Multiferroic perovskites under epitaxial strain
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Chapter 2

Experimental techniques

2.1 Pulsed laser deposition

Pulsed laser deposition (PLD) is a thin film growth technique by which a high power pulsed laser beam with short duration pulses hits a target with a certain laser energy density. The target is located inside a high vacuum chamber (with background pressures of $10^{-7}$ to $10^{-8}$ mbar) and a lens is placed just outside one of the optical ports of the chamber, to focus the laser close to the target. If the laser energy density is large enough, the material can be dissociated from the surface of the target and ablated away, with the same stoichiometry as that of the target. This process is called laser ablation. Contrary to the simplicity of the set-up, the interaction between the laser and the target is very complex [87] and out of the scope of this thesis. It is, however, important to emphasize that the laser energy density at the target is a crucial parameter, both to ensure a homogeneous ablation of the different species in the target, avoiding preferential ablation (or so-called incongruent deposition/ablation) [88] and to determine the deposition rate, the energy of the species arriving at the substrate surface and, thus, the growth mode.

The species ablated away from the target expand into the surrounding gas in the form of a plasma. The plasma forms a highly directional cloud (forward peaking phenomenon [89]) in front of the target (so-called 'plasma plume' due to its shape). The plume brings the species from the target onto a, typically, hot substrate (usually a single crystal). This is performed with a background gas, such as oxygen in the case of
oxides growth, at pressures of $pO_2=0.01-1\text{mbar}$. In the case of non-volatile species, and when the energy threshold for ablation of all the target species is reached, there is a very good stoichiometric transfer from the target to the substrate. This is one of the main advantages of PLD with respect to other thin film deposition techniques, specially for the growth of complex materials. Moreover, because of the plasma phase involved in the process, having the proper stoichiometry and a proper homogeneity of the target is important, but there is no need for phase-pure targets or targets with the crystal structure intended for the film, which can be difficult or impossible to achieve by standard synthesis techniques.

The next process occurring during pulsed laser deposition is the transition from a plasma phase to a solid (crystalline) phase at the surface of the substrate. This process can be compared to the supersaturation that takes place between the vapour and the solid phase of a material during crystallization. In the case of pulsed laser deposition, growth takes place far from the dynamical equilibrium conditions and the difference in chemical potentials between the plasma and the solid phase is also the thermodynamic force to trigger crystallization [90]. Supersaturation is thus crucial for determining the type of growth [90]. The different types of growth will be described in the section 1.2.2.

Our PLD setup allows for scanning the target in the vertical and horizontal directions during deposition to improve the homogeneity of the ablated area. The growth of multilayers is also possible thanks to a multi-target holder, which can hold up to 5 different targets. In practice, many other intercorrelated parameters should be taken into account in the optimization of the growth: The temperature of the substrate, the background pressure and type of gas (pure gas or mix of gases), the frequency of the pulses, the distance from the surface of the target to the surface of the substrate and the spot size on the target (the area defined by the defocused laser spot, and whose shape and homogeneity is controlled by a mask). Figure 2.1 shows a sketch of the vacuum chamber used in this thesis. Apart from the standard elements described above, the PLD system used in this thesis includes a Reflective High Energy Electron Diffraction.
2.1. Pulsed laser deposition

Figure 2.1: Top view of the PLD deposition chamber set-up of the Zernike Institute for Advanced Materials, University of Groningen.

RHEED is, in principle, incompatible with PLD because of the high pressure needed during growth (up to 1 mbar), which gives rise to a large scattering of the electrons before they reach the phosphorescent screen and, thus, a too low intensity collected by the CCD camera (see figure 2.1). To avoid this problem, the group of Prof. Blank in Twente (The Netherlands) added an extension to a standard RHEED-gun, consisting of a tube that goes from the gun to the substrate [91]. The electron gun and the tube are then differentially pumped with respect to the main chamber, to minimize the scattering along the incident electron path and, at the same time, avoid the breaking of the filament of the gun due to the high pressures. Moreover, the chamber is designed to keep a minimum distance between the substrate and the screen [91]. Under these conditions, RHEED-assisted PLD is possible although the alignment is more difficult than that used in Molecular Beam Epitaxy set-ups, due to the small size of the hole at the end of the tube.
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Figure 2.2: Picture of the pulsed laser deposition system at the Zernike Institute for Advanced Materials, University of Groningen, used to in this thesis.

