scans (see Figure 4.5).

Repeating the same analysis for different films (see rocking curves on Figure 4.7 (a)-(c) for different thicknesses), it appears that the domain freezing temperature extracted from the ω-scans (rocking curves) in Figures 4.6 and 4.7 varies with the thickness of the sample, as plotted on Figure 4.8. This is an important fact that allows us to establish, first, the values of the coherency strain that are relevant for the P&Z model (in other words which is the temperature that decide the misfit strain for each case) and, second, that those values vary with thickness, being this dependence particularly strong for films under 100 nm and, thus, that the thickness dependence of the coherency strain needs to be incorporated in the model.

This knowledge makes us reconsider the way in which we use the existing theoretical models. The relative coherency strain derived from the previous experiments is used in calculations for both the classical Roytburd model and the P&Z model, modified to include the thickness dependence of the strain. These models have the coherency strain and the domain
Figure 4.9: Domain period ($W$) as a function of the film thickness ($d$). Modified P&Z model (green) and Roytburd model (red) fitted to the experimental data (black circles).
wall formation energy as parameters. With these experimentally obtained strain values, the domain wall formation energy is chosen such that the theory and experiment show the best fit. Those best fits are shown in Figure 4.9 for both the Roytburd and P&Z models; while the domains wall formation energy density required to provide those fits is plotted in Figure 4.10. As observed, the domain wall formation energy appeared to be constant with thickness for P&Z model with an average value of 12.8 ± 2.2 mJ/m². With these assumptions the P&Z model fits best in low to mid thickness regime (numerically from 20 to 150 nm film thickness), with the transition from the linear-like to the square-root-like behavior happening at about 90 nm (green curve in Figure 4.9). The Roytburd square-root law and the P&Z model are equivalent for high thicknesses regime, as expected from the assumptions of the model (see section 1.5). The domain wall formation energy used to fit the experimental data with Roytburd model is 12.8 mJ/m², that is the same value as obtained from the P&Z model but in this case a constant freezing temperature of 490°C is used. The freezing temperature is assumed to be constant for Roytburd model as in the high thicknesses regime it varies negligibly (see Fig. 4.8).

4.5 Conclusion

We have experimentally investigated the temperatures at which the observed (room temperature) domain structure freezes in ferroelastic films with periodic a/c domains. This knowledge allows us to determine the relevant strain values for the formation of domains (the lattice mismatch between the film and the substrate that are responsible for the domain configuration observed at room temperature). We observe that those freezing temperatures can vary in the low thickness regime from 420°C for the thinnest films to about 490°C for films of 80 nm and above. Using the thickness dependent coherency strain to fit the experimental values within the P&Z model allows us to extract a reliable value for the domain walls formation energy density of 12.8 ± 2.2 mJ/m², which appears to be thickness independent and consistent with that obtained for the classical Roytburd model. Previously, the domain formation energy density for a/c 90° domain walls in ferroelectric PbTiO₃ thin films on a different substrate was estimated to be 50 mJ/m² [16] and theoretical value, using first principles calculations for a/c 90° domains in relaxed PbTiO₃ films by Meyer and Vanderbit [17], is 35 mJ/m², the same order of magnitude value found in
Figure 4.10: Domain wall formation energy density of a/c domains in PbTiO$_3$ thin films as a function of thickness derived from the P&Z fit to the experimental data (black symbols in Fig. 4.9); black line being the average value and the band being the standard deviation. The average value agreed with that obtained with the Roytburd’s model.

our samples.
Bibliography


Chapter 5

Super switching and control of in-plane ferroelectric nanodomains in strained thin films.

5.1 Summary

In previous chapters it was shown that highly periodic $a/c$-domains form in PbTiO$_3$ thin films and it is possible to predict the periodicity of such structure by modifying the model established by Pertsev and Zembilgotov. This was done in order gain control of the size and response of such fine structures and to use them for applications.

In order to further enhance usability and to improve ferroelectric properties of ferroelectric materials we use a combination of strain and compositions tuning. Partially substituting Pb by Sr in PbTiO$_3$ grown on the top of (110)-DyScO$_3$ substrates resulted in thin films which undergo a phase transitions from polarization out-of-plane to polarization purely in-plane at room temperature.

These strained films showed a domain structure with domains forming at two different length scales: nanodomains and superdomains. These superdomains had only been observed previously in laterally confined objects and, thus, they had been ascribed to the large in-plane depolarization fields. Here we offer a different explanation for this phenomenon taken place in extended films: the average direction of the polarization varies when averaging at the nanoscale (in the nanodomains) or at the micro-scale (in the superdomain) from the $<110>$ in-plane directions to the
<100> in-plane directions, which reflects the competition between the ground state of the single domain and the polydomain film, according to the theoretical predictions [1,2].

In addition, and very importantly, it will also be shown that despite the pure in-plane phase of the PST films it is possible to switch domains by an electric field applied from the top and the bottom surfaces of the sample using a scanning probe.

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5.2 Introduction

Understanding and controlling domain formation in ferroelectrics at the nanoscale is interesting from a fundamental point of view and also of great technological importance. Increasing miniaturization in ferroelectric materials allows the creation of complex domain structures with novel functionalities [3–6] that could be particularly useful for the development of nanoelectronic devices. Most studies in thin films focus on domain patterns with up/down polarization for ferroelectric memories, while domain structures with purely in-plane polarization have not been much investigated. However, such structures are potentially useful, for example, in optical devices where in-plane domains, with vertical domain walls, could be manipulated optically or in ultra-thin films, where avoiding depolarization field effects is necessary.

Within the past decade, complex domain patterns (such as flux-closures and vortices) have been predicted to form in ferroelectrics as their dimensions are reduced [7–13], motivating experimental work aimed to reveal such complex topological arrangements of electrical dipoles. Within the last 5 years, several experimental studies have been focused on the effect of geometrical confinement on novel nanoscale domain patterns [5,6], especially in lamellae and small-scale dots from bulk single crystals of BaTiO$_3$ [14–18], PbZr$_{1-x}$Ti$_x$O$_3$ (PZT) [19] and Pb(Zn$_{1/3}$Nb$_{2/3}$)$_{1-x}$Ti$_x$O$_3$ (PZN-PT) [20]. A few studies were also conducted on disk-shaped thin film capacitor structures of PZT [21,22]. Exotic dipole arrangements have been evidenced but their formation remains not fully understood. Recently, complex domain structures have also been observed to occur spontaneously at grain boundaries (in PZT films) [23], and heterointerfaces in thin ferroelectric films (of PZT and BiFeO$_3$) [24,25]. First results on their control by applying external electric fields (in PZT [23] and BiFeO$_3$ [3]) appear very promising for the development of new nanoelectronic devices. It is, therefore, essential to understand the effect of geometry, electrical boundary conditions and local strains on the domain architectures in ferroelectrics.

In ferroelectric thin films, epitaxial strain can be used as an additional degree of freedom to tune the domain configuration. Intensive theoretical work has thus been conducted on several ferroelectric materials in order to predict the changes of ferroelectric domain structures induced by strain [1,2,26–29]. Experimentally, epitaxial strain is typically created by growing high-quality thin films on suitable substrates [30]. A perfect con-
control of the epitaxy is crucial in order to ensure domain formation as the only mechanism to relieve misfit stresses. However, the limited number of available substrates prevents continuous tuning of the epitaxial strain in one given material. In order to control the magnitude of the epitaxial strain in a continuous manner, from compressive to tensile, and access the whole diversity of available phases, a suitable combination of composition and substrate can be used. The substitution of Pb by Sr in Pb$_x$Sr$_{1-x}$TiO$_3$ (PST) thin films grown epitaxially on (110)-DyScO$_3$ induces an increased tensile strain, predicted to stabilize a ferroelectric domain structure with purely in-plane polarization [31,32].

In this work, we used epitaxial growth and strain in extended PST thin films to stabilize and control a complex multiscale domain pattern with a purely in-plane polarization, which can be easily switched by 90° by a scanning probe. We showed that 90° a1 − a2 stripe domains self-organize in distinct bundles, or super-domains, at larger scales, and we propose that this happens as a result of the competition between the preferred polar direction of the polydomain and the single-domain ground states. Unlike previous reports in laterally confined objects, where significant depolarizing fields are expected to affect the domain formation, our results prove that these hierarchical domain arrangements, forming flux-closure states, can be stabilized in extended thin films, where strain-equivalent superdomains are created to emulate the single-domain ground state. Importantly, despite the inherent difficulty to switch in-plane polarizations, the hierarchical domain organization allows the polarization in these films to be manipulated from the top surface, with the in-plane electric field available through a scanning probe [3]. The control of such domain architecture at two scales offers promising perspectives to design novel electronic devices based on thin films with vertical domain walls (DWs) and no effect of depolarizing field.

