Structure and domain formation in ferroelectric thin films

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Chapter 3

Thin film technology & analysis

3.1 Introduction

Although the first pulsed laser ablation experiments took place in the mid-sixties of the previous century, it took until the discovery of high-$T_c$ superconductors in 1986 for pulsed laser deposition (PLD) to become a widespread deposition method. The relatively good stoichiometric material transfer from target to substrate and the wide choice of (oxygen) background pressures, have made PLD the leading deposition technique in research for high-$T_c$ superconducting thin films. The development of high-pressure reflection high-energy electron diffraction (RHEED) [58] and single crystal surface treatments [59], opened up possibilities to monitor the surface structure during high-pressure deposition of metal oxide thin films.

Nearly parallel in time to these developments, scanning probe microscopy has made enormous progress. This was triggered by the discovery of scanning tunneling microscopy (STM) by Binnig and Rohrer in 1982 and the atomic force microscope (AFM) a few years later [60]. Already in 1989 the first experiments with conductive tips on ferroelectrics were performed [61], setting the field of piezoresponse AFM (p-AFM). Due to the growing interest in ferroelectric thin films, p-AFM is currently a rapidly developing field of research [62].

These developments, set the background for the techniques used in this thesis work. Combined with more conventional techniques like X-ray and electron diffraction, impedance spectroscopy and CV-measurements, PLD-grown ferroelectric thin films have been analyzed. Despite the good stoichiometric transfer of material from target to substrate, thorough materials analysis remains necessary, since the stoichiometry can be disturbed by differences in the thermal properties of the materials constituents. Besides, the properties of ferroelectrics in thin film form are not yet fully understood [63],
which makes knowledge and control over a wide variety of parameters necessary. In the case of $PbTiO_3$, the main parameters to be taken care of are the lead excess necessary to compensate for lead loss at high (growth) temperatures, the oxygen pressure during deposition or annealing to prevent the formation of oxygen vacancies and the importance of the thermal history of the ferroelectric with respect to the domain structure.

3.2 Monitored thin film growth

3.2.1 Pulsed Laser Deposition (PLD)

The variety in thin film deposition techniques is so large that even extensive textbooks [6] only provide general overviews. Categorization of all these different techniques, provides a good context in which pulsed laser deposition (PLD), can be viewed. PLD is a physical deposition technique: a physical process is used to deposit a vaporized form of the material onto a surface (substrate). No chemical reactions are involved. The compound that is to be deposited, is ablated, forms a plasma and deposits onto a surface (the nomenclature is incomplete here; the material undergoes a phase transition from solid to plasma and back). In the case of PLD, the physical process is ablation by a high-power pulsed laser (in this case a Lambda Physik COMPex Pro 205 KrF ($\lambda = 248$ nm) excimer UV-laser), by which a plasma of highly energetic ions is formed. The ions in this plasma expand from a ceramic or single crystal target material towards a single crystal substrate on which the material is deposited. This process takes place in a conventional vacuum vessel ($p_{\text{background}} = 10^{-7} - 10^{-8}$ mbar) filled with oxygen gas ($p_{\text{deposition}} = 0.01 - 1.00$ mbar $O_2$). PLD can be seen as very short and rapid depositions at every laser pulse, followed by annealing in the time interval between the laser pulses. The thermodynamic model to describe the characteristics of PLD, is based on the nucleation of a solid phase from a supersaturated gas.

An important drawback of PLD is that, unlike many chemical deposition techniques, it cannot be scaled up easily. The homogeneous deposition area typically has a diameter of only several centimeter, although efforts for up-scaling are being made. On the other hand, for research purposes, PLD has a large advantage over most chemical vapor deposition techniques: ex-
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Figure 3.1: SEM images of ablated surfaces of a \( \text{SrTiO}_3 \) target with increasing energy density from \( 1.0\, \text{J/cm}^2 \), \( 1.3\, \text{J/cm}^2 \), \( 1.5\, \text{J/cm}^2 \) to \( 1.7\, \text{J/cm}^2 \) (from left to right). At \( 1.0\, \text{J/cm}^2 \) “pillars” or “droplets” are formed which is often attributed to inhomogeneous melting. Homogeneous ablation starts around \( 1.3\, \text{J/cm}^2 \); further increasing the energy density is ineffective as it will merely increase the effective temperature. An energy density of \( 1.5\, \text{J/cm}^2 \) is chosen to ensure homogeneous ablation.

tremely thin films can be easily prepared and the material transfer is stoichiometric. This stoichiometric transfer is ensured as long as the ablation is homogeneous. Because multi-component target materials are used in our experiments, and different materials ablate at different energies, or with different rates at a fixed energy, a suitable energy regime is necessary to prevent preferential ablation. These have been chosen carefully, analyzing ablated target areas using scanning electron microscopy (SEM) as shown in Figure 3.1. The differences in ablated surface morphology have been used as a guiding principle. When the ablated area shows a flat surface without extrusions, homogeneous ablation is ensured. Even with the good stoichiometric transfer of material from target to substrate, the stoichiometry of the resulting thin film can be different from that of the target material. The reason for this is the high plasma temperature and the elevated temperature of the substrate needed for single crystal growth. This can lead to loss of volatile species or decomposition of the thin film material at the substrate. In this work the volatility of lead, compared to elements like titanium and strontium, gives rise to possible lead-loss during the growth process. Therefore, we add a 3 – 8% excess lead in the \( \text{PbTiO}_3 \) target materials.

Typical deposition parameters used in the experiments described here, are summarized in Table 3.1. The PLD setup used for this work, is a TSST PLD-RHEED system\(^2\), schematically represented in figure 3.2. The heater consists of a resistive wire heating element; the substrates are attached to the

\(^2\)Twente Solid State Technology, P.O. Box 256, 7500 AG Enschede, The Netherlands (www.tsst.nl).
heater with silver glue. The laser-optics involves a UV-mirror and a lens, aligned to focus close to the target surface. A typical laser spot on the target is shown as an inset in Figure 3.2. In this case, it is the image of a 15x4mm mask, resulting in a 2.62x0.98mm laser spot. Also shown in this figure is the grazing angle of incidence (0.1-5°) for RHEED and a typical RHEED pattern as obtained from a treated $SrTiO_3$ substrate (for details, we refer to section 3.2.3).