Figure 2.2 shows the PLD system at the Zernike Institute for Advanced Materials, University of Groningen, used to grow the samples discussed in this thesis. The small pump used for the differential pumping of the electron path can be seen on the picture hanging below the electron gun. The laser is a Lambda Physik COMPex Pro 205 KrF excimer laser ($\lambda=248$nm), providing pulses of about 25ns. The long optics path is designed to achieve the laser energy densities typically needed at the target position (1-5 J/cm$^2$), using a limited range of laser voltages (19kV-26kV). In this thesis, the changes in laser energy density are obtained by changing the voltage of the laser to keep a constant spot size at the target while a fixed mask is used to select the central, most homogeneous part of the laser beam. Finally, to ensure reproducibility, the laser was refilled with new gases when the voltage required for a chosen laser energy density was too high with respect to the above mentioned conditions.

Pulsed Laser Deposition has advantages with respect to other physical deposition techniques [92]. First, PLD is an experimentally simple deposition technique, attractive for fundamental research. Moreover, it is a versatile technique which allows the
deposition of many different types of materials in various gases and various pressures. This wide range of background gas parameters makes the PLD unique because it can be used to modify the growth mode, changing the kinetic energy of the ablated particles by interaction with the background gases [92]. It is a fast process that allows the growth of high quality samples in short deposition times. Moreover, because of the very short duration of a pulse, the deposition can be regarded as instantaneous with annealing between pulses, which is advantageous for the study of growth kinetics [92]. A laser can be used along with more than one UHV chamber, making the use of PLD cost-efficient. A major drawback of this deposition technique is the scalability. Indeed, the area deposited is small compared to many other deposition techniques, making PLD difficult for large scale purposes.

### 2.2 Reflective high energy electron diffraction (RHEED)

#### 2.2.1 RHEED set-up

In RHEED, an electron beam hits the surface of a crystalline sample at a grazing angle (typically below 3°). The grazing angle provides surface sensitivity and allows to use electron diffraction in-situ during growth, with minimum interference between the electron beam and the plume. Because of this, RHEED is a very common technique for monitoring the growth of thin films, in particular for those processes using low background pressures, such as Molecular Beam Epitaxy [93]. Although, as explained in the previous section, RHEED-assisted PLD is also becoming very popular.

A RHEED set-up requires two rotation circles in order to modify the sample azimuth and the incident angle (see figure 2.3(a)). Qualitative information of the RHEED patterns can be extracted from a simple kinematical diffraction model. Most of the incident electrons are elastically scattered by the atoms at the first few atomic planes below the surface of the sample and a diffraction pattern forms at the phosphorescent screen. Moreover, the electrons are also scattered multiple times. Therefore, contrary
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Figure 2.3: (a) Sketch of a RHEED set-up, where the azimuth ($\phi$) and tilt ($\omega$) angles are shown. (b) RHEED pattern showing Kikuchi lines. The picture was taken for an TiO$_2$-terminated (001)-oriented SrTiO$_3$ substrate with a miscut of $\approx 0.1^\circ$ under an acceleration voltage of 28kV in a vacuum of the order of $10^{-6}$ mbar and at room temperature.

To x-ray diffraction, the dynamical theory of electron diffraction must be used for a full interpretation of the patterns. The inelastically scattered electrons contribute to the diffuse background. This being enhanced with increasing partial oxygen pressure in the chamber. Moreover, the multiple inelastic scattering of electrons can give rise to cones of intensity that can, in turn, be diffracted by the sample and form the so-called Kikuchi lines [94]. Kikuchi lines are often found in RHEED patterns from surfaces of high quality (see figure 2.3 (b)).

