Control of periodic ferroelastic domains in ferroelectric Pb1-xSrTiO3 thin films for nano-scaled memory devices
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Chapter 2

Experimental techniques

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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-
chrotron source. Due to the nature of the synchrotron radiation (brilliance, coherence length and wavelength tuning), it is suitable for measurements of ultra-thin films and offers better resolution for small lattice distortions. It is also possible to perform in-plane diffraction in the so-called Grazing Incidence Diffraction (GID) geometry.

For the Pb$_x$Sr$_{1-x}$TiO$_3$ (PST) films with $x$ varying from 0.50 to 1.00, we used X-ray photoelectron spectroscopy (XPS), a surface-sensitive spectroscopic technique that measures the elemental volume ratio in order to have additional control over the Pb/Sr stoichiometry of such solid solution.

### 2.3 DyScO$_3$ substrate treatment

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
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:

$$\text{Dy}_2\text{O}_3 + 3\text{H}_2\text{O}(l) \rightarrow 2\text{Dy}(\text{OH})_3(aq)$$

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) 
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 H$_2$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°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
Figure 2.2: a) (101)-DyScO$_3$ substrate as-received from supplier, no clear steps are visible; b) after thermal treatment terraces are clearly visible, the two terminations are present; c) after wet etching, terraces are still very clear. The substrates are now single ScO$_2$-terminated. Small halls (dark contrast) due to the HF etching step are present. All images are 2 µm × 2µm.

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 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-
2.4 PULSED LASER DEPOSITION (PLD)

Oxskites. 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 \( \approx 10^{-7} - 10^{-8} \text{mbar} \), 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 (poly-crystalline or single-crystalline) was prepared with the stoichiometry of the desired films and placed inside the vacuum chamber. A single crystal substrate was place 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 25\( \text{ns} \) pulses was focused...
at the target with a well-controlled fluency. 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 $\approx 2.1 \text{J/cm}^2$.

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 distance 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 expanding 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 increases the smoothness of the deposited film. PLD growth is, thus, ruled by kinetics rather than thermodynamics of the surfaces involved. Generally, 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
2.4 PULSED LASER DEPOSITION (PLD)

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 SrRuO$_3$ thin film grown on top of the DyScO$_3$ 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 \(k_0 = \frac{2\pi}{\lambda}\), 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 \(G_{hkl} = \frac{2\pi}{d_{hkl}}\), 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-
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 mode is step-flow, while
Figure 2.5: The information extracted from RHEED intensity is used to observe growth mode and thickness of the thin film. a) RHEED pattern of the SRO layer grown on top of the DSO substrate with the AFM topology image to the right; b) RHEED pattern and AFM image after 2D growth of a 12 nm thick PST layer on top of SRO layer and corresponding AFM image of the surface; c) RHEED intensity oscillations showing 30 oscillations corresponding to the 12 nm film; d) example of 3D growth as observed in a RHEED pattern. AFM images are 2 µm × 0.67 µm.

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
PULSED LASER DEPOSITION (PLD) 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:

\[ xPbO + (1 - x)SrCO_3 + TiO_2 \rightarrow Pb_xSr_{1-x}TiO_3 + (1 - x)CO_2 \]  

(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.
Figure 2.6: Heat treatment cycle for \( \text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3 \) \( (x = 0.9) \). Time axis is not to scale.

2.5 Atomic Force Microscopy (AFM)

In this work the properties of thin films as thin as 6 \( \text{nm} \) 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 \( \text{nm} \) 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 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 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-
fection 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:

$$D_i = P_i + \epsilon_0 E_i = d_{ijk}\sigma_{jk}$$

(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:

$$\sigma_1 = \sigma_{xx}$$
$$\sigma_2 = \sigma_{yy}$$
$$\sigma_3 = \sigma_{zz}$$
$$\sigma_4 = \sigma_{yz} = \sigma_{zy}$$
$$\sigma_5 = \sigma_{xz} = \sigma_{zx}$$
$$\sigma_6 = \sigma_{xy} = \sigma_{yx}$$

(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 3x3x3 tensor has been used for convenience. Therefore, the $d$ coefficients are often described by two indexes [24]:

$$D = \begin{pmatrix} D_{11} & D_{12} & D_{13} & D_{14} & D_{15} & D_{16} \\ D_{21} & D_{22} & D_{23} & D_{24} & D_{25} & D_{26} \\ D_{31} & D_{32} & D_{33} & D_{34} & D_{35} & D_{36} \end{pmatrix} = \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix}$$  \hspace{1cm} (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:

$$V(\omega) = V_0 \cos(\omega t)$$  \hspace{1cm} (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:

$$d(t) = d_0 + A \cos(\omega t + \phi)$$  \hspace{1cm} (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.

![Figure 2.7: Sketches of the effect of tip movement with the four-square photo detector. a) Vertical displacement of the tip during VPFM leads to a change in vertical deflection. b) Torsional motion of the tip during LPFM leads to a change in lateral deflection.](image)

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 wavelength, \( d_{hkl} \) 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.

![Figure 2.9: 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.](image)

### 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 rlu=\( 2\pi/\lambda \). This allows for easy comparison between measurements taken with different wavelengths. 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.c 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 became 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°. 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

![Diagram](image)

Figure 2.12: 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.

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°-0.5°. 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