5.3 Experimental

5.3.a Epitaxial growth

Pb-rich PST thin films with $x=0.55$-1 (of 6, 12, 30, 60 and 100 nm thickness) were grown on (110)-oriented DyScO$_3$ substrates (from CrysTec GmbH) by pulsed laser deposition using a pulsed KrF excimer laser ($\lambda=248$ nm), from Pb$_x$Sr$_{1-x}$TiO$_3$ targets with 4 atomic % excess lead. The substrates were treated to get a single ScO$_2$ termination [33,46], allowing the
growth of high-quality SrRuO$_3$ bottom electrodes. The growth was followed \textit{in-situ} by reflection high energy electron diffraction and the films thickness was determined from the reflection high energy electron diffraction intensity oscillations, together with X-ray reflectivity. The thickness of the SrRuO$_3$ layer was 8 nm in order to get fully strained films and thus keep the lattice parameters of the substrate for the deposition of PST. The growth parameters were tuned to optimize the epitaxial quality of PST films (temperature of 580$^\circ$C, oxygen partial pressure of 0.06 $mbar$, 2 $J/cm^2$ laser fluence, laser frequency of 10 $Hz$, spot size of 0.8 $mm^2$ and a target-substrate distance of 50 $mm$).

5.3.b X-ray diffraction

The epitaxial structure and strain state of the films were studied by XRD in both normal and grazing incidence geometry. We used the facilities of both the HASYLAB P08 beamline (Petra III-DESY, DESY), for grazing incidence measurements, and a Panalytical X’Pert MRD Cradle (four axes) laboratory diffractometer. The wavelengths used were 1.2398 and 1.5406 $\AA$, respectively.

5.3.c Atomic force and piezoresponse force microscopies

The films were characterized using AFM in tapping mode, to access the morphology, and using PFM (both in-plane and out-of-plane modes) to study the ferroelectric domain structure and switching. For PFM measurements, our Dimension V (Veeco/Bruker) microscope was equipped with conductive Co/Cr-coated silicon tips (spring constant 5 $N/m$) and an alternating voltage was applied between the tip and the SrRuO$_3$ bottom electrode at a frequency of about 25 $kHz$ for domain mapping, with a voltage amplitude in the 0-5 $V$ range.

5.4 Results

5.4.a Strain state and structure of Pb$_x$Sr$_{1-x}$TiO$_3$ thin films

In pure PbTiO$_3$ thin films grown on (110)-DyScO$_3$, a tensile strain of 1.1 \% induces a usual $a/c$ domain structure with periodic ferroelastic domains of alternating in-plane ($a$ domain) and out-of-plane ($c$ domain) ferroelectric polarization, as simply sketched in Figure 5.1 (c) [33,34,34]. In fact,
the differences in a and c lattice parameters induce a non-flat surface with a twinned roof-like structure that makes this domain architecture directly observable in the film topographic image (Figure 5.1 a) [35]. X-ray diffraction (XRD) reciprocal space mapping (RSM) shows the presence of a and c domains, as well as additional intensity oscillations in the diffuse scattering because of their periodic arrangement [33–35]. In Pb$_x$Sr$_{1-x}$TiO$_3$ films, by substituting Pb by Sr (decreasing $x$), the tensile strain can be continuously increased. Both in-plane and out-of-plane lattice parameters have been measured by XRD to precisely characterize the films strain state as a function of composition. As expected, the strain state was found to be strongly dependent on the Pb content ($x$): the higher the $x$, the larger the unit cells tetragonality and the more difficult to keep the strain when increasing the thickness. Consequently, although 6-nm thick films maintained the strain in the whole composition range under investigation ($x=0.55-1$), 12- and 30-nm thick films are only fully strained for $x \leq 0.7$ and $x \leq 0.65$, respectively. Lowering the Pb content to $x=0.55$, the films can remain fully strained up to a thickness of 100 nm or more.

First, we take a look at films of 30 nm in thickness with $x \leq 0.65$, which were fully strained, that is, they present the same in-plane lattice parameter as the DyScO$_3$ substrate. Orthorhombic (110)-DyScO$_3$ substrates do not have a totally squared in-plane lattice, however, the difference between the two in-plane parameters was small: the two in-plane lattice directions were [1-10] and [001], which we shall name a-axis and b-axis, respectively, corresponding to pseudo-cubic lattice parameter of 3.943 and 3.945 Å [36]. Along these axes lie the [100] and [010] in-plane lattice directions of the PST films. The out-of-plane lattice parameter of the films being smaller than the in-plane value indicate an in-plane orientation of the polarization in this composition range [31, 32]. This is consistent with a transition to an in-plane ferroelectric phase predicted under increasing tensile strain (blue area in Figure 5.1 b) [31]. The transition to the in-plane phase takes place at different compositions for different thicknesses (at $x=0.7$ for 6-nm thick films and at $x=0.65$ for 12- and 30-nm thick films). In this in-plane polarized phase, the domain structure cannot be evidenced from the films topography, as expected. The atomic force microscopy (AFM) images show steps of one unit cell height (Figure 5.1 d), reflecting the substrates terraces and the high quality of the epitaxial growth. The lack of out-of-plane polarization was confirmed by piezoforce microscopy (PFM) measurements, as it will be discussed later.
Figure 5.1: Topography and ferroelectric phases of Pb$_x$Sr$_{1-x}$TiO$_3$ thin films. a) AFM image (2 × 2 µm$^2$) of a PbTiO$_3$ (50 nm) film, with an a/c domain structure as sketched in c. b) Monodomain phase diagram versus composition for Pb$_x$Sr$_{1-x}$TiO$_3$ (PST) strained on DyScO$_3$ as calculated using the Landau-Devonshire theory (the misfit strain $U_m$ is defined with respect to the lattice parameters of the extrapolated PST cubic phase) [31]. AFM image (5 × 5 µm$^2$) d) and in-plane reciprocal space maps e)-g) around the (010), (-110) and (-220) reflections, respectively, of a completely strained 30-nm-thick PST thin film ($x=0.65$). The axes are in units of $2k_0$ where $k_0=2\pi/\lambda$ with $\lambda=1.2398$ Å. h) Schematic view of the two possible ferroelectric structures: aa phase with 180° domain walls (left) and a phase with 90° domain walls (right).
The domain structure in the in-plane-oriented ferroelectric phase has been studied from synchrotron XRD RSMs around various reciprocal lattice points. Such maps are presented in Figure 5.1 (e-g) for a 30-nm thick PST film ($x=0.65$). These XRD data were consistent with any in-plane ferroelectric periodic domain structure with DWs perpendicular to the in-plane <110> directions. Satellites were observed around all in-plane reflections, proving that the in-plane polarization was periodically modulated, while no modulation was found around pure out-of-plane reciprocal space lattice points (as expected for pure in-plane polarization). Around the (010) reflection, the satellites were observed along the two diagonal ([110] and [1-10]) directions (Figure 5.1 e), whereas around the (-110) reflection, these satellites were observed only along the [110] direction (Figure 5.1 f). The satellite spacing was constant for different Bragg peaks (Figure 5.1 f and g), indicating that they originate in a superstructure (unlike satellites caused by different tilting of domains/twins). From the spacing between the satellites and the Bragg peak, $\Delta k$, a modulation periodicity of $\Lambda = 2\pi/\Delta k = 40$ nm has been obtained along the in-plane <110> directions, for this particular thickness and composition. The two possible uncharged domain structures with these types of walls are presented in Figure 5.1 (h): the $aa$ phase with anti-parallel polarization 180° domains and the $a$ phase with head-to-tail polarization (also called $a1-a2$ or 90° domains) [2].

5.4.b Periodic in-plane domain architecture at two length scales

In-plane PFM has been performed in order to determine with certainty the ferroelectric domain structure in the in-plane polarized phase. The study of a fully strained 30-nm-thick PST film with $x=0.65$ is presented in Figure 5.2. First, very well-defined periodic domains with in-plane polarization were observed, with a periodicity along the <110> directions and a domain period of 46 nm, in good agreement with the XRD results. No response has been observed while measuring the vertical PFM signal (except the usual contrast attributed to the cantilever buckling effect in the presence of in-plane polarization) [16], confirming the absence of an out-of-plane component of polarization.