The reciprocal space associated with the 2D lattice of a perfect crystal surface, consists of infinite rods perpendicular to the surface of the sample and passing through the 2D lattice points (also called crystal truncation rods or CTRs), due to the relaxation of the third Laue condition [95]. So a RHEED pattern will then be determined by the intersection of the rods with the Ewald’s sphere, whose radius is inversely proportional to the wavelength of the incoming electron beam [95]. If the surface is perfectly flat, the reciprocal rods have no width and this intersection gives rise to a pattern of spots aligned along semicircles (Laue circles), as schematically shown in figure 2.4 (a).
In a RHEED pattern during PLD, in practice, only the low order diffraction spots (so called '0th Laue circle') can be seen under proper conditions of tilt ($\omega$) and azimuth ($\phi$) ($\omega_1$ in figure 2.4 (a)). By changing the tilt angle of the sample, higher order diffraction spots can be accessed, as shown in figure 2.4 (a). Moreover, as shown schematically and illustrated by an example (TiO$_2$-terminated (001)-oriented SrTiO$_3$ single crystal) in figure 2.4 (b), rotating the sample around the azimuth allows access to different planes and gives extra information about the structure of the surface.

If the surface has a roughness of the order of one monolayer, the reciprocal rods are broaden and their intersection with the Ewald’s sphere gives rise to streaks (see figure 2.5 (a)). In practice, the observation of spots or streaks for an atomically flat surface also depends on the set-up (mainly, the wavelength of the electrons that determines the radius of the Ewald’s sphere). When using RHEED to monitor the growth, we call both these patterns '2D-patterns', because they reflect an atomically flat surface.

Moreover, the tilting of the CTRs can give information about the step-terraces structure of the surface of a substrate (the length of the terraces being determined by the miscut angle), and/or possible tilt distortion of the growing film with respect to the substrate, as shown in figure 2.5 (b) and illustrated for the case of a 10nm BiFeO$_3$ film grown on SrTiO$_3$. If the roughness of the surface is increased, such as during three-dimensional (island) growth, electron transmission across islands can take place and the RHEED pattern consists of a 3D net of spots, which are not arranged along a semi-circle, as in a standard diffraction pattern (see figure 2.5 (c)).

### 2.2.2 Growth monitoring

Since the intensities of the individual spots on the RHEED patterns change according to the surface coverage and roughness, we can use these changes to follow the thin film growth. Generally speaking, the relative values of the free energies of the surface of the substrate, the surface of the film and the interface between the substrate and the film, determine the nucleation of the arriving species and the wetting of the substrate by
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Figure 2.4: (a) Side view of a schematic representation of the intersection of the Ewald’s sphere with the reciprocal lattice rods in the case of an ideal surface (left panel). The drawing represents the RHEED pattern for the electron beam oriented along the [100] direction. The reciprocal lattice rods, perpendicular to the surface, are labelled by their respective Miller indexes (h,k). The view on the right panel is the projection on the phosphorescent screen. (b) The left panel shows a schematic top view of (a), along with an illustration of a TiO$_2$-terminated (001)-oriented SrTiO$_3$ substrate with a miscut of $\approx 0.08^\circ$ under an acceleration voltage of 28kV in a vacuum of the order of $10^{-6}$mbar and at room temperature. The right panel shows the effect of rotating the substrate by $\phi=45^\circ$ (see $\phi$ angle in figure 2.3) of the same sample as shown on the left panel, highlighting the (110) planes.

the film [87]. For low supersaturation (not too far from thermodynamic equilibrium), three different growth modes have been defined: If the total free energy of the film plus the interface is larger than the free energy of the substrate surface, the arriving species will tend to form islands on the substrate (figure 2.6(a)-(b)-(c)). This type of growth
2.2. Reflective high energy electron diffraction (RHEED)

