Novel phases in ferroelectric BaTiO3 thin films

Everhardt, Arnoud

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2017

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
Chapter 2: Experimental methods

Abstract

This chapter describes the main experimental techniques used in this thesis, the film growth by Pulsed Laser Deposition, structural X-ray diffraction characterization, Piezoelectric Force Microscopy imaging of the piezoelectricity at the nanoscale and macroscopic ferroelectric polarization switching and piezoelectric displacement measurements.
2.1 Pulsed Laser Deposition

2.1.1 Introduction

Pulsed Laser Deposition (PLD), sometimes also called Laser Ablation or Laser MBE, had its origin in 1965 and is a technique that uses strong laser pulses to physically ablate material from a target into a plasma, which then crystallizes on a (hot) substrate. The technique only became big when it was demonstrated it could be used to grow epitaxial high-temperature superconductors at Bell Labs in 1987. Since then, PLD has seen a tremendous growth in research applications as it is an easy method to grow epitaxial high-quality thin films with stoichiometric material transfer from the target to the final film.\[1\] While it is possible to grow any type of material, its true power lies in the growth of oxides. It is possible to use an oxygen environment during growth, which reduces the normally common oxygen vacancies in oxides. The main drawback of PLD is that it is only a small-scale and -size laboratory technique not friendly to mass production. Not surprisingly, after such a long time mass production is still in the early phases, so far only pursued by the company Solmates, based in Enschede, The Netherlands.

2.1.2 Growth parameters

The schematic setup of the PLD system used in this thesis is given in Figure 2.1. A pulsed excimer laser with its wavelength in the UV (248 nm) is fired and will naturally produce a large laser spot with dimensions of a few centimetres. One of the main control parameters in the PLD growth process is the laser fluence (energy per unit area) on the target. The laser beam goes through an aperture to cut out the middle, most homogeneous part of the laser spot, then goes through a lens, which focuses on target. This way a sharp image of the aperture is made so a well-known can be obtained. The path lengths that should be used are determined by the lens formula,

\[
\frac{1}{f} = \frac{1}{o} + \frac{1}{i} \tag{2.1}
\]

where \(f\) is the focal length of the lens, \(o\) the object distance (between the lens and the aperture) and \(i\) the image distance (between the lens and the target). In this system the image distance is about half a meter (fixed by the size of the PLD chamber) and with this specific lens the object distance is about three meter. So the required path length for PLD system is quite large, which is why mirrors are introduced in the optical path to fit the path length in the room. It is crucial to experimentally determine the exact focus point after making the first guess using the lens formula, by shooting the laser and adjusting the positions of the lens, aperture or target to achieve the best focus. After finding the focus it is, in principle, not needed to ever adjust those positions again, but in real setups there are often small changes in the setup over time. It is important to determine for each system which element is the most likely to change with time, and then to align that element before every run of depositions. In most systems, the laser path changes over time due to small changes in laser alignment, so then it is easiest to change the lens position. In old systems with the target holder on a long stick, the target holder will often bend and thus change its position, even if it is just a little. So in that case, the target holder position should be adjusted to achieve focus.

While PLD can operate without a lens system, the sample-to-sample reproducibility within one lab and between labs is far greater by using a well-defined fluence. Unfocussed and not-well focussed PLD systems will deliver a fluence gradient on the target, so it is no longer simple to describe the fluence by a single number. A quite good approximation with similar results for most depositions can be made nonetheless by using the average fluence. It is important to keep all mechanical parts at the exact positions because already for a millimetre change in the mechanical parts, the fluence can be 10% off.

In the PLD process, the laser hits a target, which is a ceramic material with the right composition, to ablate the material into a plasma of individual ions.\[2\] Loose powders or a low density of this
Experimental methods

ceramic material makes it too easy to ablate grains and particles into the plasma, which later will be deposited onto the substrate, so it is important to strive for the highest possible density. The maximum density is achieved in single crystals, so they are preferred, if available for the required material. The target is often scanned while the deposition is ongoing, so the laser spot hits the target at a larger area, to make an average of the local inhomogeneities on the target surface and to prevent burning deep holes on the target at such a single spot. The way the plasma travels towards the substrate (its energy, momentum and shape) depends on the gas environment, which is oxygen for oxide materials. The oxygen fulfills two functions: it provides extra oxygen to prevent oxygen loss from the oxide material and it reduces the kinetic energy of the plasma. Argon can also be used, which will then only reduce the kinetic energy but will not prevent oxygen loss. So argon can be used for the growth of non-oxide materials or when oxygen vacancies are desired in the final film. The distance between the target and the substrate and the pressure perform a similar role in the growth process. So for more stable operation, it is recommended to lock the target-substrate distance to get better mechanical stability in the system.

The plasma arrives with high energy on the substrate, enough to overcome nearly all thermodynamic barriers, which is why PLD is said to be kinetically controlled[3]. The substrate can be heated to high temperatures (~500-900 °C) to give better crystallization.

In the process of growing thin films of new materials, the film growth has to be optimized by changing some of the parameters to find the films with desired properties. This optimization process can take many iterations and is a complex interplay of all the interdependent, available parameters, which include the fluence, the spot size of the laser on the target, the laser pulse frequency, the target quality, the total pressure and the oxygen partial pressure in the chamber, the target-substrate distance, the substrate material and surface, and the substrate temperature. Generally flat, 2-dimensional films are desired, but sometimes lower structural quality is found to give rise to better physical properties such as low leakage or high magnetism.

2.1.3 RHEED

Reflection High-Energy Electron Diffraction (RHEED) is a tool commonly used in low-pressure surface science to study the surface morphology. Electrons, accelerated by a ~30 kV high voltage arrive at grazing incidence (< 1° incidence angle) onto the substrate. After interaction with the surface, they travel to a phosphorus screen which reveals the diffraction pattern, recorded by an optical camera. Strong interaction with the material, together with grazing incidence means the electrons cannot penetrate further than a few unit cells, so the technique is only sensitive to the surface.[3] The main uses for RHEED diffraction patterns are in determining the surface ordering (Figure 2.2) and the unit cell size (Figure 2.3) of the surface.
RHEED can be used during growth to monitor the growth mode. By following not the type of diffraction pattern, but the intensity of any of the diffraction spots, it is possible to understand which growth mode is taking place. Two common growth modes for flat, 2-dimensional structures, are layer-by-layer (Figure 2.4) and step-flow (Figure 2.5) mode. The growth of a thin film does not have to be exclusively one type or the other, for example the growth of SrRuO$_3$ on SrTiO$_3$ starts initially with a layer-by-layer growth and after two unit cells transforms into a step-flow-like growth mode because the diffusivity of the atoms on the already formed SrRuO$_3$ surface is increased.$^6$

### 2.2 X-Ray Diffraction

#### 2.2.1 Diffraction conditions

X-Ray Diffraction (XRD) is a common technique in research and routine analyses outside of research, extremely versatile in both the information it can provide and its exceptional accuracy. Applications are related to resolving structural parameters, which are positions of atoms and associated electron densities. Examples are the accurate measurement of bond lengths up to 0.0001 Å$^7$ and the full structural characterization of protein structures.