The three colors observed on the 0° and 90° PFM scans (bright, medium, dark) correspond to different projections of the polarization along the direction of sensitivity (positive, zero, negative projection). As an example, these three phase contrast levels are associated to projections of polarization on the horizontal axis in Figure 5.2 (a): bright color for
Figure 5.2: Ferroelectric-ferroelastic domain architecture by in-plane PFM. AFM and PFM pictures of an in-plane polarized 30-nm-thick PST film with $x=0.65$. (a,d,e and Figure 5.3 f,h) Lateral PFM phase images (color scale range is 0-70 °) of areas of $2 \times 2 \mu m^2$ a), d) and e), $2.8 \times 2.8 \mu m^2$ (Figure 5.3 f) and $10 \times 10 \mu m^2$ (Figure 5.3 h), measured by rotating the film by 0° a) and d), 90° e) and 45° (Figure 5.3 f,h) with respect to the [100] axis. The direction of sensitivity to the polarization is indicated as double black arrows. The square area under investigation is visible in all scans and is marked surrounded by a dashed line. (Figure 5.3 g) topographic picture corresponding to the PFM phase picture (Figure 5.3 f) (scale bar range, 0-4 nm). From these images (plus images in Figure 5.3), four types of areas are observed (marked by the blue squares on a), defining coarse-scale ‘superdomains’. The polarization orientation in the nanodomains is directed along the a- and b-axis, in agreement with the a phase, and is represented by blue arrows for the four types of 90° rotated variant. The boundary between two ‘superdomains’ can be 180° (enlarged image b) or 90° domain walls (DWs; enlarged image c). Wide blue arrows on d) demonstrate the net polarization within the ‘superdomains’, with an example of 180° DWs, 90° DWs and a more complex flux-closure pattern.
Figure 5.3: Ferroelectric-ferroelastic domain architecture by in-plane PFM. For the detailed description see Figure 5.2 caption. Size of image f) is $2.8 \times 2.8 \mu m^2$, g), h) - $10 \times 10 \mu m^2$.

left-to-right polarization, medium color for polarization along the vertical axis of the scan (back-to-front or front-to-back), and dark color for right-to-left polarization. The two colors observed on the $45^\circ$ scans indicate that the polarization has a component along the [110] direction in all do-
mains: either a positive component (bright color) or a negative one (dark color). If we consider the area marked by the blue square on the top right of Figure 5.2 (a), the alternating left-to-right and back-to-front polarization directions in the domains produced alternating bright and medium color stripes along the [110] direction. The same area gave alternating medium and dark color stripes on the 90° scan (Figure 5.2 e) and alternating bright and dark color stripes on the 45° scan (Figure 5.2 f). Another area of the film (marked by the blue square on the bottom left of Figure 5.2 a) shows domains with right-to-left and back-to-front polarization directions, producing thus dark and medium color stripes along the [-110] direction on the 0° scan, medium and dark color stripes on the 90° scan, and an homogeneous dark color area on the 45° scan since all domains have the same polarization component along the [110] axis. Thus proves that the in-plane polarization phase is the \(a\) phase presented in Figure 5.1 (h) with favourable head-to-tail polarization.

As observed in Figure 5.1 (b), the Landau Devonshire approach predicted an \(aa\) phase in that region of the phase diagram [31]. This is the same ground state as found for pure PbTiO\(_3\) under tensile strain [2, 29]. However, in both cases, domain formation was neglected. Taking domain formation into account, calculations have shown the stabilization of the \(a\) phase, instead of the \(aa\) phase, for the region of the phase diagram with purely in-plane polarization [1], which is in agreement with our experimental results. In the \(a\) phase, the domains were not only ferroelectric but also ferroelastic, unlike in the \(aa\) phase. Although domain formation would not be expected in the \(aa\) phase, in the \(a\) phase it can be easily understood as an efficient way to minimize the elastic energy [37]: PST is tetragonal with a Curie temperature (depending on the Sr content and strain) between room temperature and the films growth temperature. While the films coherently grow on the substrate in the cubic phase, epitaxial strain develops while the films are cooled down and the PST unit cell becomes tetragonal, since the films have to fit the (nearly) square lattice of DyScO\(_3\). If the tetragonal axis of PST is aligned along one of the cubic directions of DyScO\(_3\), compressive epitaxial strain will be present in the polarization direction, while in the direction perpendicular to the polarization the strain will be tensile. Therefore, in order to minimize the epitaxial strain, the two polarization orientations alternate along the substrate a and b axes, creating two domain variants, as shown in Figure 5.1 (h). The good epitaxial quality of the films prevents defects formation and thus ensures the domain
formation to be the only mechanism to relieve the strain. In the $aa$ phase, on the contrary, the $a$ and $c$ axes of the tetragonal unit cell of PST would be along the $<110>$ directions of the substrate. In this scenario, it is not possible to think of neither elastic nor electrical driving mechanism for the formation of domains.

These small scale nanodomains were seen to be arranged in four types of areas, related by 90° rotations, as observed on the lateral PFM pictures (marked by the blue squares in Figure 5.2 a). These variants define micron-size superdomains with a resultant inplane component of polarization along the [110] and [110] directions (see wide blue arrows). Similar patterns have been observed in single crystals of BaTiO$_3$ (lamellae and dots) [14,16,17], dots of PZT [19] and lamellae of PZN-PT [20], as well as in relatively thick PZT and PbTiO$_3$ films [38,39], which included a fraction of domains with out-of-plane polarization and partial strain relaxation by dislocations. The DWs between superdomains were observed along both $<100>$ and $<110>$ crystallographic directions (see Figure 5.2 h). We have found 90°-type superdomain walls (Figure 5.2 c), if the periodicity direction rotates by 90°, and 180°-type superdomain walls (Fig. 5.2 b) with no change of periodicity direction. The latter type appeared to be less abundant in the PST thin films. Within the PFM resolution, these two types of DWs between superdomains seem to be locally charged. However, McGilly et al. [16] have recently investigated such type of apparently charged 180° DWs in BaTiO$_3$ by transmission electron microscopy and they evidenced zigzagbundle boundaries composed of local 180° DWs, forming continuous chains of adjacent flux closure and quadrupole states. It is likely that we have similar structures in our PST films, which would then form charge-neutral 180° superdomain boundaries.

In some areas of the PST films, the four superdomain variants were present and arranged in 90° DWs to create flux-closure patterns at larger scales, in which the resultant in-plane polarization step-rotates from one quadrant to the next (Figure 5.2 d). Different quadrant arrangements can be observed, such as a fourfold vertex and several threefold wall junctions that are connected to each other by 180° DWs. Four 90° domain boundaries that intersect at a single point will create energetically unfavourable core singularities and rarely were observed in our PST films. Instead, flux closure objects are split into two threefold junction points connected by a 180° superdomain boundary, as discussed in [20].

Complex domain patterns with flux closure objects at two different
length scales have only been reported in ferroelectrics recently and their physical origin has remained unclear [20]. In dots of single crystals, significant in-plane depolarizing fields can be present, because of the reduced objects lateral size, and induce flux closure loops. Such strong effect of lateral depolarizing fields has been reported by McGilly et al. in BaTiO$_3$ single crystals dots [15,17]. A favourable formation of quadrants facilitating fluxclosure at the mesoscale has been observed in vacuum [15], whereas 180° superdomains have been evidenced in air [17], showing the effect of surface charges and depolarizing fields on the domains architecture.

The present work shows that strong lateral depolarizing fields are not needed in order to create hierarchical domain structures with flux-closure objects on continuous films. According to the predictions, although 90° stripe $a1-a2$ nanodomains are the ground state of the polydomain strained film [1], a hypothetical single domain strained film would show an $aa$ phase with polarization along the in-plane pseudocubic $<110>$ directions [31]. The formation of superdomains mimics such single-domain ground state by creating strain-equivalent regions with average polarization oriented along the $<110>$ directions.

### 5.4.c Thickness dependence of domain structure

In the in-plane ferroelectric phase (composition range $x=0.55-0.7$) [31], the domain size (or domain periodicity) does not appear to change much with the Pb content, most likely because of the relatively small changes in the magnitude of the strain in this composition range. However, the domain periodicity was strongly affected by the film thickness. The well-defined periodicity of the nanodomains increased with the film thickness, as it is well known for ferroelastic domains. The RSMs around the (-110) Bragg peak of PST films with $x=0.55$, in Figure 5.4, showed that the satellite spacing decreases when increasing thickness. The evolution of the in-plane a domain period ($w$) with the thickness ($d$) for completely strained films is presented in Figure 5.4 (d). It is worth noticing that for this composition a film thickness higher than 6 nm is required to develop enough strain and induce domain formation. The measured domain period as a function of film thickness was consistent with Roytburds square root law for ferroelastic domains [40,41], as also observed in 90° $a-a$ domains in BaTiO$_3$ lamellae [14]. For fitting the experimental data to Roytburds model, we used the lattice parameters of the film and the substrate (and thus the strain values) at room temperature, as the domain freezing temperature was not known at
108 SUPER SWITCHING AND CONTROL OF IN-PLANE FERROELECTRIC NANODOMAINS IN STRAINED THIN FILMS.