Figure 2.5: (a) Schematic representation of the effect of low roughness, of the order of one monolayer, on the RHEED pattern. A picture, seen on the right panel, has been added to illustrate this effect. The picture was taken along the [100] direction of SrTiO$_3$ for a 20nm BiFeO$_3$ film. (b) Effect of miscut or film tilt on the crystal truncation rods. The picture to illustrate the effect, on the right panel was recorded in vacuum for a 10nm BiFeO$_3$ film on a SrTiO$_3$ having an overall tilt of the order of 0.2° with respect to the lattice planes of the substrate. (c) Schematic representation of the effect of a rough surface, leading to transmission through the three dimensional 'islands'. This is also illustrated for the case of a SrTiO$_3$ film grown on SrTiO$_3$ with a RMS roughness of the order of 1nm (3-4 unit cells).

mode is seen as a sharp decrease of the RHEED intensity and a '3D' RHEED pattern of spots (see previous subsection). It is referred as 3D growth or Volmer-Weber growth.
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Figure 2.6: Typical modes observed in thin film growth close to thermodynamic equilibrium and the corresponding evolutions of the RHEED intensity. (a) Arrival of species at the substrate. (b)-(c) 3D island growth (Volmer-Weber). (d)-(e) 2D layer-by-layer growth (Frank-Van der Merwe). (f)-(g) 2D step-flow mode.

For total free energies of film plus interface equal to or smaller than the free energy of the substrate surface, the film will wet the substrate, leading to 2D layer-by-layer growth (figure 2.6(a)-(d)-(e)). This mode is seen as RHEED oscillations that keep the same amplitude with time. This type of growth is also known as Frank-Van der Merwe growth. The intermediate mode is also frequently observed in heteroepitaxy: After a few monolayers, the interfacial energies lead to a decrease of the wetting and the growth switches from 2D to 3D mode. This can be seen by RHEED oscillations whose maxima decreases as the thickness increases until the oscillations fade away. The final RHEED pattern also usually displays 3D-like spots (i.e. not aligned on a Laue circle). This type of growth is known as Stranski-Krastanov growth (not shown in the figure).

The misfit strain between the film and the substrate, specially at high misfit values, can modify considerably the growth modes during deposition. Indeed, the first monolayers are heavily strained on the substrate so that their chemical potential is considerably modified with respect to that of the bulk. The chemical potential of the film is then thickness (t) dependent ($\mu(t)$), approaching the bulk value as the thickness increases [90].

Moreover, in PLD, supersaturation is large and the growth takes place far from ther-
modynamic equilibrium. Limited diffusion creates different growth modes than those explained above and other parameters, such as the miscut angle of the substrate, become important. The presence of a miscut angle (substrate steps) and large supersaturation can give rise to the step-flow mode (2.6(a),(f),(g)). In this case, after a first decrease and further increase of the RHEED intensity, no RHEED oscillations are observed because the film morphology does not change during growth. The steps can rapidly move over the surface with different velocities leading to step bunching and an atomically flat surface with few steps, for high enough thicknesses. In this case, very high quality films can be grown but no layer-by-layer control is possible.

2.3 X-ray diffraction (XRD)

2.3.1 Crystal truncation rods and specular scans

In the case of an infinite three-dimensional crystal, the x-ray diffracted intensity is proportional to a delta function for allowed values of integers (h,k,l), giving rise to spots in a diffraction pattern. However, for a cleaved crystal such as a substrate, a relaxation of these conditions occurs perpendicular to the cleavage direction and streaks of scattering appear, along this direction [95]. A crystal with a perfect surface can be mathematically expressed as the multiplication of the electron density of the bulk crystal, $\rho(z)$, with $z$ being the normal to the cleavage plane, with a step function, $h(z)$. The scattered amplitude is then proportional to the convolution of the fourier transforms of $\rho(z)$ and $h(z)$. The fourier transform of the electron density being a delta function whereas the fourier transform of the step function is proportional to the inverse of the wavevector along the direction perpendicular to the cleavage direction [95]. In practice, the use of typical $2\theta - \omega$ scans (where $2\theta$ and $\omega$ are, respectively, the angles that the detector and the sample form with the incident beam) allows to monitor the profile of intensity along the CTRs in the (00L) direction, which is proportional to the square of the inverse of the wavevector [95]. When a film is grown on a perfect substrate surface and
the film is thin enough, the x-rays can penetrate through the film and the interference effects from reflections at the surface and the interface with the substrate, produce fringes (Laue fringes) in the CTRs, whose periodicity can be related to the thickness of the film.