The easiest way to understand XRD is by using Bragg’s law,

$$n \lambda = 2 \ d \ \sin \theta$$

(2.2)

where $\lambda$ is the wavelength of the X-ray, $d$ the measured distance between two periodic planes, and $\theta$ the angle between the X-ray source and the detector. From this law it follows that X-rays in the order of a few Å are best to image lattice constants in materials. A good and full explanation of how XRD works is given in the book by J. Als-Nielsen and D. McMorrow in Ref.$^8$. 

Figure 2.2 Taken from Ref.$^4$ RHEED patterns from the cubic material SrTiO$_3$ with different surface morphologies, here discussing only the diffraction spots and not the Kikuchi lines. a) A perfectly smooth surface (usually of the substrate) gives strong diffraction spots. These spots will move under rotation of the substrate since the crystallographic axis along which diffraction occurs rotates as well. b) A smooth surface, with single unit cell terraces on top. The diffraction spots slightly smear out into lines and weak new diffraction spots can be seen. c) The surface gets more disordered, but a smooth two-dimensional surface is still within reach of the electrons with their penetration depth of a few unit cells. d) A true three-dimensional, polycrystalline surface creates patterns associated to transmission of the electrons through the islands. These spots will not move under rotation of the sample.

Figure 2.3 RHEED pattern of a cubic SrTiO$_3$ (a) and an orthorhombic NdScO$_3$ (b) substrate. Differences in the in-plane distance can be observed between the two structures, which are inversely proportional to the surface unit cell size. The pseudocubic lattice constants for both materials are about 4x4 Å, but the real orthorhombic crystal symmetry of the NdScO$_3$ enlarges the surface cell size to about 8x8 Å$^5$, which gives the observed halving of the distance between the diffraction peaks. Following the distance between the diffraction peaks during deposition reveals information about the crystal symmetry.
Bragg’s law works in real space, but to acquire more insight into XRD it is important to consider reciprocal space which is what is actually measured by XRD as drawn in Figure 2.6. The Laue condition to fulfill the XRD condition, equivalent to Bragg’s law, reads

\[ Q = K \] (2.3)

where \( K \) is the reciprocal lattice vector (or equivalently the Bragg peak) and \( Q = k_{in} - k_{out} \), and \( |k| = k_0 = \frac{2\pi}{\lambda} \). The reciprocal space for a cubic system is drawn in Figure 2.7a. It can be seen that it has Bragg peaks distributed evenly over the whole reciprocal lattice along the [h00] and [00l] directions of the reciprocal space. The [001] direction is the line where the condition

\[ \omega = \frac{1}{2} 2\theta - \delta \] (2.4)

is held with \( \delta = 0 \), also called specular reflection. This is when the source and detector are symmetric with respect to the sample, and only purely out-of-plane Bragg peaks can be found. It is called off-specular when \( \delta \neq 0 \) and both in-plane and out-of-plane components of the crystal are measured. The relationship between the measured \( \theta \) and \( \omega \) angles and the reciprocal lattice is described by the equations

\[ K_{per} = \Delta K \cos \delta, \] (2.5)

\[ K_{par} = \Delta K \sin \delta, \] (2.6)

Figure 2.4 Layer-by-layer growth. Initially there is a flat surface and the RHEED intensity of the direct reflection and the diffraction spots are maximum. Once atoms start arriving on the surface, destructive interference between the two layers takes place and the intensity starts to drop. The intensity is minimum for a coverage value of 0.5 and starts to increase again afterwards, when the layer starts to fill up. For a full layer, the intensity is fully recovered. This oscillation takes place for each layer grown, which makes it possible to count the amount of layers during thin film growth. In real thin film growth, the oscillations are usually damped because each successive layer adds a little more roughness.

Figure 2.5 Step-flow mode. A substrate is cut not perfectly along a high-symmetry axis, but under a small angle which introduces a terraced surface. The atoms arriving during step-flow growth are highly mobile and they diffuse over the surface until they find one of the step edges, and stick to that position. So the film essentially grows by moving the step edges constantly. RHEED oscillations are not observed in this mode, but rather a constant intensity as the roughness of the film does not change periodically during growth. Due to the nature of the step edge growth during this growth mode, the step edges tend to be more randomly distributed and have less resemblance to the original step edge shape; while the original step edge shape is largely conserved in layer-by-layer growth.
Chapter 2

\[ \Delta K = 2 \, k_0 \sin \theta \]  \hspace{1cm} (2.7)

which are used to convert between angular and reciprocal space.\(^5\)

It is possible to determine the crystal symmetry and all atomic positions when the full reciprocal space along h, k and l is known. Cuts along certain [h0l] or [0kl] planes are shown for several common crystal symmetries in Figure 2.7. Figure 2.7a shows the cubic case where the Bragg peaks are evenly distributed in the [h00] and [00l] directions. Once one removes the a = b constraint, Figure 2.7b is obtained where the Bragg peaks have different spacings along [h00] and [00l]. An orthorhombic unit cell would find that a ≠ b, so in the [0kl] cut yet another in-plane spacing is found, while those two reciprocal spaces would be equal in tetragonal systems.

A common symmetry found in perovskites are pseudocubic crystals, where the basic structure is cubic, but a small distortion lowers the symmetry. One of the pseudocubic distortions found in scandate substrates\(^10\) is in reality an orthorhombic symmetry, but it is described by a pseudocubic symmetry. Figure 2.7c shows that this pseudocubic orientation is like a normal orthorhombic crystal symmetry with a ≠ b in the [0kl] cut. But the [hol] cut in Figure 2.7d introduces the angle \(\beta \neq 90^\circ\), and then the Bragg peaks are no longer symmetric along the specular line. Rhombohedral, or rhombohedrally distorted pseudocubic crystals, in Figure 2.7d,e have equal angles and asymmetry around the specular line in both the [hol] and [0kl] cuts.

These reciprocal spaces can be used to determine the crystal symmetry of both the substrate and the film. Thin films have low diffracted intensity (since the volume is only small), so measuring the full reciprocal space takes too much time to obtain high-quality data. If the crystal shows domains, then it is possible to take a few small cuts from the reciprocal space, called Reciprocal Space Maps (RSM) and to deduce the crystal symmetry from there. The RSM around the (001), (002) and either the (103)’s or (204)’s is enough to obtain all the information needed about the crystal symmetry, as the other Bragg peaks follow similar symmetry. The (103) and (204) are usually the highest-intensity off-spectacular peaks for perovskites. Those off-spectacular RSMs should be taken for the (103) and (-103) (or (204)/(-204)) peaks, for both the [hol] and [0kl] cuts. The different cuts can be obtained by rotating the sample 90° around the [00l] axis (strictly only if in the system \(\gamma = 90^\circ\)). The (103) and (-103) can be obtained either by taking the negative value of \(\delta\), or by rotating the sample 180° along [00l].