Figure 5.4: Evolution of domain size. X-ray in-plane reciprocal space maps around the (-110) reflection of completely strained PST thin films for x=0.55 at different thickness a) d=12 nm, b) d=30 nm and c) d=100 nm. Axes are in units of 2k_0, where k_0=2π/λ with λ=1.2398 Å. The intensities scales (colour differences) are in logarithm scale. d) Domain period (w) of the nanodomains as a function of the films thickness (d) in the a phase. The solid line is the linear fit, in agreement with Royburds law [40, 41].

This point. The experimental data of our PST-strained films were well fitted using a DW formation energy density of 26 mJ/m^2. This value for a-a 90° DWs in strained films is 50 mJ/m^2 estimated by Stemmer et al. [42] for a/c 90° DWs (that is, walls between in-plane and out-of-plane polarized domains) in relaxed PbTiO_3 films and the 35 mJ/m^2 calculated by Meyer and Vanderbilt [43] using first principles calculations for a/c 90° domains in relaxed PbTiO_3 films (at 0K and excluding substrate clamping).

We also observed that one of the four superdomain variants became more favourable when the film thickness increases (Figure 5.5), lead to a
very long anisotropic periodic nanodomains with a most favourable resultant polarization along one of the four in-plane $<110>$ diagonals. This is clearly seen in PST films at $x=0.55$ that can stay fully strained up to thicknesses of 100 nm. As the film thickness increases, the elastic energy associated to the formation of walls between the superdomain variants increases, so that it becomes energetically more favourable to present only one type of variant [44].

5.4.d Switching of in-plane polarization

Interestingly, we were able to switch the polarization in a phase PST films. An in-plane electric field is available in the standard out-of-plane geometry, that is, by applying a bias between the bottom electrode and a metallic AFM tip, as reported by Blake et al. [3] Figure 5.6 (a) shows the as grown domain structure in an a phase 30-nm thick PST film ($x=0.65$). The switching of the in-plane polarization in nanodomains is associated to a rotation by 90° of the DWs (and, thus, to a switching by 90° of the resultant in-plane polarization) in the superdomains (marked by big blue arrows on Figure 5.6 b and c). The in-plane switching mechanism is described in more detail in the next paragraph.

All PFM pictures on Figure 5.6 were obtained by a fast (slow) tip scanning along the $a$-axis ($b$-axis). During the poling, the bias was applied to the tip while scanning the sample in the $b+$ direction (from bottom to top of the picture) or in the $b-$ direction (from top to bottom of the picture), in the square delimited by dashed lines. In the as-grown state, the four types of superdomain variants can be observed. After applying a tip bias (positive or negative), a stabilization of two variants with the same polarization along the $b$-axis (slow scanning axis) is clearly obtained (see Figure 5.6 b and c). Applying a positive tip bias while scanning in the $b-$ direction allows stabilizing the same set of variants (Figure 5.6 (b), dark color) as after applying a negative tip bias while scanning in the $b+$ direction (Figure 5.6 d). A positive tip bias with a scanning in the $b+$ direction (Figure 5.6 c) has also the same effect as a negative tip bias with a scanning in the $b-$ direction (Figure 5.6 e): a stabilization of the two variants with a negative polarization along the slow tip scanning axis.

This switching mechanism of in-plane polarization is possible due to the in-plane electric fields existing around the biased tip, as reported by Balke et al. for BiFeO$_3$ films (showing both in- and out-of-plane components of polarization) [3]. Sketches of the tip orientation and the in-plane
Figure 5.5: Effect of film thickness on domain structure. Lateral PFM phase images on PST films with $x=0.55$ (at the in-plane polarized $a$-phase) and thicknesses of 30 nm (a, picture size is $2 \times 2 \, \mu m$), 60 nm (b, picture size is $3 \times 3 \, \mu m$) and 100 nm (c, picture size 3 $\mu m$). The latter sample shows completely parallel domain walls for areas as large as 10 $\mu m$ (d, picture size is $10 \times 10 \, \mu m$). Colour scale range=0-70°.

Electric fields are presented on Figure 5.6 for each type of tip bias sign and scanning direction. While a negative tip bias induces in-plane electric
Figure 5.6: Control of the in-plane polarization switching (30-nm-thick PST film, $x=0.65$). PFM phase pictures (scale bar, 70-100°) of the as-grown state (a) and after applying a bias of 4V (b) and -4V (c). The tip orientation and the in-plane electric fields causing the switching during scanning in the $b$-direction (d) and Figure 5.7 (e) and (f) are presented in sketches (same manner as in Balkes article [3]). All images are $4 \times 4 \mu m^2$ scale; dashed square area is $2 \times 2 \mu m^2$. All images are presented in sketches (same manner as in Balkes article [3]).
Figure 5.7: Control of the in-plane polarization switching (30-nm-thick PST film, $x=0.65$). For the detailed description see Figure 5.6 caption. All images are $4 \times 4 \, \mu m^2$ scale; dashed square area is $2 \times 2 \, \mu m^2$. 
fields towards the tip, a positive tip bias has the opposite effect. If the tip is not scanning, the in-plane electric fields would change only locally and isotropically the in-plane polarization in the films. On the contrary, by scanning the tip, it is possible to switch anisotropically the in-plane polarization of the films along the slow scanning axis. Due to the back-and-forth scanning along the fast scanning direction, there is no average effect of in-plane electric fields along the \( a \)-axis. However, the directional scanning along the \( b \)-axis, allows stabilizing an in-plane component of polarization along this slow scanning axis (\( P_{in} \)). The direction of \( P_{in} \) is defined by the orientation of the in-plane electric field (marked by a red arrow on the sketches) applied to the films area just after the tip motion. For example, motion in the \( b \)- direction of a tip biased with positive voltage (Figure 5.6 b), resulted in a domain pattern that consisted of domains aligned along the \( b \)-axis, allowing to stabilize two domain pattern variants (the domains with polarization along the \( a \)-axis are not affected by the tip bias since the effect of in-plane electric fields along the fast scanning axis cancel each other during the trace and the retrace). Reversibly, by applying a negative, instead of positive, voltage to the tip (while keeping the scanning direction, Figure 5.6 e) or by changing the scanning direction from \( b \)- to \( b+ \) (while keeping a positive voltage to the tip, Figure 5.6 d), the directions of the in-plane electric fields were reversed. Consequently, the motion along the negative (positive) slow scanning axis of a tip biased with negative (positive) voltage resulted in a domain pattern that consists of domains aligned in the opposite direction along the slow scanning direction, allowing to stabilize the two other superdomain variants.

Looking at the data, though, the mechanism of in-plane switching seems more complex, with an associated 90° rotation of the DWs. Simply switching by 180°, the in-plane polarization in the nanodomains along the slow scanning axis (vertical in the figures) would induce charged DWs between nanodomains. Although charged DWs can exist under certain conditions [45], it is often not the most favourable configuration and, indeed, Figure 5.6 shows that head-to-head and tail-to-tail domain configurations are avoided in this case. Thus, the experiments have revealed that the in-plane electric field induces, next to the 180° switching of some particular areas, the 90° rotation of the polarization on the adjacent areas, changing the orientation of the domains walls and avoiding head-to-head and tail-to-tail configurations. Sketch on the Figure 5.8 shows our model for in-plane polarization switching in PST, with the resulting 90° rotation
of the domain walls, which is clearly observed in the experiments (see Figure 5.6). The pre-switching polar orientations are plotted as blue arrows and the post-switching polarizations are plotted as red arrows. The domain walls before and after switching are marked with blue and red lines, respectively. A particular region of a nanodomain has polarization along the same direction as the in-plane field but in opposite sense (see central area) and would be able to orient along the electric field avoiding charged domain walls if four directly adjacent areas of similar size simultaneously rotate their polarization by 90°. Notice that the diagonally adjacent areas do not need to switch. That implies that 1/9 of the total switched area (Figure 5.6 a) switches 180°, 4/9 of the area rotate by 90° and 4/9 do not switch at all. This seems to be a very efficient mechanism by which four ninths of the sample can remain unswitched, nevertheless producing a net total moment in the desired direction.

![Figure 5.8: Model for in-plane polarization switching.](image)

As discussed previously in this chapter, the structure of PST films is close to cubic, with a relatively small $a/c$ ratio, which most likely enables the 90° rotation. Modelling polarization dynamics would help better understand the switching mechanism of purely in-plane polarization under the PFM tip. Such study would require a precise determination of the electric field components under the tip, but is beyond the purpose of this thesis.