2.3.2 Reciprocal space mapping

In addition to the structural information that can be extracted from standard $2\theta - \omega$ scans, the epitaxial relationships between film and substrate can be investigated by mapping different areas of the reciprocal space, in particular, around non-specular Bragg peaks. This is done by performing series of $2\theta-\omega$ scans (radial scans) for different $\omega$ angles. Figure 2.7 shows a sketch of the reciprocal space mapping principle. The radial ($2\theta-\omega$) scans change the length of the scattering vector, $\Delta K$, while keeping its direction, whereas the $\omega$ scans keep the length constant but change the direction of the scattering vector.

The recorded angles ($\theta, \omega$) are then transformed to reciprocal units ($K_\perp, K_\parallel$) using the simple following relationships: $K_\perp = \Delta K \cos \delta$ and $K_\parallel = \Delta K \sin \delta$, where $\delta = \theta - \omega$ is called the offset and $\Delta K = 2 k_{in} \sin \theta$.

2.3.3 Grazing incidence diffraction

When characterizing the structure of the films, standard diffraction geometries have limited use. As explained above, in the standard Bragg-Brentano geometry, the finite thickness of the films gives rise to Laue oscillations along the crystal truncation rods [95] that limit the resolution in the direction perpendicular to the surface. Although, as shown in the previous section, information about the in-plane structure can be obtained in this geometry, the small volumes of material involved in the scattering event leads to a considerable reduction of the diffracted intensities. In addition, the much more intense substrate peaks often hide the film reflections.
2.3. X-ray diffraction (XRD)

Figure 2.7: Reciprocal space mapping using x-ray diffraction. The control of the motion of the sample and the detector allows the spanning of the shaded area. The collected data are plotted in a 2D contour plot, where the horizontal and vertical axes correspond to $K_{\text{par}}$ and $K_{\text{perp}}$, respectively.

In order to have access to the in-plane structure of the films with scattering vectors fully contained in the plane (and, therefore, be insensitive to the finite thickness of the films and the presence of the substrate), grazing incidence x-ray diffraction (GIXD) is performed. The setup for GIXD is plotted in figure 2.8. The wave $k_{\text{in}}$ is incident on the surface at a very small angle $\theta_0$, just below critical angle for total reflection, which is about 0.2-0.3° for most materials. In total reflection conditions, with the absence of wavevectors propagating perpendicular to the surface, an evanescent wave is produced, which is only significant close to the surface and decays exponentially into the films. This evanescent wave is able to scatter with the in-plane lattice planes. If the sample is rotated around its surface normal, thus preserving the small angle $\theta_0$, the wave $k_{\text{in}}$ can fulfill the Bragg condition with some atomic planes perpendicular to the
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Figure 2.8: Grazing incidence diffraction geometry.

surface at some angle $\theta_B$, giving rise to the diffracted wave, $k_{\text{out}}$.

GIXD also allows to perform depth dependence measurement by tuning of the incident angle $\theta_o$ [95]. Another advantage of GIXD is that, due to the small penetration depth of the evanescent wave, the substrate peak is not seen. The disadvantage of this technique is that it requires specific motion of the detector and the sample stage that are not available in many diffractometers. Moreover, since the evanescent wave is very weak, and the incident angle needs to be well defined, it requires the large intensities and highly collimated beams of synchrotron sources. The GIXD experiments in this thesis were performed at HaSyLab (DESY, Hamburg) on the beam line W1 and at the ESRF (Grenoble, France) on the beam line BM28.