![Diagram of PLD system](image)

*Figure 3.2:* Schematic top-view of the PLD-system at the Zernike Institute for Advanced Materials. The target material is ablated by a focused pulsed UV-laser beam that enters the vacuum vessel via a quartz window. The ablated material forms a plasma whose ions land on the heated substrate. Using an electron gun and phosphorus screen, the growth is monitored by RHEED. The temperature, pressures and several positionings are computer-controlled. As insets, on the left, a typical RHEED pattern is shown and, on the right, a picture of an ablated target area.

### 3.2.2 Supersaturation & growth modes

Whereas in homoepitaxy, the growth is fully determined by kinetics, for heteroepitaxy, thermodynamics plays an important role too. The very short and
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<table>
<thead>
<tr>
<th>material</th>
<th>pO$_2$ (mbar)</th>
<th>T(°C)</th>
<th>E$_d$ (J/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbTiO$_3$</td>
<td>0.13</td>
<td>570-580</td>
<td>2</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>0.10</td>
<td>800-850</td>
<td>1.5</td>
</tr>
<tr>
<td>SrRuO$_3$</td>
<td>0.06</td>
<td>600-700</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 3.1: Deposition parameters: From left to right the material, oxygen pressure, substrate temperature and laser energy density. In general, all targets are sintered ceramics, the background pressure in the vacuum vessel before gas inlet is typically below $10^{-7}$ mbar, target-substrate distance is 48 mm, laser repetition rates are in the range between 0.5 and 15 Hz and the spot size ranges from 0.76 to 2.46 mm$^2$. Deviations from these settings are mentioned in the pertinent chapters.

rapid depositions at every laser pulse, followed by annealing in the time interval between the laser pulses, as described earlier, gives rise to supersaturation. Formally, supersaturation is the difference in chemical potential between two phases of a material. In PLD practice, the plasma phase is far from equilibrium and has a very high vapor pressure. Upon expansion of the plasma, the vapor pressure exceeds the saturation pressure and supersaturation is established. The atoms nucleating on the surface, act as condensation centers for crystal growth.

The supersaturation is expressed in terms of the difference in chemical potential for different aggregations ($\Delta \mu$), which is zero between pulses but enormous during the laser pulse. This equals

$$\Delta \mu = kT \cdot \ln \frac{P}{P_0} = kT \cdot \ln \frac{R}{R_0}$$

(3.1)

where $T$ is the temperature, $P$ and $P_0$ are the vapor pressure during deposition and at the equilibrium, respectively, and $R$ and $R_0$ are the corresponding deposition rates.

The way in which the material nucleates on the substrate is then determined by the supersaturation. This can be adjusted by a number of interdependent parameters in the PLD process, of which the main ones are the target-substrate distance, the laser energy density, the (oxygen) pressure and the substrate temperature.

For heteroepitaxy, the materials differences between the impinging parti-
cles and the substrate which determine the relationship between the substrate and film surface free energies and the misfit strain, also play an important role in the nucleation. The nucleation on the sample surface determines the growth mode of the thin film. In general, three modes can be distinguished: island (or Volmer-Weber (Figure 3.3a)), layer (or Frank-Van der Merwe (Figure 3.3b)) and Stranski-Krastanov (Figure 3.3c) growth [6].

Layer growth resulting in atomically flat thin films, is preferred because

![Figure 3.3: General classifications of growth modes](image)

our aim is to measure intrinsic thin film properties and grow superlattices. Volmer-Weber and Stranski-Krastanov growth are generally (more) useful for the fabrication of (periodic) morphological structures [64]. In the next section more details on the distinction between these growth modes by reflection high-energy electron diffraction (RHEED) during the growth process will be given.

Two sorts of layer growth can be distinguished: step flow and layer-by-layer growth. Step flow mode is best described by the propagation of the steps because impinging particles have sufficient energy to move to the terrace step before the next particles arrive. In layer-by-layer growth, impinging particles have a somewhat lower energy, leading to the formation of unit-cell high islands, which grow and merge to fill a whole layer, before the next layer will start forming. Although step flow growth results in the highest film quality, experimentalists using RHEED prefer layer-by-layer growth because that enables them to monitor the thin film grow layer-by-layer.

Besides these layer growth modes, we observed Stranski-Krastanov-like (SK) growth modes several times. In Stranski-Krastanov, the first few monolayers grow in a layer mode and then the energy balance between solid, liquid and vapor changes, causing a change in growth mode to island growth. This means that in the SK growth mode, the surface roughness increases with thickness. We have also observed two other but similar growth modes, which differ from SK by the absence of roughening with thickness. One of them is very similar to the growth mode recently described in literature as a “pseudo-
two-dimensional” growth mode [65]. Shin et al. [65] show that the surface roughness is constant when the film thickness is increased. Therefore, we think the mode we observe is not SK, but pseudo-two-dimensional (Figure 3.4a). The second one is similar to that described by Sánchez et al. [66] and named “mound” growth. In this growth mode, islands nucleate on the terraces and start growing in a layer-by-layer fashion. The terraces sometimes remain visible, but superimposed to them are unit-cell-stepped islands (Figure 3.4b).

We have also observed Volmer-Weber growth modes (see section 5.2.2): First, we observed a growth mode in which islands nucleated on an initially two-dimensional surface. After this initial island nucleation, the surface turns two-dimensional again. In the intermediate regime, fingerprint-like structures are observed due to the merging islands (see Figure 5.2). And finally, we have observed true three-dimensional growth, for example when $PbTiO_3$ was grown at room temperature on $SrTiO_3$ with polymer nanorods (chapter 6).

3.2.3 Reflection High Energy Electron Diffraction (RHEED)

In RHEED, an electron beam is aligned under a grazing incident angle ($0.1 - 5^\circ$) on the surface by which it is diffracted (Figure 3.2). The diffraction pattern is collected at a phosphorus screen and contains information on both the crystal structure and morphology of the top-most atomic layers of the surface. RHEED is highly suitable to monitor PLD growth since it can -via differential pumping [58]- be applied in high oxygen pressures and interfere minimally with the deposition process. When care is taken, the observation of intensity oscillations of the specular RHEED intensity can be linked to the layer-by-layer growth rate [67, 68]: An initially flat surface is highly reflective and upon island nucleation, the reflected intensity drops. In a layer-by-layer growth mode, this decrease in intensity continues until half a monolayer is filled. Then the islands coalesce, the surface retains flatness and the reflected intensity increases until an entire crystal monolayer is grown. This observation has made of RHEED a suitable technique to monitor layer-by-layer growth with atomic resolution. In the ideal case that one oscillation corresponds to one unit cell, it can also be used to monitor the thickness of the deposited layer.