Even if the exact mechanism of in-plane polarization switching remains to be theoretically proven, our results clearly demonstrate that it is possible to switch a purely in-plane polarized thin film using PFM. The reason why this is possible is the selfarrangement of the nanodomains in super-
domains with spaceaveraged polarization pointing along the diagonals of the pseudocubic lattice. It is the presence of superdomains that allows switching of the purely in-plane polarization because, unlike the nanodomains, the different superdomain variants are strain-equivalent and they are therefore not elastically pinned to neighbouring superdomains. This type of switching mechanism is favoured by the small tetragonality of the samples and the very small barrier for the motion of 90° DWs [43]. Because we have shown that superdomains are formed also in regular extended samples with competing (single-domain versus poly-domain) ground states, this work paves the way towards a more deterministic writing of in-plane domain structures in ferroelectric films.

5.5 Conclusion

Combining both strain engineering and composition tuning we were able to find the predicted in-plane polarized phase, which proves an existence of a morphotropic phase boundary in Pb$_x$Sr$_{1-x}$TiO$_3$ thin films grown on DyScO$_3$ substrate. We showed that with sufficient control of the epitaxial growth and strain in extended thin films, it is possible to stabilize and control complex domain architectures at two different scales, yielding periodic ferroelectric nanodomains with purely in-plane polarization and organized in strain-equivalent superdomains, so far mainly observed in laterally confined samples. Such multiscale domain arrangement emerged from the differences in the ground state of the poly-domain and single domain strained films (superdomains emulate the single-domain ground state) and it facilitates domain switching. In this way, a pure in-plane polarization can be switched from the top surface with the in-plane electric field created by a scanning probe.
SUPER SWITCHING AND CONTROL OF IN-PLANE FERROELECTRIC NANODOMAINS IN STRAINED THIN FILMS.
Bibliography


Chapter 6

Nanostructuring ferroelectrics for memory applications.

6.1 Summary

In previous chapters we have studied ferroelectric thin films of PbTiO$_3$. The films are interesting due to the highly periodic $a/c$-domains, for which the period is robustly determined by the thickness of the film and the growth conditions (see Chapter 3). We have developed a modification of the theoretical model by Pertsev and Zembilgotov (P&Z model) [1], in order to be able to predict domain periodicity with better accuracy, taking the kinetics of the domain formation into account (see Chapter 3 and 4).

In this chapter, such gained knowledge is used to manufacture ferroelectric nano-structures. We apply the known phenomenon of selective wet etching by polar surfaces [2–4] and use HF acid to preferably etch part of the periodic $a/c$-domain structures in our PbTiO$_3$ films. The aim is to leave only one of the domains untouched while etching the other one. The resulting domain mesh is studied with piezo force microscopy in order to investigate its ferroelectric response. In a first step towards investigating its potential for ferroelectric memory devices, single and multiple bit manipulation is performed.
6.2 Introduction

As discussed in Chapter 1, ferroelectric materials are good candidates for active elements in memory devices [5]. In this chapter we use PbTiO$_3$ thin films with domains to test their capabilities as memory elements. These films show periodic $a/c$-domain patterns with 90° domain walls, which are reported to aid domain switching [6]. In addition, 90° walls are also responsible for the enhancement of the piezoelectric response in nano-islands [6]. Reducing the lateral size of the ferroelectric thin film down to the order of the film thickness, decreases clamping of the film to the substrate and allows to measure the piezo-response of such an island [7].

Focused ion-beam [8] and electron-beam lithography [9,10] are the most efficient ways for nano-structuring of oxides. Hard alumina mask during Pulsed Laser Deposition (PLD) has also been used to fabricate standalone PbZr$_{1-x}$Ti$_x$O$_3$ nano-capacitors [11]. All mentioned methods have common features: a pattern is fabricated with the help of a mask, which defines the size and period of the nano-objects. Utilizing self-assembling mechanisms that occur spontaneously during the materials deposition is an alternative approach to manufacture nano-objects. The advantage of this method is that it needs less production steps and resources and, importantly, that it can give easier access to sizes below 100 nm, which are hard to obtain with the other methods, while maintaining the oxide structural and chemical integrity. High-density ferroelectric memory cells using self-assembled nano-electrodes on a continuous film have previously been reported [12] but the nano-islands had no registry. Indeed, using masks for fabrication has the big advantage of giving rise to ordered arrays of equally spaced nano-structures suitable for memory applications, while the self-assembly approach tends to produce island of diverse sizes and at rather random positions, unless one uses a combined strategy such as block-copolymer templating [13,14].

In this Chapter in order to overcome this problem, and as an attempt to simplify the process with respect to the use of a template, we intend to use the process of domain formation in ferroelectric/ferroelastic materials, and our control on the domain sizes, in order to fabricate switchable nano-structures. For that we take advantage of the different surface polarity of the different domain variants, defect sites in the crystal lattice (like domain walls) and the preferential etching that they display [2–4]. We use thin PbTiO$_3$ films grown as described in Chapter 3. In these films, as a release mechanism for internal strain, induced by the DyScO$_3$ substrate, highly
periodic and well ordered \(a/c\)-domains form and their registry is close to that obtained with the help of masks (although more work is needed to optimize this feature).

In addition, the periodicity of such pattern can be as small as 27 \(nm\) for our films (see Chapter 3). The periodicity mainly depends on the coherency strain [1] and thus on the mismatch between the substrate and film lattice parameters, and the film thickness. Variation of these parameters allows to vary the \(a/c\)-domain periodicity and, thus, allows to control the density of nano-structures, which is important for applications: a memory cell with capacity of 1 \(Tbit/in^2\) (as the memory roadmap establishes), requires one ferroelectric bit per 25 \(\times\) 25 \(nm^2\).

6.3 Results

\(PbTiO_3\) thin films grown on the top of \(SrRuO_3\)-buffered (110)-\(DyScO_3\) substrates were prepared by PLD. The substrate preparation and growth conditions are described in Chapter 2 and 3 (here we use the fast grown films there described). As described in Chapter 3, such films exhibit very periodic \(a/c\)-domains structure easily detectable by XRD and AFM measurements. In order to measure the piezoelectric response and to reveal the domain structure, some films were studied with Piezo Force Microscopy (PFM) (see Chapter 1, section 4.3.1 for setup and operating principle).

To proceed with nano-structuring by wet etching, a 120 \(nm\) thick \(PbTiO_3\) sample was chosen. As seen in Figure 6.1, the \(a/c\)-domains are highly periodic, especially along one of the two in-plane directions (see Chapter 5 for discussion about the in-plane anisotropy). An average size of a \(c\)-domain for this sample is 112 \(\pm\) 16 \(nm\), which is 80 % of total domain period. We have made samples with much smaller domains size; for example, a 17 \(nm\) thick film has only 27 \(\pm\) 5 \(nm\) period, which would be better suitable for high density memory applications. However, in order to establish proof-of-concept, a sample with rather large \(c\)-domains is used to ease the sample treatment and characterization. Before proceeding any further with the sample its ferroelectric structure was investigated with PFM and the results are depicted on Figure 6.1. The amplitude channel shows the \(c\)-domains as bright areas with a large piezoelectric response; while in between them, the much thinner \(a\)-domains show no piezoelectric response in the out of plane direction, as expected. The phase channel shows a homogeneous contrast in the \(c\)-domains indicating that all the
c-domains are equally oriented with polarization pointing up.

![Figure 6.1: PFM images of a 120 nm thick PbTiO$_3$ film. a) topography; b) and c) amplitude and phase channel, respectively, of VPFM.](image)

Selective etching on ferroelectric $a/c$-domains was performed by buffered 12.5% HF acid. This was done in 3 subsequent steps:

1.1 the sample was submerged into acid for 2 minutes and the beaker containing the acid was placed in ultrasonic bath (Branson 2510) to the aid chemical reaction;

1.2 the reaction was stopped by placing the sample into beakers with di-ionized water. 3 different beakers with water were prepared and the sample was subsequently submerged into each one for 20 seconds in order to make sure there is no acid residue left on the sample;

1.3 an AFM topology measurement was performed in order to check the state of the sample.

All the steps were repeated when necessary. On the Figure 6.2, PFM images are shown of the sample where the selective etching of $\approx 18$ nm of parts of the film is seen. The interpretation of the in-plane piezo-force channels is complicated by the cross-talking with the topography.