Comparing the positions of those off-spectacular peaks and determining the lattice parameters and the angles along the different directions, one can find the crystal symmetry by comparing them to Figure 2.7. The symmetries given in Figure 2.7 are not exhaustive, for example monoclinic phases can also be found, which act as a bridge between two of the phases tetragonal, orthorhombic and rhombohedral. Structurally they should have features which are an intermediate between the two parent phases. Triclinic symmetry is found when a symmetry is found which obeys none of the symmetry elements lined out here.
Experimental methods
Next to the determination of crystal symmetries, the RSM can also be used to determine the strain state of the thin film, who are always close in reciprocal space as the lattice parameters of thin films cannot differ more than a few percent to get epitaxial growth. Figure 2.7f shows a substrate and thin film. The orientation is equal for both films, but the film is not fully strained because the in-plane lattice parameters are not equal. Figure 2.7g shows the same substrate and film, but now the film is fully strained to the in-plane lattice parameter of the substrate. Figure 2.7h shows a RSM of a material with two different orientations (twinning), with the [00l] axis not fully out-of-plane for one of the two materials. That means a tilt in the reciprocal space.

2.2.2 Measurement setup

The measurements in this thesis are performed on a lab PANalytical four axes X’Pert MRD Cradle with a Cu X-ray source with wavelength $\lambda = 1.540598$ Å (Figure 2.8a). The source gives X-ray radiation collimated into a line beam, which is very well defined in the $2\theta$ direction, but very broad in the perpendicular direction, which does not contain information in the $2\theta$-plane in the measurements. The detector is a PIXcel 3D detector, which can measure $255 \times 255$ individual pixels (width $2.5 \times 2.5$ °) in the $2\theta$ and its perpendicular direction. Since the beam is long along the perpendicular direction, those individual pixels are integrated into a single value and the detector is used to measure $255 \times 2\theta$ simultaneously, significantly speeding up certain measurements.

Next to this standard out-of-plane diffraction, it is also possible to use in-plane surface diffraction where the X-ray beam has incident rays nearly parallel to the surface and is diffracted in the [hko] plane. This requires a point source X-ray beam as a line focus perpendicular to the surface will have low intensity and a line focus parallel to the surface will have diffraction from multiple points in the sample, giving apparent different $2\theta$ values and thus poor $2\theta$ resolution. The lab X-ray optics are not able to both achieve high enough intensity with sufficient $2\theta$ resolution, so those measurements are performed in the PETRA III P08 beamline at DESY, Hamburg (Figure 2.8b) with a 9 keV acceleration voltage corresponding to a $\lambda = 1.37761$ Å. The beam is focused to 600x400 μm diameter in this setup.

The incident beam to the sample in the in-plane configuration is taken at grazing incidence. Since the refractive index for materials in the X-ray regime is slightly smaller than 1, X-rays will have total internal reflection when the angle is below the grazing incidence angle $2\theta_c$, which for perovskites is around 0.5 °. This physically means that an evanescent wave is formed in the surface, which travels within the surface until being diffracted. This means that the intensity of diffracted X-rays is greatly enhanced.11

2.2.3 Truncation rods

Focussing on pure out-of-plane XRD, the pattern for a thin film grown on a substrate typically looks like Figure 2.9, with a sharp Bragg peak for the substrate and a broad peak for the films, of which the maxima roughly correspond to the lattice parameters, through Bragg’s law. There are also thickness fringes from the film, which are a measure of the film thickness. Those two features of the film XRD are described by Crystal Truncation Rods: since the film is finite in size, it is called
Experimental methods

truncated and its reciprocal space is not infinitely sharp and rods, or fringes, are obtained.

It is possible to simulate the XRD patterns of such a thin film system by following the approach of Thompson et al.\[12\]. It starts with defining the X-ray scattering from the individual atoms, the atomic form factor $f$, in the material by

$$f = \sum_{j=1}^{5} \left( a_j \exp \left[ -b_j \left( \frac{q}{4\pi} \right)^2 \right] + f_1 + i f_2 \right) e^{-B \left( \frac{q}{4\pi} \right)^2}$$ \hspace{1cm} (2.8)

where $a_j$ and $b_j$ are the atomic form factor coefficients for each of the atoms (which can be found in ref.\[13\]), $q$ is the experimental wave vector (equal to $(4\pi \sin \theta) / \lambda$), $f_1$ and $f_2$ are wavevector independent dispersion corrections and $B$ is the Debye-Waller factor, which is a temperature-dependent intensity-correction factor\[14\]. The atoms are then arranged inside a unit cell, the structure factor $F$, by

$$F = \sum_{j=1}^{n} f_j e^{i q z_j}$$ \hspace{1cm} (2.9)

where $n$ is the amount of atoms inside the unit cell and $z_j$ is the position of the specific atom in the unit cell along the out-of-plane direction. The atoms not only diffract, but also absorb part of the X-rays and this absorption correction, $\varepsilon$, for the X-rays for each material is given by

$$\varepsilon = \frac{4\pi}{\lambda} \rho \sum_{j=1}^{n} \frac{m_n}{m_{\text{total}}} \mu_n$$ \hspace{1cm} (2.10)

where $n$ is again the amount of atoms in the unit cell, $\rho$ the density of the material, $m_n$ the mass of that atom, $m_{\text{total}}$ the combined mass of all the atoms inside the unit cell and $\mu_n$ the atomic scattering cross-sections, taken from ref.\[15\].

The structure factor $r_{\text{film}}$ for the film is calculated as

$$r_f = \frac{i 4 \pi R}{a_f^2 q} f_f \left( 1 - \exp[-c_f t_{f,n} (i q + \varepsilon_f)] \right) q e^{-\sigma_f \sigma (q-q_{001})^2}$$ \hspace{1cm} (2.11)

with $R$ the Thomson radius of an electron, $2.82 \cdot 10^{-5}$ Å, $a_f$ the film in-plane lattice parameter, $c_f$ the film out-of-plane lattice parameter, $t_{f,n}$ the thickness of the film (in amount of layers $n$), $\sigma_f$ a standard Gaussian film surface roughness with $q_{001}$ for a (001) Bragg peak equal to $(2\pi l) / c_f$. A similar structure factor $r_s$ can be calculated for the substrate, assuming an infinite thickness since $t_f \ll t_s$, by

$$r_s = \frac{i 4 \pi R}{a_s^2 q} f_s \left( 1 - \exp[-c_s (i q + \varepsilon_s)] \right)$$ \hspace{1cm} (2.12)
which now contains the substrate parameters instead of those of the film. This kinematic expression for the substrate can be corrected for extinction by using

\[ r_{s,\text{cor}} = \frac{2 r_s}{1 + (1 + (2 r_s)^2)^{1/2}} e^{-\frac{1}{2} a_2^2 (q - q_{00})^2} \]  

(2.13)

with the surface roughness correction applied only here. The film and substrate structure factors can be combined into \( r_{\text{total}} \), adding a phase shift and an absorption correction, by

\[ r_{\text{total}} = r_f + r_{s,\text{cor}} e^{-c_f (t f n + \delta) (i q^2)} \]  

(2.14)

where \( \delta \) is added to allow for a unit cell contraction or extension at the interface. The intensity for different \( q \) vectors can then be found by

\[ I = |r_{\text{total}}|^2 \]  

(2.15)

which was done in Figure 2.9, by fitting the film parameters to the measured experimental data.