A RHEED pattern contains a plethora of information: the pattern pro-
Figure 3.4: AFM images of thin films grown in different observed growth modes. a) “Pseudo-two-dimensional” growth, observed when SrTiO$_3$ was grown on SrTiO$_3$, full z-scale Δz=7 nm (top) and when SrTiO$_3$ was grown on DyScO$_3$, Δz=4 nm (bottom). This growth mode has also been observed several times for PbTiO$_3$ on SrRuO$_3$ on DyScO$_3$ and PbTiO$_3$ on SrTiO$_3$ (not shown). b) “Wedding cake” or “mounds” growth observed when PbTiO$_3$ is grown on SrRuO$_3$ on DyScO$_3$, Δz=10 nm (top) and 5 nm (bottom) and when SrRuO$_3$ is grown on DyScO$_3$ (not shown).

provides information on the surface crystal structure and reconstruction, the lattice parameters can be calculated from the spot spacings, the pattern symmetry of the spots and its behavior upon sample rotation reveal the morphology (two- or three-dimensional) and, as mentioned before, the specular spot intensity as a function of time gives information on the growth mode and layer thickness. Here we will only deal with elastically scattered electrons, since they are scattered by the outermost atomic layers, which is the region of interest for thin film growth monitoring. As an in-situ growth monitoring tool, mainly the two- versus three-dimensional patterns and intensity oscillations as a function of deposition time have been used. These will be treated here in some more detail.

A perfect two-dimensional surface is never present in epitaxial thin film growth, but a nearly two-dimensional surface, with one unit cell steps (in
3.2. Monitored thin film growth

Figure 3.5: Schematic top-view of the RHEED setup in real space (a), linked with its interpretation in reciprocal space (b+c). (a) Top-view showing the grazing incident and diffracted angle ($\theta_{in}$ and $\theta_{out}$) and the in-plane sample rotation ($\phi$) in real space. Top- (b) and side-view (c) showing the reflected diffracted signal and its construction using the Ewald’s sphere and the crystal truncation rods. In the measurement setup, the pattern is projected on the fluorescent screen.

the case of oxide perovskites ~3.9 Å) every few hundreds nanometer, can be regarded as two-dimensional (2d). A RHEED pattern corresponding to a 2d surface during thin film growth, can be the result of either step flow or layer-by-layer growth. The diffraction pattern from a 2d surface is constructed by the crystal truncation rods intersecting the Ewald’s sphere. The radius of the Ewald’s sphere is determined by the wavelength (energy) of the electrons (in RHEED generally a large radius, the wavelength we typically use is only 44 pm) and the spacing between the crystal truncation rods by the in-plane crystal structure and lattice parameters (Figure 3.5). The RHEED pattern of a 2d surface is, therefore, sensitive to the in-plane orientation of the sample: upon rotation around the sample normal, diffraction spots should move and (dis)appear, unlike that of a three-dimensional surface, for which a diffraction pattern of the protruding material in transmission mode is obtained. This diffraction pattern is insensitive to orientation, since it is a powder-like
The intensity oscillations observed by RHEED on layer-by-layer growing thin films, are well described by a simple empirical model in which the specular intensity is inversely proportional to the number of up and down steps on the surface [69]. Every step can act as a diffuse scatterer so a maximum of steps corresponds to a minimum in specularly reflected signal and a minimum in steps to a maximum in specularly reflected signal. Using this model and the pulsed nature of PLD, the relaxation time $\tau$ for the deposited materials to diffuse, can be calculated with a relation of the form

$$I \propto I_0 (1 - e^{-\frac{t}{\tau}})$$  \hspace{1cm} (3.2)

This relaxation time depends on the laser fluence, substrate temperature and film/substrate combination and it can be used to determine an appropriate laser frequency and deposition rate, which facilitates sustainable layer-by-layer growth.

### 3.3 Substrates

Layer-by-layer growth requires lattice-matched substrates in order for the deposited material to grow epitaxial onto a substrate. To investigate the lattice match, typical single crystal substrates with lattice parameters similar to those of perovskite metal oxide ferroelectrics are summarized in figure 3.6. As a function of temperature, the lattice parameters of $PbTiO_3$ and several perovskite substrates like $SrTiO_3$, $DyScO_3$, $GdScO_3$, $KTaO_3$ [40], $SrRuO_3$ [70], $LaAlO_3$ [71], $NdGaO_3$ [72] and $MgO$ [73] are plotted. Chemical compatibility makes metal oxide substrates more suitable than, for example, metallic substrates like $Pt$ (cubic $a=3.9231$ Å at room temperature) which have a very good lattice fit to $PbTiO_3$. Only recently, scandate perovskite substrates have become commercially available with lattice parameters in the range below $2\%$ misfit strain with $PbTiO_3$ [72, 74].

An important prerequisite for epitaxial growth and to attain a sharp substrate-film interface on these metal oxide substrates, is a single terminated surface. Besides, the termination of perovskite substrates determines the electronic structure and chemical properties of the interface [75]. For the $ABO_3$ perovskite substrates in use, those with large differences in chemical prop-
3.3. Substrates

Figure 3.6: Lattice parameters as a function of temperature of PbTiO$_3$ (solid line; including the hypothetical cubic low temperature phase) and several perovskite substrates like LaAlO$_3$(001)$_c$ (dashed, plusses), NdGaO$_3$(110)$_o$ (dash-dotted, > triangles), SrTiO$_3$(001)$_c$ (dashed, crosses), SrRuO$_3$ (dashed, diamonds), DyScO$_3$(110)$_o$ (dash-dotted, circles), GdScO$_3$(110)$_o$ (dotted, squares), KTaO$_3$(001)$_c$ (dotted, asterisks) and MgO(001)$_c$ (dash-dotted, < triangles).