In this particular case, the etching process was repeated 9 times until no further height difference was measured, and the etched height was recorded in Figure 6.3, with a resulting 90 nm total height difference. Due to the limited resolution of the technique (tip radius 20-40 nm), it is not totally clear if the whole sample thickness (120 nm) has been etched. For the last two data points of Figure 6.3 there was no change in height difference observed.

According to the literature, HF should etch faster at positively charged surfaces and at lattice defects [2–4]. In our case, it looks like active etching
Figure 6.2: PFM images of the same PbTiO$_3$ film of Figure 6.1 after selective etching. The height difference between etched and unetched areas in this image is 18 nm. a) topography; b) and c) out-of-plane piezo-response, amplitude and phase channels respectively; d) and e) in-plane piezo-response, amplitude and phase channels respectively.

Figure 6.3: Height difference between etched and unetched areas versus etching time, as measured by atomic force microscopy. Average etching rate is 5.5 nm/minute.
takes part at domain walls. With time, a dip is etched near the domain wall exposing the c-domain side and $a$-domain side (positively charged) to the acid, see Figure 6.4 (a). The etching rate of exposed $a$- and $c$-domains sides are significantly less than that at the domain wall according to the literature [2–4]. This is supported by TEM measurements in Figure 6.4, where a cross-section TEM image of an HF partially treated sample is depicted. From Figure 6.4 (a) it is clear that the conical shaped material, left after the HF treatment, follows the tilt of $a$-domains (the domain walls) and that the etching takes place mainly in the $c$-domains. On the other hand, we found a few places where an $a$-domain is etched alongside with the adjacent $c$-domain, like shown by red dashed lines on Figure 6.4 (b). An explanation for this phenomena will be given later in this chapter.

![Figure 6.4: Bright field TEM images of a partially etched PTO sample. a) Conical shape of unetched material has its side slopes defined by the tilt of $a$-domains, marked by black dashed lines; letter ”$a$” and ”$c$”, respectively marks $a$- and $c$-domains; black arrows depict polarization orientation and red pluses show positively charged exposed $a$- and $c$-domain sides. b) Red dashed lines confine an $a$-domain, which is etched along with adjacent $c$-domain. Bright field TEM images were taken using a FEI ”Titan” microscope by Cesar Magen (INA, Zaragoza, Spain).](image)

In Figure 6.5 there are topology images of the maximally etched sample, which clearly shows profiles and maximum depth of 90 nm. Only when the unetched areas are too close to each other and the tip cannot penetrate, a smaller apparent depth is measured. Once these images are compared
to the images of the untreated sample and TEM images on the Figure 6.4, it becomes clear that the unetched material, although selected by the presence of $a -$domains at the top surface, mainly consists of $c -$domains in the bulk of the film and it is patterned in the in-plane direction by nice and straight domain walls in one direction and wavy walls in the perpendicular direction (see Figure 6.5).

![AFM topography images of the fully etched sample with crosscuts.](image)

**Figure 6.5:** AFM topography images of the fully etched sample with crosscuts. a) $2 \mu m \times 2 \mu m$ topology image; c) height crosscut along the white line of image (a). The measurements show a 90 nm height difference on the left-side of the image. The size of the tip ($\approx 30-50 \text{ nm}$) prevents measuring the full height on the right-side of the images, where the pattern is denser; the profile line shows a 90 nm height difference; (b) and (d) show similar measurements in a $5 \mu m \times 5 \mu m$ area.

As explained in relation to Figure 6.2 the correlation between the topography and the piezo-response makes it difficult to interpret the PFM images, especially the in-plane response. Thus, in order to study the elec-
trical polarization of the etched sample, it is better to perform PFM measurement at a fixed point in the sample: on the top of an unetched domain the PFM tip was placed, then a DC bias was applied to the tip, and it was slowly cycled from -5 V to +5 V. The piezo-response was measured with an AC voltage of 2 V in magnitude at a frequency of 25 kHz. The collected data is shown on the Figures 6.6 (a) and (b), as the amplitude and phase channels of the measured response, respectively. These measurements show that coercive voltage for this particular sample-tip system is around 3.8 V. Further measurements revealed that the coercive voltage stays within 4 ± 0.5 V for all tips and different areas used and that it is possible to fully switch down the vector of spontaneous polarization by applying +5 V and more to the tip (same applies in reverse, using negative bias voltage in order to switch the polarization up).

![Figure 6.6: PFM hysteresis loops of an unetched part of the sample. a) and b) are, respectively, amplitude and phase signal during a hysteresis cycle. Trace data (voltage ramped from -5 V to +5 V) are in blue and retrace data (voltage ramped +5 V to -5 V) are in red.](image)

Taking into account the results of the previously described PFM loops, the next natural step is to switch a larger area on the sample surface. This is a simple and efficient way to probe the piezo response of etched, unetched areas and borders between them. Switching is performed by PFM tip scanning over an area of 4 µm × 4 µm with a +7 V DC bias being applied to the tip and with no AC voltage to aid switching. Then the DC voltage is removed and a bigger area of 5 µm × 5 µm is scanned. The AC voltage well below the coercive field is then applied to the tip to probe piezo-response of the sample surface. In order to prove the reliability
of the method, a part of the switched area (2 μm × 2 μm) was switched back to the initial state by applying a negative DC bias to the tip while scanning the area. The results of the switching manipulation are presented on Figure 6.7. Interestingly, it was only possible to switch an unetched part of the sample (bright areas that become dark on the phase channel of Figure 6.7 (c) after switching), while the areas remained under the etched region were not switchable (these areas always stay bright in the phase channel on Figure 6.7(c) before/after the switching). From that, we conclude that, either, the deep areas were completely removed till SrRuO₃ bottom layer (which efficiently resists HF) during the acid treatment, or that the remaining PbTiO₃ layer is too thin and thus experiences too much clamping for the piezo-response to be measured.

Figure 6.7: Ferroelectric switching inside an area of 5 μm × 5 μm. Rows are sketches (top), phase channel (middle) and amplitude channel (bottom) for different states of the sample: a) images before switching; b) an area of 4 μm × 4 μm switched by applying +7 V DC bias to the tip; c) an area of 2 μm × 2 μm switched back to the initial state by applying -7 V DC bias to the tip.
Thus it is possible to manipulate the polarization of the unetched parts of the film while the etched regions serve as natural separators between them. In the following then, we will investigate the switching characteristic of the unetched domains in more detail. For this, a PFM tip was placed in the middle of an unetched area of one of the straight domain lines running vertically in the figure (see Figure 6.8). Then a $+7$ V DC pulse was applied to the tip for a duration of one second. A clear contrast in the phase is seen on the "1 bit" phase image in Figure 6.8, indicating that an area of the domain with vertical size of 190 nm has been switched (horizontal dimension is the whole unetched region, of about 180 nm). Correspondingly, a dark line appears in the amplitude image, confirming that a domain wall between up and down polarized domains has been created. Then the PFM tip was moved by 200 nm up in the (image) vertical direction and the switching procedure was repeated. In this way 7 points ("bits") were switched. The resulting bits have an average vertical size of $170 \pm 20$ nm, while the horizontal size occupies the complete width...
of the unetched regions (see ”7 bits” image on Figure 6.8).

It can be seen on Figure 6.8 that the shape of the bits is rather unusual: laterally, it is symmetrically confined by the width of the unetched region, as expected. However, in the vertical direction of the image, the switching (always under the same +7 V DC bias applied for 1 second) appears to be non-symmetric and also confined by, on the one hand, the intersection with the horizontally running domains (what produces a wedge-like shape in the switched bit) and, on the other hand, by what looks like internal boundaries in the material, all parallel to each other and having the same wavy shape across the unetched domains. A close inspection of the amplitude image at the top of Figure 6.8, shows that these features are indeed there and produce some amplitude contrast in the image taken before switching. They are also observed in the other amplitude images of Figure 6.8 also on the unswitched domains. This phenomenon is explained by the presence of extra $a$–domains under the unetched domains, like the one depicted on Figure 6.9, which shows that not all $a$–domains get to the surface, due to the interaction with previously existing domains.

![Figure 6.9: Strain map obtained by Geometric Phase Analysis (GPA) of a TEM image of an etched PTO sample. Two $a$-domains in the center of the image are tilted towards each other and one of them does not get to the surface (so-called “ghost” $a$-domain). Strain map was prepared using a FEI ”Titan” microscope by Cesar Magen (INA, Zaragoza, Spain).](image_url)
The switching in the middle of the areas in between two crosses (points where the unetched areas running along perpendicular directions define junctions of four domains, see black circle mark in Figure 6.11 (a)) has also been investigated and the results are presented on Figure 6.10. A +5 V DC voltage pulse was applied during 1s to the spots on the sample marked with a red dot on Figure 6.10 (a). These positions are chosen such that each switching center is in the middle of a section in between crosses with different length (each section is bigger than the previous one from top to bottom of the image (the size evolution across the series is marked with white dashed lines on Fig. 6.10 (a)). The resulting phase image on Figure 6.10 (b) shows the switched domains in the middle of the section also being limited by the internal boundaries previously discussed and that there is no clear dependence with the length of the section in between two crosses (see Figure 6.10 (c)).