2.4 X-ray photoelectron spectroscopy (XPS)

X-Ray Photoelectron spectroscopy allows the chemical analysis of surfaces by gathering information of the elemental composition, valence and electronic states. XPS requires ultra-high vacuum (UHV) conditions (typically $10^{-9}$-$10^{-10}$ mbar). XPS spectra are obtained by irradiating the material with a beam of monochromatised x-ray photons produced from aluminum or magnesium sources. Electrons, within a depth of a few nanometers, can absorb the x-rays and leave the material with a characteristic ki-
netic energy, directly related to their binding energy \( (E_{\text{binding}}) \). A typical XPS spectrum is a plot of the number of electrons arriving at the detector as a function of the binding energy of the collected electrons. \( E_{\text{binding}} \) of each emitted electron can be calculated by:

\[
E_{\text{binding}} = E_{\text{photon}} - E_{\text{kinetic}} - \Phi_{\text{sp}},
\]

where \( E_{\text{photon}} \) is the energy of the absorbed x-rays, \( E_{\text{kinetic}} \) is the kinetic energy of the emitted electron, as measured by the analyzer, and \( \Phi_{\text{sp}} \) is the work function of the spectrometer, taking into account the difference of kinetic energy seen at the detector with respect to the kinetic energy seen at the sample. These characteristic peaks, or binding energies, identify the atoms present at the surface and their electronic configuration. Moreover, XPS is a non-destructive technique that can measure the surface chemistry of any material and is not restricted to crystals. The measurements using this technique have been performed in a SSX-100 (Surface Science Instruments) photoemission spectrometer, with a monochromatic Al K\( \alpha \) X-ray source (\( h\nu = 1486.6 \text{ eV} \), base pressure during measurement: \( 10^{-10} \text{ mbar} \)), belonging to the Surfaces and Thin films research group at the Zernike Institute for Advanced Materials.

### 2.5 Atomic force microscopy (AFM)

The Atomic Force Microscope (AFM) consists of a microscale cantilever with a sharp tip at its end that is used to scan a sample surface. The cantilever is typically silicon or silicon nitride with a tip radius on the order of 10 nanometers. When the tip is approached to the sample surface, forces between the tip and the sample lead to a deflection of the cantilever. Typically, the deflection of the cantilever is measured by detecting the movements of a laser spot that is reflected from the top of the cantilever into an array of photodiodes.

The AFM can be operated in a number of modes, depending on the application, but most of the AFM images presented in this thesis were performed using the AFM in tapping mode, which is more gentle on the sample and the tip than the contact mode.
In tapping mode, the cantilever vibrates with a frequency close to its resonance frequency. The amplitude of this oscillation is typically 100 nm. Due to forces acting on the cantilever when the tip is approaching the surface, the amplitude of the vibration decreases. The height of the cantilever is modified by the system electronics using a piezoelectric actuator, in such a way that a constant amplitude of the cantilever vibrations is kept during the scanning of the surface by the AFM tip. Tracking the cantilever height results in a map of the area that represents the topography of the sample.

2.6 Magnetization measurements

The measurements of the magnetization of the thin films produced in this thesis were performed using a Quantum Design Magnetic Property Measurement System MPMS7. The (MPMS) is composed of a liquid-helium cooled SQUID (Superconducting QUantum Interference Device) that measures the changes in the magnetic flux as the sample moves through a superconducting detection coil. This device acts as a very sensitive magnetometer, since it can detect changes as small as one flux quantum. The MPMS system at the Zernike Institute for Advanced Materials, used in this thesis, allows the measurement of the magnetic properties from around 2K up to 400K under magnetic fields up to \( \pm 7T \). The sensitivity of the measurement is \( 10^{-6} - 10^{-8} \) emu, depending on the setup. However, despite this high sensitivity, measurements on non-ferromagnetic ultra-thin films (below 50nm) are very difficult, as the signal from the layer can be below the sensitivity value and the signal of the substrate may mask that of the film.