Properties of the AO and BO$_2$ layers, can be used to obtain nearly perfect single terminated surfaces. SrTiO$_3$(001)$_c$ is the ABO$_3$ perovskite with the best-established procedure to achieve single terminated surfaces. The procedure to obtain nearly perfect single terminated surfaces is thoroughly described elsewhere [59]. The chemistry involved is described by merely two chemical equations (TiO$_2$ is stable in water):

\[
\begin{align*}
SrO(s) + H_2O(l) & \rightarrow Sr(OH)_2(s) \\
Sr(OH)_2(s) + HF(l) & \rightarrow Sr-\text{complex (aq)}
\end{align*}
\]

This chemical procedure is followed by thermal annealing at 960$^\circ$C in a modified tube furnace. The modification consists of a replacement of the thermocouple which provides the feedback-loop signal. This thermocouple is placed inside the tube right next to the substrates, ensuring that the substrate temperature is controlled with the highest precision. During heating and cooling, a small flow of oxygen ($< 200 ml/min$) is applied to prevent the formation of oxygen vacancies within the substrate.
A similar procedure results in single terminated surfaces for $LaAlO_3$ and $NdGaO_3$ substrates [76], but the misfit with $PbTiO_3$ is quite large. Too large misfits (especially at the growth temperature) are detrimental for epitaxial growth, which also eliminates $MgO$. The thermal properties of $KTaO_3$ are problematic for high-temperature crystal growth: Potassium (K) is very volatile, which can easily lead to K-loss accompanied by $K_2Ta_4O_{11}$ formation [77].

We are, therefore, left with $SrTiO_3$, $SrRuO_3$, a typical electrode material,

*Figure 3.7: AFM images of as-received and treated substrates. a) As-received $SrTiO_3$ cleaned with acetone and ethanol in ultrasound (full z-scale $\Delta z=2$ nm). b) Cleaned and thermally treated $SrTiO_3$ ($\Delta z=1.5$ nm). c) Cleaned, chemically and thermally treated $SrTiO_3$ ($\Delta z=2.5$ nm). d) As-received $DyScO_3$, cleaned with acetone and ethanol in ultrasound ($\Delta z=2$ nm). e) Cleaned and thermally treated $DyScO_3$ ($\Delta z=2.5$ nm).*
and the scandate perovskites $GdScO_3$ and $DyScO_3$. Because of the small misfit with $PbTiO_3$, especially for $T > T_c^{PbTiO_3}$, $DyScO_3$ is an ideal substrate material. A proper treatment procedure is hard to obtain for this crystal, due to the similarities in chemical properties between the $DyO$ and $ScO_2$. Whereas the first metal oxide is soluble in acids, the second is soluble in hot acids [78]. Reactions with water lead to etch pits and, although etching with a $HNO_3$ solution in methanol has been reported [79], etching with $HNO_3$ in ethanol lead in our case to etch pits, most likely due to the residual water in this solution. Ultrasonic cleaning in acetone and ethanol, rubbing with acetone and optical tissue, no etching and a thermal treatment of 24 hours at $1020^\circ C$ gives unit-cell stepped terraces with reasonably straight steps, as depicted in figure 3.7e.

$SrTiO_3$ and $DyScO_3$ are selected based on lattice match and chemical compatibility, but the remaining materials aspects also need to be investigated. The electronic properties are the most important aspect, since they play a crucial role in thin film growth and domain formation in ferroelectric thin films. The conductivity and dielectric constant of the substrate, determine the domain formation, so knowledge on these properties is of vital importance. $SrTiO_3$ is a widely studied dielectric material. It is a wide-bandgap semiconductor with an indirect band gap of $3.16\,eV$ at $10K$ [80]. The structure is cubic above $T_c = 105K$ and tetragonal below. It is a so-called quantum paraelectric: the dielectric constant increases extraordinarily with lowering temperature and stabilizes at values over $10^4$ below $10K$ without showing a ferroelectric phase transition [81]. The dielectric constant is approximately 300 at room temperature [82] and $\sim 10^2$ at temperatures above $1000K$. The dielectric constant depends heavily on doping and $SrTiO_3$ can even be doped to become a conductor or pseudo-ferroelectric. The resistivity of pure $SrTiO_3$ single crystals is $\rho > 10^7\,\Omega m$ at room temperature and drops to $\rho < 1$ for temperatures above $1500K$ and below $100K$ [77].

Data on the electrical properties of $DyScO_3$ are not widely-spread in literature. The material is a wide band gap semiconductor as well, with a band gap around $5.7\,eV$ [83]. The dielectric constants at room temperature in the three different crystallographic directions of $DyScO_3$ are $\epsilon_{11} = 22.0$; $\epsilon_{22} = 18.8$ and $\epsilon_{33} = 35.5$ [84]. To our knowledge, no studies have been performed on the temperature-dependence of the dielectric constants of bulk $DyScO_3$. But probably the temperature dependence of the dielectric constant
has a relatively flat profile over the 300-1000\(K\) temperature range, as it has been reported for relatively thick \(DyScO_3\) thin films [85].

Last, but not least important, is the internal charge distribution in these crystal substrates possibly leading to polar surfaces. Whereas \(SrTiO_3(001)_c\) can be thought to be built up by alternating layers of \(SrO\) and \(TiO_2\) which are both charge neutral, \(DyScO_3(110)_o\) is built up of layers of \(DyO^+\) and \(ScO_2^-\) giving rise to a polar surface. Besides the usual atomic reconstruction at crystal surfaces, this polar surface can lead to electronic reconstruction, an interesting effect in itself [86], but that can cause a complex charge distribution at the interface complicating the description of the electrical boundary conditions of the ferroelectric.

### 3.4 Targets and stoichiometry

Besides a single commercial target (of \(SrTiO_3\))\(^3\), all targets have been prepared in-house by solid state reactions of metal oxide powders. The standard process consisted of powder weighing, ball milling with ethanol, drying, grinding, sieving, powder sintering, grinding, sieving, pellet pressing and finally pellet sintering. Sintering of the powders and pellets has been performed in a standard tube furnace in a closed crucible with some excess \(PbO\) powder at temperatures and times in the range of 700-850\(^\circ\)C and 1-4 hours.

The final target stoichiometry has been determined by powder X-ray diffraction. Due to the excess of lead (\(Pb\)), only \(PbTiO_3\)-like phases and \(PbO\) were allowed to ensure the proper stoichiometry. In Figure 3.8 the diffractograms of a \(PbTiO_3\) target and a \(PbTiO_3\) target with excess lead (in the form of \(PbO\)) are shown. We preferred to use the latter because of the volatility of lead at the growth temperatures we have employed.

Other techniques, like inductively coupled plasma-optical emission spectrometry (ICP-OES) and scanning electron microscopy/energy dispersive X-ray (SEM/EDX), have been employed to verify the stoichiometry, but could not give a reliable element composition: Because our target materials are not even soluble in aqua regia, ICP-OES analysis could not be performed. Oxygen is too light to be detected by EDX (detection range \(Na - U\)), so only the

\(^3\)Obtained from SCI Engineered Materials, 2839 Charter Street Columbus, OH 43228, USA (www.superconductivecomp.com).
metal ratios have been determined but the small electron penetration depth (typically $\sim 1\mu m$) and dependence on surface morphology of EDX measurements have led to inconsistent results from one measurement to the other.