**Figure 6.10:** Switched domain size versus unetched "piece" size. DC = +5 V, pulse duration is 1 second. a) Topology image, red dots are marks for PFM tip position, white dashed line shows evolution of domain piece size determined by two subsequent "cross" centers; b) phase image. c) resulted plot.
The same switching procedure described for a single bit (+7 V during 1 second) was applied to the “cross”. Each side of a “cross” is switched one after the other. The results are depicted on Figure 6.11. It is known that physically confined objects with spontaneous polarization that experience strict mechanical and electrical boundary conditions can result in unexpected polar configurations [11, 15]. We have not found such unexpected states but, interestingly, we have observed that each side of the cross can be manipulated independently and there is no cross-talking among the four domains (see Figure 6.11 (b) and (c) for horizontal and (d) and (e) for the vertical domains).

![Figure 6.11: "Cross" switching without cross-talking. a) Topology (left) and PFM phase (right) of the sample before switching. Black and white circles mark the "cross" to be switched, respectively. b)-e) Subsequent stages of the switching with sketch on the left, of the area where the tip was placed (in black) and resulting phase image on the right. Bright in the phase image means polarization up and dark means polarization down.](image-url)
The DC bias pulse duration is an important parameter which determines the size of the switched bit. In order to investigate this dependence, a PFM tip was used to switch a part in the middle of an unetched areas by applying +7 V DC pulse with different durations. Figure 6.12 (a) is a phase image of the switched bits with the pulse duration in seconds marked above the image. A summary of the observed dependency is plotted in Figure 6.12 (c), where it is clear that the switched areas are increased with pulse duration in the short time range from 0.1 to 2 seconds and then become less dependent on time. This type of logarithmic behavior is also found in literature [16,17]. It can be seen that the switched area increases with pulse duration, but it never fills the whole section in between two domains junctions or crosses, again limited by the internal "ghost" domain boundaries discussed earlier. In order to check the robustness of
such boundaries, a +8 V DC pulse was applied during 300 seconds. The resulting phase image of the switched area is in Figure 6.12 (b). Even with such strong electrical driving force it was not possible to switch the whole section between two crosses (see red line surrounding the non-switched bit on blow-up on Fig. 6.12 (b)), while the rest of the unetched domain were switched (see green line on blow-up on Fig. 6.12 (b)).

These results show that there is the opportunity to use these samples as memory devices, where the memory bits are naturally separated, cross-talking of close-by bits is avoided and the writing conditions are not critical. The size of each bit is defined by width of the unetched areas, which depends on the original domain width and the etching time (this is about 200-300 nm in the present example but it can be made smaller, even down to 30 nm) in one direction. In the vertical direction the size is limited by internal boundaries (most possibly ghost a-domains, as discussed above).

![Figure 6.13: PFM manual manipulation with the sample surface. The letter 'R' has been written bit by bit.](image)

To visualize sample performance as a memory device, switching of bit patterns were performed. Two approaches were used: manual and automated writing (performing switching according to a pre-determined pattern). Manual patterning was done by placing the PFM tip manually to each position on the sample. A resulted phase PFM image is on Figure 6.13. A clear 'R' letter can be seen on it, which consists of single bits. The bits were switched separately one by one. Accuracy in the tip position is an advantage of this method but, on the other hand, it is very time
consuming. The tool "NanoMan" in the NanoScope software package by Veeco (now Bruker) was used for automated manipulation. On the Figure 6.14 (a) there is a phase image of the sample before patterning. An image was fed to the software, see Figure 6.14 (b). As a result, the software moves the PFM tip across the sample accordingly applying the required voltage. The phase image recorded after manipulation is on Figure 6.14 (c). This method allows for fast and efficient patterning but it is not possible to position PFM tip accurately on the desired place of the sample.

![Figure 6.14: Automated manipulation of ferroelectric bits by PFM software. The text “RuG for Infinity” (the motto of the 400 anniversary of the University of Groningen, celebrated this year) has been designed and provided to the software (b). The PFM tip with a bias voltage applied to it follows the image automatically and reproduces it on the ferroelectric sample (a) sample before- and c) after- automated bits writing).](image)

### 6.4 Conclusion

We have used the ferroelastic/ferroelectric domain patterns investigated in previous chapters to obtain a highly periodic selective etching and thus nano-structuration of a 120 nm thick PbTiO$_3$ film. The treated sample has its average vector of spontaneous polarization pointing out of the plane of the sample. This feature allows to switch a single bit by applying field normal to the sample surface. Apart from other factors like the magnitude of the applied voltage or its duration, the size of a single bit is mainly and robustly determined by the width of the unetched regions and the original domain width, which are in turn, controlled by the film thickness and growth conditions (see Chapter 3). Writing an area on the sample according to the pattern shows the possibility to automate the switching process, which is crucial for the next step in a memory development.


Summary

This dissertation focuses on investigation of the room temperature ferroelectric PbTiO$_3$ and its solid solution Pb$_x$Sr$_{1-x}$TiO$_3$ under epitaxial strain. Great control over the internal crystal structure of these materials has been achieved in the form of thin films. It is shown that, by substituting Pb with Sr, it is possible to modify the strain induced in the film and, thus, introduce more control to tune the properties of PbTiO$_3$. Moreover, in this way we can create features like domains and domain walls with nanoscale sizes. Nanostructuring of the resulting films is introduced in order to study the potential use of these materials for high density, non-volatile and energy efficient memory applications.

Chapter 1 contains introductory information about ferroelectric materials and, in particular, PbTiO$_3$. Information on composition tuning and strain engineering of PbTiO$_3$, which are the methods used here to make novel materials, is provided. The domain formation mechanisms and the theoretical models used to describe domain formation are also discussed.

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 width of ferroelastic 90° domains (a/c twins) in the thickness regime from 10 nm to 240 nm using PbTiO$_3$ films grown on SrRuO$_3$-buffered (110)-DyScO$_3$ substrates. Periodicity of ferroelastic a/c twins depends not only of the epitaxial strain and the thickness of the film, but also greatly on the growth kinetics. This is demonstrated by the different scaling exponents that have been found for the domain width as a function of thickness for series of thin films grown with different laser frequencies and, thus, very different growth kinetics. In order to get understanding of the formation of a/c-domains and to control and predict the domain width, we have modified the model developed by Pertsev and Zembilgotov to take kinetic effects into account. This modified model allows us to predict the experimental behavior of a/c-domains with great
In Chapter 4 we go one step further toward understanding the formation of $a/c$ domains in real films by investigating the behavior of domains as the films are cooled down from the growth temperature. X-ray diffraction experiments were performed as a function of temperature. They revealed that the temperature at which the domain walls freeze varies with the film thickness. In particular, we observe that the ferroelastic domain freezing temperatures of epitaxial PbTiO$_3$ films on a DyScO$_3$ substrate can vary in the low thickness regime from 420$^\circ$C, for the thinnest films, to about 490$^\circ$C for films of 80 nm and above. This, in turn, implies that the coherence strain that determines the final domain configuration, is also thickness dependent. We use the so-called Pertsev & Zembilgotov model modified to include the observed thickness dependent coherence strain. This model allows us to extract a reliable value for the domain wall formation energy density of 12.84 ± 2.21 $mJ/m^2$, which appears to be thickness independent. These values are significantly smaller than the 50 $mJ/m^2$ previously reported for $a/c$ 90$^\circ$ domain walls in ferroelectric PbTiO$_3$ grown on different substrates, which may explain the higher quality and better registry of the periodic domain structures often observed on scandate substrates.

In Chapter 5, we perform strain engineering in Pb$_x$Sr$_{1-x}$TiO$_3$ thin films, grown with very accurate control of the epitaxy. We were able to stabilize and control complex domain architectures at two different scales: periodic ferroelectric nanodomains with purely in-plane polarization, organized in strain-equivalent superdomains (with micron size). We suggested the mechanism by which the two length scales coexist in the films: the competition between different ground states for single-domain and polydomain films. In-plane ferroelastic domains are typically very hard to switch. Nevertheless, 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$^\circ$ domains in PbTiO$_3$ thin films utilizing wet etching. The etching process is based on the fact that bHF acid has faster etching rate at positively charged surfaces rather than neutrally or negatively charged ones. Thus etching mainly occurs on the surface of $c$-domains of the PTO sample. Selective etching in combination with the high domain periodicity has led to a quasi-periodic mesh, with no complicated nano-lithography methods. Electric measurements of
the sample showed clear ferroelectric and piezoelectric loops, which prove that it is possible to utilize the mesh as memory bits, which can be manipulated independently from the top surface of the sample, applying the electric field using an AFM-tip.

