Strain and composition effects in epitaxial ferroelectrics
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Chapter 4

Ferroelectrics grown in the ferroelectric phase

4.1 Introduction

In theoretical descriptions of ferroelectricity, the ferroelectric phase is considered to be a distortion of the paraelectric high-temperature phase. For PbTiO$_3$ this means that the cubic paraelectric unit cell is distorted by some self-strain resulting in the tetragonal ferroelectric unit cell [34]. In addition most theoretical approaches to domain formation explicitly or implicitly assume domain formation upon cooling from a paraelectric phase [14, 15, 22]. In most bulk ferroelectrics this approach is valid as the processing temperatures are typically much higher than the ferroelectric transition temperature. [111, 112] Thin film growth typically uses lower processing temperatures than bulk solid state reactions. Moreover, the application of epitaxial strain is known to increase the transition temperature of ferroelectrics. [1, 3, 44] In PbTiO$_3$, these combined effects lead to the interesting case in which the ferroelectric transition temperature is increased above the growth temperature.

To study the effect of growing thin films in the ferroelectric phase, fully strained thin films of Pb$_x$Sr$_{1-x}$TiO$_3$ were grown on SrTiO$_3$ substrates. Strontium substitution was used to tune the transition temperature. Temperature dependent XRD
Figure 4.1: 2θ-ω scan of a 23 nm thick PbTiO₃ thin film on SrTiO₃. The crosses are the experimental data. The solid line is a simulation of the data as described in section 3.5.

was used to study the polarization evolution and transition temperatures.

4.2 Experimental

4.2.1 PbTiO₃ on SrTiO₃

Epitaxial thin films of PbTiO₃ were grown using MBE as described in section 2.5. Figure 4.1 shows a XRD 2θ-ω scan of a 23 nm thick PbTiO₃ film grown on a (001) oriented SrTiO₃ substrate. The solid line is a simulation of the experimental data around the (001) reflection using the method described in section 3.5. The out-of-plane lattice parameter c is found to be 4.115 Å and the roughness is 2 Å. The thickness and roughness obtained from the simulation are in good agreement with the values obtained from x-ray reflectivity measurements and atomic force microscopy, respectively.

The epitaxial coherence of the films is verified using off-specular reciprocal space maps (RSM) around the (103) reflection. At room temperature, the difference between the bulk PbTiO₃ a lattice parameter (3.904 Å) and the cubic SrTiO₃ lattice parameter (3.905 Å) is very small. [60] This can make it difficult to verify epitaxy from a RSM measured at room temperature. At elevated temperatures this
4.2 Experimental

Figure 4.2: Reciprocal space map (RSM) around the (103) reflection of a PbTiO₃ thin film grown on SrTiO₃ measured at 625°C after heating to 800°C and, thus, reaching the paraelectric phase. The peak appears at (0.196,0.572)-2k₀ and the substrate peak at (0.196,0.572)-2k₀, where k₀ = \( \frac{2\pi}{\lambda} \) and \( \lambda = 1.540 \text{ Å} \).

difference increases, and it becomes easier to distinguish between a fully epitaxial and a relaxed film. Figure 4.2 shows a (103) RSM of a PbTiO₃ film measured at 625°C. It can be seen that the in-plane film lattice parameter is identical to the substrate lattice parameter.

As the films are confirmed to be coherently strained, linear 2θ-ω scans can be used to determine the tetragonality. By measuring the tetragonality as a function of temperature, the temperature behavior of the polarization and the transition temperature can be obtained (see section 3.4). Figure 4.3 shows the tetragonality versus temperature for a 18 nm thick PbTiO₃ film on (001) SrTiO₃. Below the ferroelectric to paraelectric transition temperature, the tetragonality decreases with increasing temperature, as the polarization decreases. Above the transition temperature the tetragonality is nearly constant with temperature, since the thermal expansion for the film and the substrate are nearly identical. From figure 4.3 it can be seen that upon heating for the first time (filled circles), \( T_C = 725°C \), which is higher than the bulk value of 490°C. This increase in \( T_C \) is in agreement with Ginzburg-Landau theory. [3] Upon cooling of the film (open circles), the transition temperature and the tetragonality in the ferroelectric phase have decreased. When the experiment is repeated on the same film (filled and open squares), no further changes are observed. Therefore, three key observations are made upon heating to the paraelectric phase.
and cooling down for the first time: A decrease in $T_C$, a decrease of the tetragonality in the ferroelectric phase and no significant change of the tetragonality in the paraelectric phase. A priori, possible explanations for these observations are sample damage through the loss of lead from the film, relaxation of the epitaxial strain or an increase of the effective depolarization field.