The stoichiometry of thin films has been measured by Rutherford backscattering (RBS) and X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectroscopy (XPS) is present in our laboratory, while for RBS, facilities at Utrecht University have been used. Both techniques are non-destructive; the main disadvantage of XPS compared to RBS is the effective probe depth, which is only $\sim 15$ Å for XPS and $\sim 200$ Å for RBS. Another important advantage of RBS is that it does not require composition standards [6], while the main drawback is that light-element substrates have to be used (in our case, preferably MgO), which do not reproduce the strain conditions of the films on $SrTiO_3$ or $DyScO_3$. 

Figure 3.8: Powder X-ray diffractograms of a $PbTiO_3$ target (black) and a $PbTiO_3$ target with excess $PbO$ (gray). The black indexation and black circles are based on Glazer and Mabud [41] for $PbTiO_3$ at T=$25^\circ$C. The gray indexation and squares are based on Boher et al. [87] for $PbO$ at T=$27^\circ$C.
3.5 Structural and morphological characterization

Besides stoichiometry, the structure and the quality of the interfaces are two of the most important factors influencing the properties of thin films [6]. Therefore, several characterization techniques have been used in this work to determine the morphology and structure of thin films. The in-situ surface characterization technique used in this work, RHEED, has been introduced previously in this chapter. A graphical overview of RHEED and the ex-situ techniques based on the probe area and probe depth, is given in Figure 3.9. A short description of the different techniques can be found in this paragraph, while more extensive descriptions are available in literature and textbooks [88, 89].

![Figure 3.9](image-url) Graphical representation of the utilized characterization techniques, based on the probe area and probe depth. All abbreviations and techniques are described shortly in this section. Note that the probe depth of X-TEM is not very well defined since samples are cut, what we mean here is the probe depth of the electrons, while for cut samples as used in X-TEM the whole film is probed along the original film normal.
3.5.1 Structural characterization

X-Ray Diffraction (XRD)

Routine X-ray diffraction experiments have been performed on a Panalytical X’Pert four axes diffractometer with Anton Paar heating stage. This setup is equipped with a Cu X-ray generator tube, supplying X-rays with a wavelength of 1.540598 Å (Cu Kα). In parallel beam configuration, both X-ray reflectivity and out-of-plane diffraction measurements at temperatures up to 900°C can be performed, providing information on film thicknesses and lattice parameters (see Figure 3.10a for the general setup). The (in)coherency of the thin films and domain formation has been studied by recording reciprocal space maps (RSMs), mainly in the [H0L]-plane.

For high-resolution X-ray diffraction and grazing incidence diffraction (GID), beamline W1 at HASYlab, DESY (Hamburg, Germany) has been used. The 6+2 circle diffractometer at this beamline can be used both for high-resolution routine-like measurements as for grazing incidence diffraction (see Figure 3.10b). The intense X-ray beam is obtained via a wiggler and the photon energy can be tuned between 6 and 11 keV. In GID, the X-ray beam comes in at a grazing angle below the critical angle for total reflection, giving rise to an evanescent wave, propagating along the surface. Bragg diffraction of this wave provides information on the in-plane structure of the surface of the thin film. This enables the recording of RSMs in the [HK0]-plane.

Although excellent overviews and reviews of X-ray diffraction tech-

![Figure 3.10: Schematic representation of the typical setup used in (a) normal diffraction experiments and (b) grazing incidence diffraction (GID). In both cases, the length of the incoming and outgoing k-vectors is defined by the diffraction angles ω and θ. In normal diffraction, the orientation of the k-vector is determined by offsets in ω and θ and possible rotation of sample and detector around the z-axis. In the case of GID, the orientation of the k-vectors can only be in-plane, since the grazing angles αi,f determine the probe depth of the X-rays.](image)
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Techniques are widely available [90, 91], some background and detailed information on the measurements performed will be treated here. We will focus especially on RSMs and the possibilities to simulate diffraction patterns. The recording of RSMs has proven its value in structural analysis of epitaxial systems with anisotropic and inhomogeneous strain relaxation and layer tilting [92]. The amount, presence or absence of epitaxial strain can easily be monitored non-invasively. Over time, RSMs have shown not to be useful solely for this purpose, but also to obtain information on the polarization state [93] and the domain structure [1, 94] of e.g. ferroic thin films. The length scale at which polarization and periodic strain relaxation occurs and its ordered nature, allows for X-ray diffraction to monitor these as a function of temperature, electrical boundary conditions, etc. Due to the relatively complex nature of these polarization and strain relaxation profiles and their dependence on boundary conditions, RSMs are a key method to monitor these.

The recording of RSMs is based on scanning two angles independently in your diffractometer. We will treat the most simple and common case of RSMs recorded in the [H0L]-plane, but the general idea can be applied to any diffraction plane. Recording $2\theta - \omega$ scans ($2\theta$ being the detector angle and $\omega$ the angle between the incident beam and the sample surface) for a range of different $\omega$ values, allows to convert these scans to a reciprocal space map. The scan in angle space over $2\theta - \omega$ changes the length but not the direction of the scattering vector $\Delta K$ in reciprocal space. While scanning $\omega$ in angle space is equivalent to changing the direction of the scattering vector $\Delta K$ in reciprocal space, but not its length. The combination of the $2\theta - \omega$ and $\omega$ angles produces a two-dimensional reciprocal space map with information on the length and direction of the scattering vector. In this reciprocal $k$-space, distances are measured in units of Ewald’s sphere diameter ($\frac{4\pi}{\lambda}$). This enables comparison between measurements taken with different wavelengths. In order to compare measurements on different substrates, these units can be made dimensionless by normalizing with respect to the substrate lattice parameter $a_0$ (axes in reciprocal space units, r.l.u.). When $k$-space is normalized in this way, $q$-space plots are obtained. In formulae, the transformation from angle space to reciprocal $q$-space, is given by

$$q_\perp = \frac{2a_0}{\lambda} \sin(\theta) \cdot \cos(\omega - \theta)$$

(3.3)
\[ q_{\parallel} = \frac{2a_0}{\lambda} \sin(\theta) \cdot \sin(\omega - \theta) \] (3.4)

Where the last term determines the direction of the scattering vector and the other terms determine the length of the scattering vector in \( q \)-space.