In conclusion we have engineered well periodic a/c-domain structures with 90° domain walls in ferroelectric PbTiO$_3$ thin films grown on SrRuO$_3$-buffered (110)-DyScO$_3$ substrate. We have got control over domain periodicity by defining the growth conditions and the thickness of the film. Successful prediction of the domain periodicity in real samples has been obtained by including kinetics effects in the established thermodynamical models. Nanostructuring of the sample via selective wet-etching of self-assembled a/c-domains was used as a proof of concept for ferroelectric memory fabrication with little production steps and resources. In addition, strain engineering in combination with chemical substitution has been used to create more complex domain architectures, which have led to domain formation at nano- and micro-scale co-existing in one sample, allowing for switching pure in-plane polarization.
Samenvatting

Deze these focust zich op het onderzoeken van het op kamertemperatuur ferroelektrisch materiaal PbTiO₃ en het verwante, door het maken van een vaste stof oplossing, PbₓSr₁₋ₓTiO₃ door middel van epitaxiale strain (de spanning die in een materiaal aanwezig is). In de these is grote controle bereikt over de interne kristalstructuur van deze materialen in de vorm van dunne lagen. Het is aangetoond dat, door Pb te vervangen door Sr, het mogelijk is om de genduceerde strain in de film te veranderen, en er dus een extra methode gaintroduceerd is om de eigenschappen van PbTiO₃ bij te stellen. Bovendien kunnen we op deze manier eigenschappen verkrijgen zoals domeinen op de nanoschaal en de bijbehorende afscheidingen ertussen, de domeinmuren. Het nanostructureren van de resulterende dunne lagen wordt gaintroduceerd om het potentieel van deze materialen te bestuderen voor onvergankelijke en energie-efficiënte opslag van gegevens met hoge dichtheid.

Hoofdstuk 1 bevat inleidende informatie over ferroelektrische materialen, in het bijzonder PbTiO₃. Informatie wordt gegeven over het bijstellen van de samenstelling en het regelen van de strain van PbTiO₃ en welke methodes daarvoor gebruikt worden om deze nieuwe materialen te maken. De mechanismes voor het vormen van de domeinmuurtjes en de theoretische modellen die daarvoor gebruikt worden, worden ook besproken.

Hoofdstuk 2 beschrijft de experimentele technieken die gebruikt worden gedurende het werk dat leidt tot deze these. In hoofdstuk 3 onderzoeken we de dikte-afhankelijkheid van de breedte van de 90° domeinen (a/c twins) in het dikteregeime van 10 nm tot 240 nm voor dunne lagen van PbTiO₃ op SrRuO₃-gebufferde (110)-DyScO₃ substraten. De periodiciteit van ferroelastische a/c twins hangt niet alleen af van de epitaxiale strain en de dikte van de dunne laag, maar ook voor een groot deel van de groeikinetiek. Dit wordt gedemonstreerd door de verschillende schalingsexponenten die zijn gevonden voor de domeinbreedte als functie van de dikte voor een
serie van dunne lagen die gegroeid zijn met verschillende laser frequenties, en dus erg verschillende groeikinetiek. Om te begrijpen waarom de a/c-domeinen gevormd worden en om de domeinbreedte te controleren en voorspellen, hebben we het model dat ontwikkeld is door Pertsev en Zembilgotov aangepast om rekening te houden met de kinetische effecten. Dit aangepaste model stelt ons in staat om het experimentele gedrag van de a/c domeinen met grote nauwkeurigheid te voorspellen.

In hoofdstuk 4 zetten we een stap naar het begrijpen van het vormen van de a/c domeinen in echte dunne lagen door het gedrag van de domeinen te onderzoeken bij het afkoelen van de dunne lagen vanaf de groeitemperatuur. Hiervoor werd temperatuursafhankelijke rntgendiffractie experimenten uitgevoerd. Zij lieten zien dat de temperatuur waarop de domeinnaturen bevriezen afhangt van de dikte van de dunne laag. Meer specifiek nemen we waar dat de temperatuur waarop ferroelastische domeinen van PbTiO₃ op DyScO₃ substraten bevriezen, varieert van 420°C voor de lage diktes tot 490°C voor dunne lagen van 80 nm of dikker. Dit laat op zijn beurt zien dat de coherente strain die de uiteindelijke domeinconfiguratie bepaalt, ook dikte-afhankelijk is. We gebruiken het zogeheten Pertsev & Zembilgotov model, aangepast om de waargenomen dikte-afhankelijke coherente strain mee te nemen. Dit model geeft ons de mogelijkheid om een betrouwbare waarde te verkrijgen voor de dichtheid van vormingsenergie van de domeinmuurtjes van 12.84 ± 2.21 mJ/m², die dikte-onafhankelijk lijkt te zijn. Deze waarden zijn significant kleiner dan de 50 mJ/m² die voorheen gerapporteerd werden voor 90° domeinmuurtjes in ferroelektrisch PbTiO₃ gegroeid op verschillende substraten, wat mogelijk de hogere kwaliteit en nauwkeurigheid van de periodieke domeinstructuren die vaak gezien worden op scandaat substraten verklaart.

In hoofdstuk 5 gebruiken we strain engineering in dunne lagen van PbₓSr₁₋ₓTiO₃ die zijn gegroeid met erg nauwkeurige controle over de mate van epitaxie. We waren in staat om complexe domeinarchitecturen te stabiliseren en controleren op twee verschillende lengteschalen: periodieke ferroelektrische nanodomeinen met de polarisatie volledig in het vlak van de dunne laag, die weer georganiseerd zijn in strain-equivalente superdomeinen met groottes van micrometers. Wij stellen een mechanisme voor waarbij beide lengteschalen naast elkaar in de dunne laag kunnen bestaan: de competitie tussen de verschillende grondtoestanden voor dunne lagen met maar n, of met veel domeinen. De polarisatie van ferroelastische domeinen met de polarisatie in het vlak is gewoonlijk erg lastig van
richting te wisselen. Niettemin maakt de aanwezigheid van domeinen op verschillende lengteschalen en strain neutrale gebieden het ons mogelijk om de polarisatie in het vlak van de dunne laag van richting te laten veranderen door het aanbrengen van een elektrisch veld op de punt van een AFM microcoop.

In hoofdstuk 6 beschrijven we het nanostructureren van 90° domeinen in dunne lagen van PbTiO₃ door middel van vloeistof etsen. Het etsproces is gebaseerd op het feit dat bHF-zuur een grotere etssnelheid heeft voor positief geladen oppervlaktes dan voor neutrale of negatief geladen oppervlaktes. Dus het etsen gebeurt voornamelijk op het oppervlak van c-domeinen van PbTiO₃. Selectief etsen in combinatie met de hoge domein-periodiciteit heeft geleid tot een quasi-periodieke maas, zonder de noodzaak van ingewikkelde nanolithografie. Elektrische metingen aan het monster laten duidelijke ferroelektrische en piezoelektrische lussen zien, die bewijzen dat het mogelijk is om de maas als opslagbits te gebruiken, die onafhankelijk van elkaar aangestuurd kunnen worden vanaf het oppervlak door gebruik te maken van een elektrisch veld van op de punt van een AFM microcoop.

Concluderend hebben we periodieke a/c-domeinstructuren met 90° domeinmuren gebouwd in ferroelektrische dunne lagen van PbTiO₃ die gegroeid zijn op SrRuO₃-gebufferde (110)-DyScO₃ substraten. We hebben controle over de domeinperiodiciteit door de groeiconditionen en de dikte van de dunne laag aan te passen. Het is gelukt om succesvol de domeinperiodiciteit te voorspellen in echte monsters door kinetische effecten mee te nemen in de gevestigde thermodynamische modellen. Het nanostructureren van het monster door selectief te etsen met vloeistof op de zelf-geassembleerde a/c-domeinen is gebruikt als demonstratiemodel voor het bouwen van ferroelektrische opslag met weinig productiestappen en -middelen. Bovendien is strain engineering in combinatie met chemische vervanging van elementen gebruikt om complexe domein-architecturen te maken die hebben geleid tot domeinvorming op zowel nano- als microschaal binnen hetzelfde monster, dat het mogelijk maakt de polarisatie in het vlak van de dunne laag van richting te laten wisselen.
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