**Figure 2.9** Measured (black dots) and simulated (blue line) XRD pattern along the specular direction around the (001) Bragg peaks for the substrate NdScO₃, with films SrRuO₃ and BaTiO₃ grown on top. The x-axis is given in units of 2θ, which is the typical measurement axis. \( c \) designates the out-of-plane lattice parameter for the materials and \( \ell \) the thickness of the thin films.

### 2.2.4 Diffuse scattering

X-rays can not only scatter from periodic arrays of atoms, but also from defects in the crystal, which is described by diffuse scattering. If the defects are distributed randomly over a crystal, it only adds to random background scattering. But if, on the other hand, the defects have a periodic arrangement, it can create a change in the structure factor and produce more localized spots in reciprocal space.[16]

A source of defects studied in this thesis are domain walls. Those can order periodically, which makes it possible to detect them as modulations in the diffuse scattering. Diffuse scattering is weak by itself[16], so they are detected only close to lattice Bragg peaks where their intensity is enhanced. The enhancement is only possible if the defects have some symmetry elements in common with the lattice Bragg peaks. Scattering from domain walls in a BaTiO₃ thin film with a domain wall inclination 45 ° to the substrate is given in Figure 2.10. Clear intensity peaks can be
Experimental methods

seen away from the specular direction, with indeed the same 45° orientation with respect to both in-plane and out-of-plane directions. The direct distance between the Bragg peak and the diffuse scattering peak equals the reciprocal distance between the parallel domain walls, while the pure in-plane distance between those two peaks equals the top-view, in-plane domain size.

The diffuse scattering is seen around both (001) and (002) Bragg peaks with the same reciprocal distance. This is in contrast to twinning as in Figure 2.7h, which is the coexistence of two or more crystal orientations. Twinning creates a tilt in the reciprocal space, which gives larger distances between peaks for higher order reflections. So if the origin of these intensity peaks had been twinning, then the distance between the peaks in reciprocal space would have been doubled for the (002) Bragg peak.

The BaTiO$_3$ film has a continuous strain gradient, from fully strained lattice parameters equal to the substrate, towards fully relaxed lattice parameters equal to the bulk BaTiO$_3$ material. Such a strain gradient will give weak scattering around the Bragg peak, but only up to the bulk lattice parameters (in reciprocal space). When both the strain gradient and the domain wall diffuse scattering are present, they enhance each other. The reciprocal space area with scattering from the strain gradient is larger around the (002) Bragg peak than around the (001) Bragg peak. This explains the additional intensity peak seen around the (002) Bragg peak: this higher-order diffuse scattering peak is still within the area of the strain gradient scattering, while around the (001) Bragg peak, this second-order peak lies outside of the strain gradient area. (Note that there is also space for higher-order diffuse scattering in the right lower corner for the (002) Bragg peak. It is probably too weak to be measured.)

2.3 Scanning Probe Microscopy

2.3.1 Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a technique developed in 1986\cite{17} to allow the imaging of any surface, whether it is conductive or insulating. AFM and the many derivations it has produced have grown to become the most important of the family of Scanning Probe Microscopy (SPM) techniques in the years after its discovery. It can not only probe topology, but also magnetic structures, piezoelectric response, force-distance curves, etc.\cite{18}

The standard setup of an AFM system contains a cantilever which is scanned over the surface of a sample, while a laser checks the height or the amount of bending of the cantilever by reflecting on a Photosensitive Detector (PSD)\cite{19}. In normal contact mode, the cantilever is pressed on the surface of the sample until it starts to bend. This bending causes an offset in the deflection measured on the PSD. One of the key settings in an AFM system is the amount of bending of the cantilever, which is governed by a constant offset in the deflection measured in the PSD, the deflection setpoint. The higher the deflection setpoint, the higher the bending and pressing on the sample. The feedback while scanning will try to keep the specified deflection setpoint constant. Sample height is the most obvious way in which the bending of the cantilever is changed and thus the measured deflection. The magnitude of the feedback signal sent back to the cantilever to recover the deflection setpoint is a measure of the sample height at each specific point on the sample.

The name Atomic Force Microscopy has the important word force in it, which means that not only height, but also for example friction, adhesion and electrostatic forces will influence the deflection while measuring. When measuring the height of the sample, it is better to reduce those other forces as much as possible to avoid difficult interpretation. One standard technique to achieve that goal is by using Tapping Mode AFM: the cantilever no longer continuously touches the sample, but has a constant oscillation above the sample, while lightly “tapping” the sample at each downward swing. This technique minimizes most of the unwanted atomic forces, such as adhesion and friction.
Chapter 2

in contact mode or electrostatic forces by oscillating the cantilever further above the sample.\[^{19}\]
The deflection in this mode is a measure for the oscillation amplitude, or more intuitively for how strong the cantilever taps on the sample. The feedback keeps this deflection constant, changing the cantilever-sample distance in order to keep the oscillation amplitude equal at each point. The oscillation amplitude is a parameter that is set by the driving voltage to the cantilever. On one hand small amplitudes are better for higher sensitivity since a small height change results in a relatively large oscillation amplitude change. On the other hand, too low amplitudes will run the risk of losing the sample surface as the amplitude is not large enough to ‘tap’ the surface anymore when the height is changed too much.

The phase lag of the oscillations is recorded simultaneously with the height and it is generally found to be dependent on properties such as adhesion and viscoelasticity.\[^{20}\] Different chemical surfaces will thus, even if the height is the same, generate a different phase due to different adhesion properties. Step edges will also give changes in the recorded phase. When you fall from a step edge (going from a larger height to a lower height), the contact between the tip and the sample is temporarily less strong and the adhesion will be lower. The reverse is found when climbing up a step edge and the adhesion will be increased. This feature can be used to distinguish phase lag due to chemical reasons or height changes: if the cantilever scans one line on the sample and its reverse track, and if the phase lag at a specific location is equal for both scans, it is chemical in nature; while it is due to a height difference if the phase lag is opposite for the two scans.