**Reciprocal space maps: coherency, superstructures and domains**

First of all, the use of RSMs enables to determine the coherency between a substrate and a thin film. But RSMs can also be used to observe and study superstructures (e.g. periodic domains), which appear in a RSM as a superimposed periodicity. Tilted layer growth or twinning within a thin film, is observed as a lattice which is tilted by its (small) tilt angle with respect to the reference lattice. And finally, finite size effects are reflected in peak size broadening in the transverse directions. This allows us to extract information on domain sizes, orientations and periodicity from the RSMs.

As an example, the interpretation of RSMs will be treated here in somewhat more detail. Figure 3.11 shows a comparison of RSMs around the (103) Bragg reflection of 30 nm \( \text{PbTiO}_3 \) on a \( \text{SrTiO}_3 \) substrate and of 30 nm \( \text{PbTiO}_3 \) on 10 nm \( \text{SrRuO}_3 \) grown on three different substrates: \( \text{SrTiO}_3 \), \( \text{KTaO}_3 \) and \( \text{LaAlO}_3 \). In general, the substrate peaks are more intense and sharper than the film peaks, due to effects of finite size and diffuse scattering from the film. The observed lattice parameters are indicated and, while the layers are coherently grown both on bare and on \( \text{SrRuO}_3 \) electroded \( \text{SrTiO}_3 \) (substrate and film are on the same vertical, meaning they share the same in-plane component of the scattering vector), this is not very clear on \( \text{SrRuO}_3/\text{KTaO}_3 \) and it is surely not the case on \( \text{SrRuO}_3/\text{LaAlO}_3 \). On \( \text{KTaO}_3 \), the \( \text{PbTiO}_3 \) film peak is rather weak, probably caused by the \( K \)-volatility at the employed growth temperature (570\(^\circ\)C). In combination with the well-established substrate treatment procedure \[59\], this makes \( \text{SrTiO}_3 \) the substrate of choice of these three substrates to grow \( \text{PbTiO}_3 \) onto, as explained in section 3.3. Besides, it shows that the presence of a \( \text{SrRuO}_3 \) buffer (electrode) layer does not influence the epitaxial relations visibly.

Superstructures and domains require a more detailed analysis of RSMs. For ferroelectrics, in which the up and down polarized states are associated with oppositely displaced atoms, the structure factor of these two states is

\(^4\)These thin films have been obtained from Arjen Janssens at the University of Twente.
Figure 3.11: RSMs around the (103) Bragg reflections of (a) 30 nm PbTiO$_3$ on SrTiO$_3$ and (b) of 30 nm PbTiO$_3$ on 10 nm SrRuO$_3$ on SrTiO$_3$; (c) KTaO$_3$ and (d) LaAlO$_3$. Axes are in reciprocal lattice units (1 r.l.u. = $\frac{2\pi}{b}$); i.e. normalized to the substrate lattice which have lattice constants 3.905 Å for SrTiO$_3$; 3.988 Å for KTaO$_3$ and 3.793 Å for LaAlO$_3$. The vertical lines act as a guide to the eye.

different. Using the general formula for the structure factor of the unit cell:

$$ F(\mathbf{q}) = \sum_{j=1}^{N_a} f_i(\mathbf{q}) e^{i\mathbf{q} \cdot \mathbf{r}_j} d^3 \mathbf{r} $$

(3.5)
with \( N \) the number of atoms in the unit cell located at \((a_1, a_2, a_3)\) and all with their own atomic scattering factor \( f_i(\mathbf{q}) \). This can be applied to a ferroelectric perovskite with general formula \( ABO_3 \) with \( A \) cations (in our case \( Pb \)) at \((0, 0, 0)\), \( B \) cations \((Ti)\) at \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2} \pm \delta)\) and oxygens at \((0, \frac{1}{2}, \frac{1}{2}), (\frac{1}{2}, 0, \frac{1}{2})\) and \((\frac{1}{2}, \frac{1}{2}, 0)\). With \( A \) being the displaced atom, and reducing the problem to two dimensions since the two in-plane directions are equivalent, this gives rise to an “up” polarized unit cell structure factor (“up” being associated with a polarization pointing upward thus an upward ion displacement, see Figure 3.12):

\[
F_u(\mathbf{q}) = f_A \cdot e^{2\pi i(qx(n)+qz(m))} + f_B \cdot e^{2\pi i(qx(n+\frac{1}{2})+qz(m+\frac{1}{2})+\delta)} + f_O \cdot \left[ e^{2\pi i(qx(n+\frac{1}{2})+qz(m))} + e^{2\pi i(qx(n+\frac{1}{2})+qz(m+\frac{1}{2}))} \right]
\]  

(3.6)

and a “down” polarized unit cell structure factor:

\[
F_d(\mathbf{q}) = f_A \cdot e^{2\pi i(qx(n)+qz(m))} + f_B \cdot e^{2\pi i(qx(n+\frac{1}{2})+qz(m+\frac{1}{2})-\delta)} + f_O \cdot \left[ e^{2\pi i(qx(n+\frac{1}{2})+qz(m))} + e^{2\pi i(qx(n+\frac{1}{2})+qz(m+\frac{1}{2}))} \right]
\]

Where \( qx(n) \) and \( qz(m) \) indicate the in-plane and the out-of-plane directions, respectively, and are functions of \( n \) and \( m \), which are the unit cell indices over which we will sum to “construct” an entire crystal. Since \( Pb \) and \( Ti \) are the main scatterers, it is a good approximation to omit the \( O \)-terms. With these simplified structure factors of up and down polarized unit cells, the intensity of the diffraction pattern of a periodic up/down polarized crystal can be calculated. Before we construct the whole crystal, one more step is required: we construct a unit of \( M \) unit cells high, consisting of “up” polarized unit cells from the 1st to the \( N \)th unit cell and “down” from the \( N + 1 \)th
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Figure 3.12: Graphical representation of a periodic 180° domain pattern and a highlight of a “down” (left) and an “up” (right) polarized unit cell and their associated atomic coordinates (the displacements are not to scale).

\[
F_{u-d}(qx, qz) = \sum_{m=1}^{M} \sum_{n=1}^{N} F_d(qx(n), qz(m)) + \sum_{n=N+1}^{2N} F_u(qx(n), qz(m))
\]  
(3.7)

Which has a 180° domain periodicity of 2N unit cells. Subsequently, an entire crystal of 2NXe by MYe is “constructed” by summation over these “up/down” units:

\[
F_{tot}(qx, qz) = F_{u-d}(qx(n), qz(m)) \sum_{X=1}^{Xe} e^{2\pi i(2NX-qx)} \sum_{Y=1}^{Ye} e^{2\pi i(MY-qz)}
\]  
(3.9)

And the intensity measured by XRD is proportional to the square of the structure factor, thus:

\[
I_{total} = |F_{tot}(qx, qz)|^2
\]  
(3.10)

This leads to the conclusion that due to the difference in structure factor of “up” and “down” polarized ferroelectric domains, periodic 180° domains in
thin films give rise to the observation of an in-plane superlattice. There is one exception to this rule: This superlattice can only be observed around Bragg peaks with non-zero $L$. When $L = 0$, it can easily be seen from equation 3.5 that the $\mathbf{q} \cdot \mathbf{r}_j$ term equals zero, no matter what vertical displacement. The presence of superlattice peaks around [00L]-reflections and their absence around [H00]-reflections is shown in Figure 3.13.