Indeed, sample damage through loss of PbO is something to consider when working with PbTiO$_3$ at elevated temperatures. PbTiO$_3$ can decompose to TiO$_2$ and gaseous PbO. Decomposition leads to residual TiO$_2$, which is not ferroelectric. However, this would be a surface process and thus, it is unlikely that decomposition would lead to a smaller overall lattice parameter of the perovskite phase as observed. The creation of Pb defects throughout the films is another mechanism for lead loss. This has been reported to decrease both $T_C$ and the tetragonality in bulk PbTiO$_3$ [113]. However in this case, the paraelectric lattice parameters should also be affected, which does not agree with the observations. Moreover, one would expect the formation of lead vacancies to be a continuous process leading to a decrease $T_C$ and tetragonality at each cycle, contrary to our experimental results.

The second possible explanation is that a higher compressive strain leads to a higher polarization and a higher $T_C$, and therefore relaxation of that strain would lead to a smaller $T_C$ and tetragonality. Strain relaxation can thus explain two of
our key observations. Such a strain relaxation model for the thermal history dependence was proposed by Venkatesan et al. for thicker PbTiO$_3$ films grown by PLD [25]. However, a difference in the paraelectric phase between heating up and cooling down is expected. In the as-grown sample, during heating from room temperature, the strain is large, leading to a high $T_C$. This high strain would lead to a tetragonally deformed paraelectric unit cell. If (some) of this strain is released after crossing $T_C$ for the first time, the tetragonality of the paraelectric phase should go down as well. This is not in agreement with the observations of figure 4.3.

The depolarization field opposes the polarization and thus acts to suppress the ferroelectric distortion. A larger depolarization field would lead to both a smaller $T_C$ and a smaller tetragonality, as observed. Moreover, the paraelectric phase would be unaffected, as there is no polarization and thus no depolarization field. An increasing depolarization field thus seems to be the most likely explanation. However, when looking at the XRD patterns (figure 4.4) and AFM images (figure 4.5) in more detail, however things appear to be more complicated.

The reflectivity scans in figure 4.4a clearly show a decrease in thickness of the film after the first heating run. Moreover the critical angle also shifts to lower values, which would indicate a decrease in electron density. Simulations of the reflectivity curves [94] give a thickness of 23.0 nm for the as-grown film, which decreases
Figure 4.5: AFM topography images for 23 nm PbTiO3 on SrTiO3. a) As grown b) After 2 heating cycles. On the edges of the image recrystallization features can be seen.

to 21.7 nm after the first run. This change is much bigger than would be expected from the observed lattice parameter change (4.1157 Å versus 4.1015 Å). Also the electron density decreases from 1.97 eÅ⁻³ to 1.8 eÅ⁻³. Both are consistent with sample damage and loss of Pb. In the 2θ-ω scans shown in figure 4.5b, extra peaks appear after heating. The extra peaks (when compared to figure 4.1) are observed at 28.55° (3.12 Å), 37.91° (2.37 Å) and 43.40° (2.08 Å). The peak at 2.37 Å appears already at room temperature and comes from the sample holder. The peak at 2.08 Å appears occasionally irrespective of the film material. Most likely it is related to silver from the sample holder, as the peak position is relatively close to the (002) peak of silver (2.04 Å) [114]. The origin of the peak at 3.12 Å does not seem to be of extrinsic origins and may originate in the decomposition of PbTiO3. Wider 2θ-ω scans also show a lower order peak at 6.24 Å. These peaks are possibly pyrochlore phases such as Pb₂Ti₂O₇ or PbTi₃O₇ [115] (the latter is more likely as it is lead-poor).

AFM images before and after two heating cycles are shown in figure 4.5. Figure 4.5a shows the morphology of the as-grown film surface. Unit cell steps are visible, the RMS roughness is 3 Å. After heating there are two different features on the surface: 1) the unit cell steps are not visible anymore and a network of crossing lines is visible (figure 4.5b). 2) big (re)crystallized features are also observed (edges of figure 4.5b). The network of lines observed in figure 4.5b resembles a dislocation grid [116] and thus may be interpreted as a sign of strain relaxation. The recrystallization may be related to the pyrochlore peaks observed in XRD.
4.2 Experimental

The experimental data of pure PbTiO$_3$ on SrTiO$_3$ is not conclusive as to what mechanism is responsible for the irreversible change observed upon cooling from the paraelectric phase for the first time. Although there are clear signs of sample damage and relaxation, a change in effective depolarization field qualitatively provides the best model to the data in figure 4.3. Moreover it is unclear, if this anomalous behavior originates from the fact that the films are grown in the ferroelectric phase. More insight about this issue will be given in the next sections.