The type of cantilever used is important for the deflection setpoint that can be used. Cantilevers with large force constants will need to be pressed hard on the sample to create large enough bending to be able to measure changes (on which the AFM principle works). Cantilevers with low force constants do not have to be pressed hard to create bending. Cantilevers with large force constants have higher sensitivity, as they operate at higher frequencies which reduces typical low frequency noise. Hard samples will benefit from large force constants as they can survive the hard pressing of those cantilevers and benefit from a good contact between cantilever and sample. Soft samples as organics and biological materials will need a cantilever with a low force constant or the samples will be damaged. If a cantilever with large force constant is nonetheless used to get highest sensitivity (for any sample), it can help to reduce the deflection setpoint to a compromise that will not destroy the sample but that still enough bending is remaining to be able to operate the AFM. In this thesis, for Tapping Mode AFM a phosphorus doped (n) silicon cantilever with a small chromium coating is used with a force constant of 5 N/m and a resonance frequency of 150-189 kHz.

The feedback loop tries to keep the deflection setpoint constant, so it reacts to changes in deflection. The strength of this reaction is another important parameter in AFM studies. A widely-used PID controller is used for this, which uses a Proportional, Integral and Derivative feedback mode. All AFM systems use the Integral parameter, which gives a feedback signal based on the total difference in the whole scan between the measured and setpoint deflection. It is a slow, but reliable way to get to the setpoint. The higher the parameter of the integral value, the more aggressive it tries to minimize this difference in setpoints. A value too low will result in not fast enough changes to large height differences, a value too high will result in unstable oscillations which decreases sensitivity, so a smooth sample can use lower integral values. Some AFMs also use the Proportional value, which gives a feedback signal related to the current difference in deflection. In AFM this parameter has not shown to be very important and is usually set to 10% of the integral value. Most AFMs do not use the Derivative parameter, which is based on the rate of change between the deflections.

The piezo element which determines the distance between the sample and the cantilever is driven by a large voltage (400 V for the Veeco NanoScope V) which changes its length. When approaching the sample with the cantilever, it is usually fully extended and then a mechanical motor slowly lowers the cantilever. When the PSD measures that the cantilever reached the surface of the sample, the feedback will automatically contract the piezo element and the measurement can
Experimental methods

start. The 400 V on the piezo element is equal to a certain maximum length in the z-direction (called z-limit). Changes in the sample height that are larger than this maximum length cannot be measured, or, in the worst case, the tip or machine will break from mechanical crashing. When a relatively flat sample is used, a maximum voltage lower than 400 V can be applied, corresponding to a lower change in maximum length. Since the 400 V is obtained by an amplifier, a lower value voltage amplifier can be used and this will create a higher sensitivity for the piezo element.

An image made by AFM always consists of many linescans over the surface of the sample, which, when aligned, form an area image. Since the stability of an AFM is not perfect, the highest sensitivity is gained in the fast scanning direction of the AFM, while quite large errors can be obtained in the slow scanning direction where many lines are aligned together. The most common correction for this lower sensitivity, and for not-flat samples, is to use a form of levelling where the slopes of each individual line are taken and subtracted, to give a zero average slope. While this usually results in the best presentable images, it could create artifacts. When there are straight lines on a sample, the fast scanning direction should be perpendicular to those lines or the levelling will, in the most perfect measurement, remove all differences between those lines. Large particles will furthermore give a hugely different slope, and the area next to a large particle in the fast scanning direction will appear to have a very different slope than the surrounding area without such a particle. Raw data without levelling should always be saved to make sure that the correct post-processing for the images can be used without creating those kind of artifacts.

2.3.2 Piezoelectric Force Microscopy

Piezoelectric Force Microscopy (PFM) is a type of SPM which uses electromechanical contact between the tip and the sample to measure the material’s surface. Since it is an electromechanical technique, a voltage needs to be applied to the tip and thus a conductive cantilever must be used. This is done by using a thin metallic coating on a normal tip or by using doped diamond tips to prevent wearing of the coating. An AC voltage is applied to the cantilever and the sample will create a height difference related to that voltage, by

$$\Delta z = d_{33} V_{AC} + 2 \frac{Q_{333}}{t} V_{DC} V_{AC}$$  \(2.16\)

where $d_{33}$ is the piezoelectric coefficient, $Q_{333}$ the electrostrictive component of the material, $t$ the thickness and $V_{DC}$ the DC voltage applied to the material. The electrostrictive component is only weakly dependent on the material and is much smaller than the piezoelectric effect in ferroelectrics, so it will only create a constant offset. PFM can be used as a tool to distinguish different polarization directions in ferroelectrics (Figure 2.11). The signal picked up in the PSD is compared to the AC voltage input signal in a lock-in amplifier to obtain only the electromechanical signal. The amplitude and the phase of the signal are recorded which are related to the magnitude and the sign of the piezoelectric effect, respectively.

The easiest application of PFM is to record the amplitude and phase signals against a DC offset. The resulting images will look like a macroscopic piezoelectric butterfly loop and ferroelectric hysteresis loop for the amplitude and phase signals respectively (Figure 2.12). The standard method (off-field) to record these images is to first apply a DC offset, remove it and then measure the piezoelectric response by the AC voltage. This method will make the electrostrictive effect zero as no DC voltage is applied while measuring. The DC voltage will at a certain point be strong enough to induce remanent switching of the domains locally under the cantilever and switching can be observed.

Loops that look very much like these types of loops can also be found in non-ferroelectric materials, so such a loop alone does not prove ferroelectricity. One method to try to differentiate ferroelectric and non-ferroelectric materials is to look at the on-field curve, where the DC offset is still applied while measuring the AC voltage. Another method to estimate what the origin of the loop is, is to look at the shape of the piezoelectric loop. The decrease in amplitude near the
coercive field should be rather sharp as that is the small area where domains are changing, while far from the coercive field the amplitude must be constant as there are no further changes in the ferroelectric material. A rise of amplitude, especially if it is quadratic, far from the coercive field is a certain red flag that it is not ferroelectric in origin. It is probably induced by the electrostrictive effect ($\propto V^2$), a remainder from the DC voltage applied. Next to this, the phase image should have a sharp phase change at the coercive field, comparable in width to the width of the decrease in amplitude at that point.