For $90^\circ$ domains, a similar analysis is somewhat more laborious and would involve twinning angles. A phenomenological analysis is therefore more useful. Twinning of tetragonal $a$- and $c$-domains occurs by sharing the

\[ \text{Figure 3.13: Simulation of diffraction patterns in the [H0L]-plane of a Pb-Ti lattice with a typical displacement of 0.05 unit cell (0.2 Å) in the z-direction. Along the horizontal axis is the variable in reciprocal space (varying over $\epsilon$), along the vertical axis the calculated intensity. a) } H = 1 \pm \epsilon, L = 0, \text{ the equivalent of a GID } 2\theta-\omega \text{ scan. b) } H = 1, L = \pm \epsilon, \text{ the equivalent of a GID } \omega \text{ scan. c) } H = 0, L = 1 \pm \epsilon, \text{ the equivalent of a } 2\theta-\omega \text{ scan. d) } H = \pm \epsilon, L = 1, \text{ the equivalent of an } \omega \text{-scan. The observed smooth fringes are due to finite size effects. The superlattice peaks are clearly present for } H = 0 \text{ and } L = 1 (d) \text{ and absent for } H = 1 \text{ and } L = 0 (b).} \]
zero-strain (101)-plane. Therefore, the domains tilt with respect to each other and in the case of thin films, at least one domain tilts with respect to the substrate. In a RSM, this results in different sublattices tilted with respect to one another. When this occurs periodically, superlattice peaks are present in the RSM, superimposed to this tilting.

**Double diffraction**

A phenomenon not very commonly observed and, therefore, not very well-known in X-ray diffraction of thin films, is "double diffraction" or "Umwegganregung". Whereas double diffraction in optics, electron diffraction and single crystal X-ray diffraction is observed regularly, it is a rare phenomenon in X-ray diffraction of thin films. Several reports on double X-ray diffraction on single crystals exist [95], but only few on thin films on substrates [96]. The concept is most easily explained by the "Huygens’ principle", which in essence means that every point on a given wavefront acts as a new source of wavelets that travel in all directions. For XRD on single crystals this means that two (or more) lattice points lie on the Ewald’s sphere at the same time. Although simultaneous diffraction can change the strength of a Bragg peak and can help solving the phase problem for bulk crystals, the peaks are always found at reciprocal lattice points of the crystal. For a hybrid system like a heteroepitaxial thin film on a substrate, a modified analysis is needed and can be found in recent literature [96]. The main difference with simultaneous diffraction from single crystals, is the fact that two distinct reciprocal lattices are superposed. This can lead to sums of diffraction vectors which end up at positions that belong to neither of the two primary lattices. Understanding of double diffraction peaks is not straightforward but can lead to three-dimensional information of the layer structure without having to measure in asymmetrical diffraction geometries. In other words: Reciprocal space maps of single symmetric reflections can already allow for determination of parallel and perpendicular lattice mismatches and relative lattice spacings [96].

### 3.5.2 Morphological characterization

Scanning probe microscopy provides information on the surface morphology of substrates and thin films. This technique comes in many kinds and flavors; only atomic force microscopy (AFM) and the more advanced technique
of piezoresponse atomic force microscopy (p-AFM), will be treated here. The
details on the (spectroscopic) electrical characterization via p-AFM, will be
treated in the next section on electrical characterization. In an atomic force
microscope, a -not necessarily conducting- tip is brought to the proximity of
a surface and the bending of the cantilever to which the tip is mounted, is
monitored. In this manner, a landscape based on the atomic forces between
the tip and the surface, like Van der Waals, capillary and mechanical contact
forces is measured. We have mainly used tapping mode AFM which also
allows to monitor the phase lag between applied and measured tapping fre-
quency. Although we do not present these data, we have also used this to
verify the homogeneity of surface terminations.

Piezoresponse atomic force microscopy is based on AFM. Normal AFM is
extended with a conducting tip and an electrical contact from tip via an elec-
trical circuit to the sample. By applying proper voltages, local piezoelectric
measurements can be performed. In this way the piezoelectric state of the
sample can be monitored (reading) and manipulated (writing). The tips used
for p-AFM are usually coated with a conductive coating, increasing their tip
size from a typical 10 nm tip radius for normal AFM tips to 20 nm. Still,
the configuration does not ensure homogeneous electric fields like in a flat
plate capacitor where the lateral dimensions are much larger than the longi-
tudinal dimensions. Combined with the fact that although p-AFM operates
in contact-mode, some voltage drop across the interfaces is inevitable, which
complicates proper estimations of the electric field. Therefore, the electric
fields calculated from the voltages applied and the film thicknesses is enor-
mous compared to those in macroscopic measurements (next section).

Still, contrast in piezoresponse (PR) phase and amplitude while scanning
the surface provides qualitative information on the domain structure of the
ferroelectric. The existing polarization state can be determined by scanning
with a sufficiently small AC-voltage. The coercive field can be determined
by applying a small AC-voltage while re-scanning an area which has been
scanned while applying a large DC-voltage.

3.6 Electrical characterization

Perovskite metal-oxides show a wide variety of electrical properties: from in-
sulators, via (wide-bandgap) semiconductors, magnetoelectrics, ferroelectrics
and conductors to superconductors. While this variety of properties pinpoints the potential of this material class to be incorporated in electronic devices, it shows at the same time one of the problems in the characterization of PbTiO$_3$-based ferroelectric thin films. As mentioned in chapter 1, PbTiO$_3$ is, besides a good ferroelectric, also a semiconductor [9, 97]. At room temperature, PZT single crystals have an estimated free carrier concentration of $3 \cdot 10^{18} \text{cm}^{-3}$, which means that it has considerably more free charge carriers than the standard semiconductor silicon Si ($1.1 \cdot 10^{10} \text{cm}^{-3}$). The bandgap of PbTiO$_3$ of 3.4eV [98] is significantly larger than that of silicon (1.12eV) though, while the electron mobility in PbTiO$_3$ remains unreported. This semiconducting character hinders macroscopic ferroelectric measurements on pure PbTiO$_3$.