4.2.2 Pb$_x$Sr$_{1-x}$TiO$_3$ on SrTiO$_3$

Substitution of Pb by Sr in the PbTiO$_3$ structure decreases $T_C$, the magnitude of the polarization and the size of the unit cell [117–119]. Thus Sr substitution can be used to decrease $T_C$ below the growth temperature and grow in the paraelectric phase. By comparing the results on pure PbTiO$_3$ films grown in the ferroelectric phase and Pb$_x$Sr$_{1-x}$TiO$_3$ films grown in the paraelectric phase, more information about the effect of growing in either phase can be obtained.

The growth of Pb$_x$Sr$_{1-x}$TiO$_3$ was described in section 2.5. The parameter defining the Sr/Pb ratio is the time the Sr shutter was open during the growth of each monolayer, $t_{Sr}$. Determining the absolute Sr/Pb ratio proved to be difficult. Throughout this section $t_{Sr}$ is used to define the composition. Figure 4.6 shows the dependence with $t_{Sr}$ of the ratio between area of two characteristic XPS peaks and the transition temperature. The XPS results show that the surface ratio of Sr 3$p$ and Pb

![Figure 4.6: a) Ratio between surface of the Pb 4$d$ and Sr 3$p$ XPS peaks as a function of $t_{Sr}$ b) Transition temperature as a function of $t_{Sr}$](image)
Figure 4.7: Temperature dependence of the tetragonality of Pb$_x$Sr$_{1-x}$TiO$_3$ thin films with various compositions ($t_{Sr}$). The tetragonality and $T_C$ decrease with increasing Sr content. The difference between the heating and cooling curves observed for pure PbTiO$_3$ is not observed at any Sr content.

4$d$ varies with $t_{Sr}$. The expected linear scaling with $t_{Sr}$, is not displayed in the whole range. However, there are some reasons why this parameter may not give realistic composition ratios: The surface sensitivity of XPS and the other peaks present have to be taken into account. The transition temperature, $T_C$ scales linearly with the Sr content of the films for low Sr contents.

Figure 4.7 shows heating and cooling curves for the tetragonality of Pb$_x$Sr$_{1-x}$TiO$_3$ with various compositions. In contrast to pure PbTiO$_3$, the heating and cooling lines do collapse. This is in agreement with the hypothesis that there is a difference between films that are grown in the ferroelectric phase and films that are grown in the paraelectric phase, as all Pb$_x$Sr$_{1-x}$TiO$_3$ films are grown at temperatures above $T_C$.

Figures 4.8 and 4.9 show the XRD and AFM results on Pb$_x$Sr$_{1-x}$TiO$_3$ films. The heating cycle in this case was up to a temperature of 600°C. In contrast to the PbTiO$_3$ films, no change in thickness is observed in figure 4.8a (the thickness found is 18.6 nm). The 2$\theta$-ω scans (figure 4.8b) show no additional peaks related to the sample after heating. The extra peak observed at 2.37 Å is related to the sample holder. The AFM image before heating (figure 4.9a) shows terrace steps, the RMS roughness being 2 Å. After one heating cycle, some particles appear at the surface (figure 4.9b), the terrace steps are still visible though. The RMS roughness has increased to 10 Å, due to the particles. The origin of these particles is unclear, but they seem
4.2 Experimental

Figure 4.8: XRD measurements on 18.6 nm $Pb_xSr_{1-x}TiO_3$ ($t_{Sr} = 6$ s.) on SrTiO$_3$ a) X-Ray reflectivity scans before and after the first heating-cooling cycle. No clear thickness change is observed b) $2\theta$-$\omega$ scans before and after the first heating-cooling cycle. No extra peaks appear (apart from the peak at 37.9$^\circ$ that arises from the heater).

Figure 4.9: AFM topography images for 18 nm $Pb_xSr_{1-x}TiO_3$ ($t_{Sr} = 10$ s.) on SrTiO$_3$. a) As grown. b) After 1 heating cycle.
Figure 4.10: $2\theta$-$\omega$ scan off a 18.6 nm Pb$_x$Sr$_{1-x}$TiO$_3$ ($T_{Sr} = 6$ s.) on SrTiO$_3$ after a heating cycle up to 800°C. An extra peak appears at 28.54° (3.12 Å). The peak at 37.9° that arises from the heater to be extrinsic in origin. Diffused silver from the sample holder or silver paint is a possible origin.