A better understanding of the PFM measurement can be obtained by realizing that the amplitude and phase are not the parameters measured by the system. An oscillating vector is obtained, of which the sine and cosine are taken, which are called the quadrature and inphase signal. Only by mathematically combining those signals the amplitude and phase are obtained. It is possible to apply a phase offset to the driving AC voltage, called drive phase. Changing the drive phase will change the amount of signal to the inphase and quadrature due to the sinusoidal character. For the best signal in the Veeco NanoScope V, it is important to find the drive phase where the quadrature is maximum due to the lock-in specifications.\textsuperscript{[25]}

There are many important parameters in PFM which should be set correctly to get maximum signal and reduce artifacts. The first parameter is that there must be high contact quality between the tip and the sample. A smooth surface is required with good feedback parameters, or the tip will loose contact occasionally which in that case gives no piezoresponse. Pressing harder on the surface would help for not-smooth surfaces, even though the tip coating will wear faster. Next to that, the PFM will measure some sort of average polarization through the z-direction of the film and the signal will not be clean if there are several polarization components in this z-direction. If there are no different polarization directions at all within the sample, it is also hard to get information on the sample as only a constant signal is found. This is also the case for zero-coercive field materials, where the AC voltage could actually switch the material while measuring, making it hard to
distinguish differences.

PFM is generally not considered to be a quantitative technique\[^{26}\], because there are many factors which have an influence on the final signal, such as the contact quality, tip wearing, drift and inhomogeneous fields. So, comparing the amplitude of different signals can only give hints of the polarization (or more precisely, the piezoresponse) in the sample. Only special tricks in specific setups can make it close to quantitative.\[^{26}\]

The AC voltage applied during scanning plays an important role. Ideally, it is a small AC voltage (< 1 V) to probe only linear piezoelectric effects without for example domain switching or to prevent too much charging or leakage within the sample. High voltages can nevertheless give more signal, as the signal goes up when the AC voltage is increased to 3-5 V or even higher. So a balance between clean and large signals should be sought.

Crosstalk plays an important role in PFM. The topography can often be observed in pure PFM signals, which means a certain degree of coupling between the electrical response and the topography. Usually it helps to change the contact (trying to increase the contact quality) between the tip and sample, but sometimes it cannot be avoided at all and smoother samples must be used. Next to that, cross-talk from in-plane polarization can be seen in out-of-plane polarization maps. The piezoelectric component causes shear strain which will be picked up as an apparent height modulation due to the canting of the cantilever. Only in-plane polarization along the long axis of the cantilever will be picked up by the out-of-plane PFM mode. In-plane polarization perpendicular to the cantilever will be picked up as torsion of the cantilever, which is not recorded in the out-of-plane mode, but only in the in-plane mode itself. So in-plane polarization in the in-plane mode, and as crosstalk in the out-of-plane mode, will probe perpendicular directions.\[^{27}\]

### 2.3.3 DART

A special mode in which PFM can work is the resonance mode. Piezoelectric response is greatly enhanced when the whole system vibrates at the resonance frequency, which minimizes elastic damping and increases vibration amplitude. The large advantage of resonance is that it is possible to use AC voltages as low as 500 mV, which is still in the linear regime for the piezoresponse, and still get higher signal than non-resonance modes. The drawback is that quantitative comparisons of amplitude are certainly no longer possible as it depends strongly on the elastic components in the system and the exact resonance value. The resonance frequency in PFM is usually in the range of 300-1200 kHz, but the exact position depends on the full system of sample combined with the setup. So this resonance must be determined experimentally before every measurement. Resonance frequency changes from position to position on a sample due to differences in topography, chemical environment, domain states and wearing of the tip.

A method to use resonance while scanning over surface is to track the resonance frequency and keep the frequency fixed on the resonance by a feedback loop, called the Dual AC Resonance Tracking Piezo Force Microscopy (DART PFM) mode. The setup is sketched in Figure 2.13. The cantilever uses two frequencies, on both sides of the resonance peak, with a certain bandwidth.\[^{28}\] The amplitude and phase signals on both of those frequencies is recorded and the difference between them is minimized by the feedback loop. The DART mode technically does not record the resonance frequency itself, but it does record a piezoresponse enhanced by the tail of the resonance peak. The bandwidth is thus a very important parameter in DART mode, as a small bandwidth enhances the amplitude more, but a too small bandwidth has the risk of losing the resonance frequency if it moves too fast for feedback to keep it locked on the bandwidth area. The integral gain for the resonance feedback plays a similar role as for the topography concerning the tradeoff between sensitivity and keeping the feedback on the resonance.
2.4 Electromechanical properties

2.4.1 Ferroelectric hysteresis loops

The measurement of the ferroelectric hysteresis loop is an important characterization method for ferroelectric materials. The oldest measurement method available is the Sawyer-Tower circuit\textsuperscript{[29]}, where an input voltage is applied across the ferroelectric material, and it measures the capacitance of that material relative to a known capacitor. In the current day Sawyer-Tower circuits are hardly ever longer used because of a few reasons. One is that the parallel alignment of the capacitors produces parasitic cable capacitances and also charging and discharging of the voltage detector, which in extreme cases can lead to backswitching. This method also requires a constant cycling of the material, which can cause degradation and there is no adequate way to deal with dielectric losses in the measurements.\textsuperscript{[30]}

A modern ferroelectric measurement is a charge measurement. It measures the change of surface screening charges in an external circuit due to a change in polarization. The most common method nowadays is the Virtual Ground method. It uses a current to voltage converter to determine the current coming from the sample electrodes. That method uses a type of feedback loop to ensure that both sides of the current to voltage converter have the same potential, thereby eliminating parallel parasitic capacitances. This method also has no problems to register dielectric losses, so they can be interpreted more easily.\textsuperscript{[31]}

The measured current in a ferroelectric measurement is related to the ferroelectric polarization by

\[ Q = A P \tag{2.17} \]

where \( Q \) is the total charge in the measurement, \( A \) is the area of the capacitor structure on the ferroelectric material and \( P \) is the total polarization.\textsuperscript{[30]} To obtain the polarization from the current, one has to perform an integration with respect to time,

\[ P = \frac{1}{A} \int I \, dt \tag{2.18} \]

where \( I \) is the measured current. It is interesting to find out that the applied voltage does not enter the equation and is thus irrelevant for the measured current nor polarization in ideal measurements.

It is important to note that there can be many current sources in real measurements, and it is
of utmost importance to learn to distinguish these different sources and their behavior under different measurement conditions in order to separate the effects properly. Figure 2.14 shows the typical current and polarization loops for several types of sources.

**Figure 2.14** Typical current and polarization curves from different sources, modelled using a triangular waveform. 
(a) Pure ferroelectric hysteresis loop. (b) Pure dielectric charging. (c) Pure Ohmic resistance. (d) Pure exponential leakage. (e) Mixed ferroelectric and dielectric contributions. Note how in the polarization plot the coercive field has apparently decreased due to the dielectric contribution. (f) Mixed ferroelectric hysteresis and Ohmic leakage. Note how in the polarization plot the coercive field has apparently increased due to the leakage. (g) Mixed ferroelectric, dielectric and Ohmic leakage. (h) Mixed dielectric charging and Ohmic leakage. To the untrained eye it resembles ferroelectric hysteresis, but it is not the same. (i) Small ferroelectric polarization and dielectric contribution superimposed on large exponential leakage. Note how the switching can still be weakly observed in the polarization plot.