Therefore, on pure PbTiO$_3$ only ferroelectric measurements on our thin films have been performed by p-AFM. Still, the ferroelectric response of thin films of solid solutions can be measured macroscopically. The ferroelectric hysteresis loop (and thus the coercive field $E_c$ and remanent polarization $P_r$) as shown in chapter 1 has been measured using a Radiant Technologies Precision Materials Analyzer. All other ferroelectric hysteresis loops have been measured with p-AFM by Alessio Morelli [99]. The capacitance, $C$, and losses, $\tan\delta$, of superlattices have been measured with an Agilent 4284A Precision LCR Meter. The operating principle of the Radiant apparatus is the Sawyer-Tower circuit [100]. This circuit allows to measure the hysteresis loop of a ferroelectric, while the influence of the measurement circuit is eliminated. Of the different techniques available for electrical characterization [29], we will only treat impedance spectroscopy and CV-measurements via p-AFM. Impedance spectroscopy boils down to frequency-dependent measurements of the capacitance and loss. The CV-measurements are carried out via p-AFM by a PUND-like method to measure hysteresis of the remanent polarization and the piezoelectric coefficient $d_{33}$ [99]. In this way, the intrinsic dielectric constant, piezoelectric coefficient $d_{33}$, coercive field $E_c$ and remanent polarization $P_r$ have been determined.

### 3.6.1 Impedance spectroscopy

Impedance measurements of materials that can be modelled by capacitive and resistive components and follow Debye-like relaxations, form one semicircles per relaxation process, when plotted in a Nyquist diagram (real part
3.6. Electrical characterization

along the x-axis and imaginary along the y-axis; each point corresponding to a different frequency). An equivalent circuit can be built in which conduction mechanisms are represented by resistors, $R$, and polarizabilities of the material by capacities, $C$. Every $RC$-circuit has a certain time constant which defines the frequency of the maximum loss. In a material with grain boundaries and a contact interface for example, this enables one to distinguish between intrinsic, grain-boundary and contact $RC$-characteristics (impedance and polarizability), which give three separate semicircles.

Because the dielectric constant consists of a real part $\epsilon'$ and an imaginary part $\epsilon''$, it can be written as $\epsilon \equiv \epsilon' - i\epsilon''$. Since impedance, $Z$, and dielectric constant, $\epsilon$, are related by $Z = 1/(i\omega C\epsilon)$, a Nyquist diagram of the real and imaginary part of the dielectric constant results in a similar plot, known as a Cole-Cole plot (Figure 3.14). The intrinsic materials properties are characterized by fast response, meaning that the first semicircle (closest to the origin, usually related to the high-frequency response), represents the intrinsic materials properties. The intercept of the first semicircle with the real axis is the bulk dielectric constant of the material. Real measurements will deviate from this ideal Debye theory behavior. The main deviation is the locus of the circular arc which can be off from the real axis. This deviation is described by $\alpha$, which indicates the angle between the real axis and the line between the origin and the locus of the arc [101] (see Figure 3.14). The measured capacitance and dielectric loss are converted to the real and imaginary part of the dielectric constant by

$$\epsilon' = \frac{CH}{\epsilon_0 A} \quad (3.11)$$

and

$$\epsilon'' = \epsilon'\tan(\delta) \quad (3.12)$$

in which $C$ is the capacitance, $H$ the film thickness, $A$ the effective capacitor area and $\tan(\delta)$ the dissipation factor or loss tangent.

3.6.2 CV-characteristics

A hysteresis loop of electric polarization versus electric field can be measured via CV-measurements. The CV-characteristics of a ferroelectric are determined by the coercive field $E_c$, the saturation polarization $P_{sat}$ and the remanent polarization $P_r$. Since polarization is nothing but charge separa-
tion, other mechanisms in which charge is being displaced, should be ruled out when measuring intrinsic polarization: one only wants to measure the remanent polarization, not the total switchable polarization. In practice, the response of many electronic components is easily mixed up with that of a ferroelectric, modifying the intrinsic measurement, or even worse, leading to the conclusion that a material is ferroelectric while it is not [102].

In this work, macroscopic CV-measurements have only been performed on solid solutions of $\text{PbTiO}_3$, while all measurements on thin films of $\text{PbTiO}_3$ have been performed by p-AFM by Alessio Morelli [99]. For both types of measurements, the first step in the process is to determine the electric field required to saturate the polarization. Once this is known, simple voltage sweeps while measuring the capacitance, result in CV-curves which -once integrated- give PE hysteresis loops characteristic for ferroelectrics. The electric field $E$ is the derivative of the voltage with respect to position and the polarization $P$ can be calculated using the expression for the dielectric constant (equation 3.11) combined with that for the polarization:

$$P = \epsilon_0 (\epsilon_r - 1) E$$  \hspace{1cm} (3.13)

CV-measurements by which the most reliable intrinsic properties of a ferroelectric can be measured, are performed by the so-called PUND-method. PUND stands for Plus-Up-Negative-Down, which describes the measurement pulses applied to the ferroelectric. Three parameters can be used to
perform a PUND measurement [103], which are related to the electric field 
\( V_{\text{max}} \) and the timing (pulse width and pulse delay). Similar care has been 
taken to measure intrinsic properties in the p-AFM measurements of the hys-
teresis loops of the remanent polarization. The voltage-circuitry as depicted 
in Figure 3.15 has been used. Both the \( d_{33} \) and the PR phase have been mea-
sured as a function of the applied DC voltage pulse. In this way, the intrinsic 
\( d_{33} \) is measured and besides, the coercive field \( E_c \) can be determined.

\textbf{Figure 3.15:} (a) Voltage-circuitry as used for the piezoresponse-AFM ferroelectric 
hysteresis loop measurements. (b) Piezoresponse AFM setup consisting of a normal 
AFM setup with a metallic tip and a feedback loop in parallel with an electrical cir-
cuit to apply the voltage pulses as depicted in (a) to the ferroelectric sample under 
investigation.