The transition temperature of the Pb$_x$Sr$_{1-x}$TiO$_3$ films is lower than that of the PbTiO$_3$ films, and thus, the maximum temperature used to measure the tetragonality was lower. To be able to compare the effects of high temperature with the PbTiO$_3$ films, a sample was heated to the same maximum temperature as used for PbTiO$_3$, which was 800°C. From this measurement, no change in $T_C$ was observed. The tetragonality was only slightly smaller, the decrease in tetragonality was never more than 0.001. Figure 4.10 shows the $2\theta$-$\omega$ scan measured after heating to 800°C. However, the peak at 3.12 Å, which is related to sample damage due to some Pb loss is now visible. This shows that some sample damage also occurs in the Pb$_x$Sr$_{1-x}$TiO$_3$ thin films, but this has no influence on the transition temperature.

### 4.3 Landau-Ginzburg theory simulations

#### 4.3.1 PbTiO$_3$ on SrTiO$_3$

One of the conclusions in section 4.2.1 was that an increase of the effective depolarization field could explain the observations of figure 4.3. Landau-Devonshire theory modeling was used to test this hypothesis in a more quantitative manner.

The simulations were based on the free energy expansion including epitaxial
4.3 Landau-Ginzburg theory simulations

strain, as described by Pertsev et al [3], see section 1.4.2. The depolarization field has a linear dependence on the magnitude of the polarization and is inversely proportional to the thickness. The free energy associated with $E_D$ is $E_D P$, so effectively $E_D$ is a renormalization of the $P^2$ term of the free energy. The depolarization field can be expressed as:

$$E_D = \frac{\nu}{d} P$$  \hspace{1cm} (4.1)

where $d$ is the film thickness, The scaling of the depolarization field with the polarization is represented by $\nu (m^2 / F)$. The screening length of the surface electrons and the effect of domain formation are both included in $\nu$, which is used as an adjustable parameter in our simulations. The polarization is obtained from minimizing the free energy at various temperatures. The tetragonality is obtained from the polarization using:

$$\frac{c}{a} = (1 - u_m)(1 - \frac{c_{12} u_m}{c_{11}} + \frac{g_{11}}{c_{11}} P^2)$$  \hspace{1cm} (4.2)

In this equation, $u_m$ is the misfit strain, $c_{ii}$ and $g_{ii}$ are the elastic stiffness and electrostrictive constants, respectively. [102] The misfit strain, $u_m$, in our model is taken to be independent of temperature as the thermal expansion of high temperature cubic PbTiO$_3$ and SrTiO$_3$ are very similar. [84]

The experimental results for pure PbTiO$_3$ on SrTiO$_3$ were simulated using only the misfit strain, $u_m$, and the depolarization field term, $\nu$, as adjustable parameters.
Figure 4.12: Alternative simulations of the tetragonality of a 23 nm thick PbTiO₃ film on SrTiO₃ upon cooling from the paraelectric phase for the first time. Only the misfit strain is changed compared to the simulation of the heating curve in figure 4.11.

Table 4.1: Parameters used for the simulations shown in figures 4.11 and 4.12

<table>
<thead>
<tr>
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<th>Heating 1 (fig. 4.11)</th>
<th>Cooling 1 (fig. 4.12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>t (nm)</td>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td>uₘ (%)</td>
<td>-1.01</td>
<td>-1.01</td>
</tr>
<tr>
<td>ν (m²/F)</td>
<td>0.25</td>
<td>0.67</td>
</tr>
</tbody>
</table>

The misfit strain was chosen to fit the tetragonality in the high temperature paraelectric phase. The depolarization term, ν, was chosen to fit the observed T_c. Figure 4.11 shows the simulation of some of the data in figure 4.3. The only difference between the simulations for the heating and cooling curves is in the depolarization parameter, ν. The misfit strain was -0.0101 in both cases.