The different sources most commonly obtained in ferroelectric measurements are:

- Ferroelectric switching has a switching peak in the current measurement (typically a Lorentzian lineshape\[^{[33]}\]), the maximum of which is at the coercive field. This is also where the polarization loop goes through the zero value of polarization. It is furthermore common practice to center the polarization values around zero polarization, as the absolute value of polarization cannot be measured\[^{[34]}\] and the positive and negative polarization values are usually equal to each other.
- Every dielectric material will have dielectric current charging on the surface electrodes when an external electric field is applied. The strength of this charging is the capacitance of that capacitor structure. The current contribution due to dielectric charging is equal to \( C \frac{dV}{dt} \) with \( C \) the capacitance of the material.
- There can be leakage in many different forms, such as Ohmic conduction or semiconducting exponential conductivity. They are modelled here with simple linear or exponential charge conduction. Too high leakage prohibits the measurement of
ferroelectricity of many thin film materials. This is usually a film growth or synthesis problem and the film typically needs higher quality to reduce leakage. The other trick is to go for smaller electrode sizes (10 – 50 µm diameter) to reduce the inclusion of leakage hotspots. Furthermore it can help to grow thicker films to reduce hotspots leakage, or to go for in-plane interdigitated electrodes to increase the effective measurement thickness.

- Sudden electrical discharges are possible in these measurements. If the field is too high on a capacitor structure, it might have sudden dielectric breakdown and this will create a large current peak. This is usually caused by too low material density or too high voltages (> kV) which creates dielectric breakdown of air. Measurements with these types of breakdowns cannot be used for reliable information and the measurement setup should be improved to prevent discharges.

- There are many different possible sources of noise, some of which can look like ferroelectricity. The most common source is a 50 Hz noise from the electric power supply, which interferes with measurements with frequencies close to 50 Hz.

- It is important to have good electrical contact with the measurement setup through the probes to the electrodes on the sample. The shape of the current and polarization loop typically obtained when there is no contact can be found in the manual of one of the companies that make ferroelectric measurement systems, aixACCT in Ref.[31]. Next to that, the choice of the electrode material is very important in the measurements. In oxide materials, it is important to use at least one oxide electrode to aid switching.[35] The workfunction of the metal electrode determines many details about the contact of the metal with the ferroelectric. Some electrodes will be able to get good switching in the ferroelectric, while others will inhibit switching. Due to the difficulty and the very many parameters of modelling such an electrode/thin film system, it is faster and more reliable to try out a variety of metals with different workfunctions.[36] The standard electrodes that can be tried are Pt, Ti/Au or Cr/Ti (Ti and Cr have nearly equal workfunctions), Cu, Au, or the oxide electrodes SrRuO$_3$ and LaSr$_{1/3}$Mn$_{2/3}$O$_3$.

Metallic electrodes can also be used to reduce the leakage. A Schottky diode will be formed on the interface between the metal and the semiconducting ferroelectric, with a forward and inverse current direction. When two different Schottky diodes at both electrodes are used with a reverse current direction into the ferroelectric, the leakage current will be blocked and thus reduced.[36–38]

Quantitatively some of those different contributions can be fitted by using the adequate fitting functions, as for example been performed in Ref.[39]. This is however only possible if the correct peak shape for the ferroelectric switching peak can be found, and the leakage behaves according to a proper function. A powerful qualitative tool to distinguish between the different sources is by looking at the different responses for three experimental parameters:

- The first parameter is the measurement frequency, or alternatively said, the rate of the change of field/voltage per time unit. The total polarization and dielectric charging are independent of frequency. From Equation (2.17) it follows that since the time is smaller for higher frequency, the current must increase to keep the polarization constant. The same argument holds for the dielectric contribution. So, the current contributions for the polarization hysteresis and the dielectric charging scale with frequency. Contrary to those contributions, the leakage currents are independent of frequency. So the leakage current will give different apparent polarization contributions for different frequencies. This means that higher frequencies are better for ferroelectric measurements as they give a higher contribution of polarization relative to the leakage. A too high frequency however will give more noise because there is less measurement time available.

- It is important to change the field range in the measurement. Ferroelectric hysteresis will switch at the coercive field, and once the voltage is higher than the tail of the switching current, any additional voltage will not yield additional polarization or coercive field. So
if a measurement gives higher polarization or coercive field when the field is increased, then that is not intrinsic ferroelectric polarization. This is in contrast to dielectric charging, where any additional voltage will yield more apparent polarization. Leakage will also give more apparent polarization and coercive field. Leakage gets larger for higher fields and will very often be the main source of apparent polarization at too high fields. Other effects such as unsaturated amplifiers will also increase the polarization and coercive field for higher field ranges.

Note that a change in field range often means that the rate $dE/dt$ is changed, so even though the frequency itself was not adjusted, the effect is the same as if the frequency was changed.

The voltage can be applied during the measurement using different function shapes, of which the triangular and sine waves are most common and useful. The triangular waveform means that the rate $dE/dt$ is always constant and it only changes sign at the field maxima, while the sine waveform has a continuous change of $dE/dt$ and ‘spends more time’ at higher fields. The current is integrated over time to obtain the polarization, so for the sine waveform, far more leakage is taken into account than for the triangular waveform which gives a huge increase in apparent polarization. The polarization from the ferroelectric hysteresis and dielectric contribution is not changed for the different waveforms. The raw current response from ferroelectric switching is usually not changed much (as the switching usually takes place as the field range where the two waveforms are quite similar), while the dielectric charging current is hugely changed. It follows the same $dE/dt$ shape as used in the waveform, so for a triangular waveform it will give flat lines with positive and negative signs, while for the sine waveform it will be ‘egg-shaped’.

From these observations it seems to follow that the best ferroelectric measurements can be obtained by using a triangular waveform just above the coercive field with the highest frequency that does not give too noisy measurements. In reality that last statement is actually not fully true, as there is another factor that limits the use of a too high frequency. The series resistance ($R_s$) of the measurement circuit gives a delay in how fast dielectric charging $Q$ can take place, which is modelled by charging a simple capacitor

$$Q(t) = Q_f (1 - e^{-t/R_s C})$$

with a delay factor $R_s C$. In oxide thin films, this product is typically large as the capacitance is a high number (it scales with $1/$thickness), and the thin oxide bottom electrode is not a very good conductor. The system needs a few times the $R_s C$ time constant to respond to a change in field. When the changes in field are faster than that time constant, the dielectric charging deviates from this ideal capacitor behavior. It will no longer follow the $dE/dt$ rate of the field change, and it will result in non-abrupt changes in dielectric charging for abrupt field rate changes.