The samples are inserted in the device by placing them inside a plastic straw (with a low diamagnetic signal) that is attached to the end of the MPMS probe. Most of the measurements presented here are done after zero-field-cooling (ZFC) and field-cooling (FC) conditions. For ZFC, the sample is cooled down below its transition temperature under no applied field. A field is then applied at the lowest temperature and
2.7 Dielectric measurements

Measurements of the capacitance and the dielectric loss of a material give valuable information about phase transitions and conduction processes in a dielectric [96]. However, these measurements are not so often performed due to issues distinguishing intrinsic and extrinsic behaviour. This is specially difficult in thin films, where leakage currents and interface effects can be important. In this thesis we show the usefulness of this technique when properly applied.

The capacitance and the loss of a dielectric sandwiched in between two parallel electrodes can be written as $C = \epsilon_o \epsilon' \frac{A}{d}$ and $\tan(\delta) = \frac{\epsilon''}{\epsilon'}$, where $\epsilon_o$ is the permittivity of free
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Space, $\epsilon'$ and $\epsilon''$ are the real part and imaginary part of the dielectric permittivity of the material, $A$ is the area of the electrodes and $d$ is the thickness of the sample. Peter Debye developed a model of dielectric relaxation by considering a delay of the response of a dipole under an alternating electric field due to a surrounding viscous medium [97]. According to this model:

$$\epsilon(\omega) = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + j\omega\tau} \quad (2.1)$$

where $\tau$ is the relaxation time associated with the orientation process, $\epsilon_s$ is the static permittivity (zero frequency limit), $\epsilon_{\infty}$ is the permittivity at optical frequencies, $\tau$ is the relaxation time and $\omega$ is the (angular) frequency of the applied electric field. By separating the real part from the imaginary part in the Debye equation, one obtains:

$$\epsilon'(\omega) = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{1 + (\omega\tau)^2}; \epsilon''(\omega) = \frac{\omega\tau(\epsilon_s - \epsilon_{\infty})}{1 + (\omega\tau)^2} \quad (2.2)$$

This implies that in a Debye-like relaxation, $\epsilon'$ and $\epsilon''$ show a step and a peak, respectively, at the relaxation frequency, $\tau^{-1}$.

Using impedance spectroscopy, the evaluation of different electrical functions (impedance $Z$, admittance $Y$ and modulus $M$) is possible. These are defined as: $M = \epsilon^{-1}$; $Z = (j\omega C_o \epsilon)^{-1}$; $Y = j\omega C_o \epsilon$, where $C_o$ is the capacitance of an empty cell with the same dimension as the sample. The frequency behavior at a given temperature of the impedance functions is often used to determine the equivalent circuit of a material [96] and separate the intrinsic and extrinsic dielectric behavior.

A home-built sample holder was used to measure the dielectric properties of the thin films placed in a Quantum Design Physical Properties Measurement System, or PPMS, (see figure 2.9(a)). The PPMS was used to carry out temperature or magnetic field dependence on the dielectric properties. Bottom and top contacts were deposited using pulsed laser deposition and the details about the growth of the electrode will
be given in chapter 4. Pt wires were connected to the top electrodes by using a two- component silver epoxy. The other end of the Pt wire was soldered to the sample holder contacts. Dielectric measurements were performed using an LCR Meter (Agilent 4284a) for frequencies between 20Hz and 1MHz, and under an applied ac voltage of 50 mV.

The results presented in chapter 6 of this thesis were performed with the sample placed inside a Janis probe station that allows 2 and 4 points measurements (see figure 2.9(b)). The system can be cryogenically cooled down to 10K. The capacitance measurements were performed using the same Agilent LCR Meter, as in previous experiments. The sample preparation differs slightly from the one used for the PPMS: The thin films with SrRuO$_3$ electrodes were glued on a thin glass sheet using wax, and a two-component silver glue was deposited on the top electrodes, keeping the added silver within the perimeter of the electrodes.