**Figure 2.15** Taken from Ref.[40] Modelling of polarization and current loops for an $a$-YMnO$_3$ thin film. a,b) Too low frequency: leakage dominates the signal. c,d) Good intermediate frequency gives proper dielectric and ferroelectric polarization responses. e,f) For too high frequency, the dielectric current cannot follow the field change fast enough. The final loop will appear to have higher coercive field.
Chapter 2

summarizes the too low, just right and too high frequency ranges.[40]

An excellent method to separate the ferroelectric polarization from other contributions is by using the Positive-Up Negative-Down (PUND) method[41]. This method makes use of remanent ferroelectric polarization, which is stable after removing the field used to switch it. All other effects will have the same response every time the voltage is applied. The pulses used in the PUND method are summarized in Figure 2.16a,b. Two positive field pulses are applied: the first pulse will have ferroelectric switching and will see all the other contributions, while the second pulse will not have the ferroelectric switching, but will see all the other contributions. By subtracting the second pulse from the first one, one can obtain a pure, clean ferroelectric hysteresis loop of the remanent polarization. This is also done for the negative direction to obtain the full loop in Figure 2.16c,d.

2.4.2 Piezoelectric hysteresis loops

Since all ferroelectrics are also piezoelectrics, it is possible to measure the displacement of the ferroelectric material while measuring the ferroelectric hysteresis loop. The displacement can in principle be obtained in PFM measurements, even though quantitative results are very challenging.[26] A better solution is to use laser reflections from a metallic electrode area. By measuring the change in height for this electrode pad, out-of-plane piezoelectric effects, $d_{33}$, can be measured while simultaneously, but independently, collecting the electric current to construct the ferroelectric loop.
For ceramic materials, one often uses a single laser beam and a Michelson interferometer to measure the difference in height when an electric field is applied. However, for thin films (and also for some ceramics this might play a role), substrate bending can give a huge influence (Figure 2.17). One way to filter out such substrate bending is by using a double-beam Mach–Zender interferometer which has a laser reflecting of the top surface, leading it back to the bottom surface and then interferes with a reference beam to obtain only the relative displacements in the out-of-plane direction. This has been commercialized in the aixACCT Dual-Beam Laser Interferometry (DBLI) measurement setup (Figure 2.18). A sample used in the DBLI setup must be reflective from the top and bottom surface. For thin films on a typical substrate, it means that the bottom of the substrate must be polished and coated with a reflective metal such as Pt, Au or Ag. The laser beam diameter is about 30 μm, constraining the minimum size of the electrode pad. The setup has high enough sensitivity to measure the piezoelectric coefficient of bulk quartz, which is only 2.3 pm/V. A one-hour measurement on thin film samples can reach sensitivities down to 2 pm.

In literature, typically two types of measurements are described: large-signal and small-signal measurements. This is analogous to large-signal and small-signal electrical measurements. Large-signal are the measurements which have been described in this chapter, sweeping the voltage from the maximum to the minimum field values and recording the current and displacement values at each of those fields. Small-signal measurements however, have a certain DC offset, and then impose a small AC voltage around that DC offset. For electrical measurements, that is equal to a standard-type capacitance measurement, while for the piezoelectric measurements the slope (dl/dV slope (dl the length change, dV the voltage change)) is taken. This measurement is repeated and the slopes obtained at each DC offset are taken as the piezoelectric coefficients at those DC offsets. The main difference between these two types is that the small-signal measurements only record small-field reversible processes, while large-signal measurements also record small-field non-reversible processes in the system.

Even though substrate bending is removed by using this measurement system, there are still other artifacts remaining that influence the measurement. For large electrode areas, the stress produced at the ferroelectric-substrate interface induces significant substrate bending, imposing in-plane stress on the substrate. This effectively enhances the measured deformation. For small electrode areas, the substrate bending is actually negligible and the out-of-plane piezoelectric stress from the film gives the opposite deformation in the substrate, thereby lowering the effective measured $d_{33}$. When the electrode area and the substrate thickness are equal, the two effects cancel out. Stiffer substrates makes both effects smaller.

High voltages are generally good for piezoelectric measurements as they will increase the actual deformation which is then easier to detect. Next to that, information on the deformation is interesting in all stages of the switching process in ferroelectrics, also above the coercive field. But the problem with thin films is that they are usually leaky and large leakage currents will give huge displacements by Joule heating. Even small leakage currents in the order of 100 μA in thin films are enough to give a 500 K instantaneous Joule heating during a measurement, which...
This effect is much stronger than the typical tens to hundreds of picometers for intrinsic piezoelectric effects. So the utmost care must be taken not to misinterpret large displacements in these measurements as intrinsic piezoelectric effects.

A good way to distinguish between Joule heating and piezoelectric effects is by using different waveforms: leakage is always higher at high voltages, so if more time of the measurement is spent at high voltages, it will have more time to heat up and to give larger displacements. So a sine wave will give much more displacement than a triangular wave for Joule heating, while the displacement for those two waveforms will be exactly equal for intrinsic piezoelectric effects. Another method is to use different frequencies: higher frequencies have less time for Joule heating, so they give lower displacements due to Joule heating. Joule heating is also associated with hysteresis as it takes a small, but finite amount of time to dissipate the heat since it is a thin film connected to a huge heat sink: the substrate.

Figure 2.18 Taken from Ref.[31] Laser path overview for the DBLI system. A laser beam enters the path and is separated into two beams with perpendicular polarizations by $\lambda/2$ plate P1. The polarized beam splitter PBS1 splits those two beams into a sample and reference beam. The sample beams goes onto the top surface of the sample (Wafer) comes back to PBS1, and is reflected by PBS2 towards the bottom surface of the sample. It then comes onto the beam splitter BS3. The reference beam from PBS1 is reflected from Piezo Mirror M7 and the mirrors M5 and M6 onto BS3. At BS3, both beams are merged, forming an interference pattern, and are being defocused by L3 onto the Photodetector to measure the interference pattern. The path length difference is electronically controlled by Piezo Mirror M7 to give a good interference pattern. The $\lambda/4$ plates are used to change the polarization of the beams to their perpendicular polarization orientations to ensure correct reflection from the polarized beam splitters.
2.5 Literature


AixACCT. “aixACCT User Manuals.” (2012)


L. Pintilie, I. Vrejoiu, D. Hesse and M. Alexe. “The influence of the top-contact metal on the ferroelectric properties of epitaxial ferroelectric Pb(\textsubscript{2}Zr\textsubscript{0.5}Ti\textsubscript{0.5})O\textsubscript{3} thin films.” Journal of Applied Physics 104, 114101 (2008)


G. Catalan, M. H. Corbett, R. M. Bowman and J. M. Gregg. “Influence of oxygen content on dielectric and electromechanical properties of Pb(Mg\textsubscript{0.3}Ti\textsubscript{0.7})O\textsubscript{3} thin films.” Applied Physics Letters 74, 3035 (1999)