Figure 4.12 shows another simulation of the cooling curve of the 23 nm thick PbTiO₃ film on SrTiO₃. Compared to the simulation of the heating curve in figure 4.11, only the misfit strain, uₘ, is changed to fit the lowered transition temperature. Although the tetragonality in ferroelectric phase is modeled reasonably well, this model predicts a tetragonality in the paraelectric phase which is significantly lower than the one observed experimentally. The effect of lead loss has not been modeled, as there are no Landau coefficients known for lead deficient PbTiO₃. From these simulations we conclude that strain is not the main parameter accounting for the difference between the heating and cooling runs in figure 4.11 and that the
4.4 Truncation Rod simulations

The increasing depolarization field is modeled using the parameter $\nu$, which contains contributions of charge screening and the presence of domains. If the sizes of up and down domains are exactly equal, all surface charges are compensated and there would be no depolarization field. Short circuited electrodes with zero screening length would have the same effect. In principle, separating the influence of domains and electron screening is impossible without experimental evidence about either effect.

In section 3.5 it was shown that simulations of the CTR profiles give information on the fraction of domains in either the up or down polarization direction.

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**Table 4.2:** Parameters used for the CTR simulations shown in figures 4.4

<table>
<thead>
<tr>
<th></th>
<th>As-Grown</th>
<th>1 Heating Cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (ML)</td>
<td>49</td>
<td>47</td>
</tr>
<tr>
<td>$a_{\text{SrTiO}_3}$ (Å)</td>
<td>3.903</td>
<td>3.903</td>
</tr>
<tr>
<td>$c_{\text{PbTiO}_3}$ (Å)</td>
<td>4.115</td>
<td>4.10</td>
</tr>
<tr>
<td>Domain fraction up</td>
<td>0.75</td>
<td>0.45</td>
</tr>
<tr>
<td>RMS roughness (Å)</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Thickness FWHM (ML)</td>
<td>2.5</td>
<td>2</td>
</tr>
<tr>
<td>PbO coverage</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

**Figure 4.13:** Simulations of the CTR profiles of a 20.4 nm PbTiO$_3$ film on SrTiO$_3$. a) As grown. b) After heating to the paraelectric phase
Therefore, applying this method to $2\theta$-$\omega$ scans measured before and after heating to the paraelectric phase could give quantitative information on the change in domain structure. Figure 4.4 shows $2\theta$-$\omega$ scans around the (001) reflection measured before and after heating. The solid lines are the simulations using the parameters given in table 4.2. It was assumed for the simulations that the top surface PbO layer present in the as-grown film has evaporated during the heating cycle. The thickness decrease during the heating cycle is 2 unit cells, in addition to the lost PbO top layer. Combined with the change in $c$ lattice parameter this makes a total thickness decrease of 11 Å, which is comparable to the thickness decrease observed from reflectivity for a similar sample (see section 4.2.1). Surprisingly, no change is found in the roughness and thickness variation before and after heating.

The domain fraction up is found to change from 0.75 in the as-grown film to 0.45 after heating. Qualitatively this change can be noticed by the extra fringe right of the SrTiO$_3$ substrate peak in figure 4.4. This fringe can only be modeled reasonably well using a majority polarization down, whereas the majority polarization is in the up direction before heating. This shift in majority polarization shows that there is a quite significant change in domain structure. The uncompensated domain fraction, $n = |n_{up} - n_{down}|$, which should scale with the depolarization field parameter, $\nu$, decreases from 0.5 in the as-grown film to 0.1 after heating.

From the Landau theory simulations it was found that $\nu$ increases to give a lower transition temperature. Although the numbers from the truncation rod simulations have to be treated carefully, an improved domain balance after cooling from the paraelectric phase is found. This implies that a different mechanism has to be responsible for the increase in depolarization field.

### 4.5 Discussion

The observations shown in figure 4.3 (a different behavior after the film has visited the paraelectric phase for the first time) can, in principle, originate in strain relaxation, lead loss or a change in the effective depolarization field. Qualitatively,
the Pb loss and strain relaxation hypotheses are not able to explain the behavior in the paraelectric phase, as both predict a lowering of the tetragonality also there. Landau-Ginzburg theory simulations have also shown that a strain relaxation model does not fit the experimental data very well, quantitatively (see figure 4.12). However, experimental data does indicate the presence of some Pb loss. AFM results suggest the presence of dislocations (see figure 4.5), but reciprocal space maps measured at high temperature after heating to the paraelectric phase still shows a perfect lattice match (see figure 4.2). Combining these experimental observations and the Landau-Ginzburg modeling, leads to the conclusion that despite the possible presence of dislocations, the overall strain state is maintained and that strain relaxation is not the driving force for the transition temperature change that is observed. Heating Pb$_x$Sr$_{1-x}$TiO$_3$ films to the highest temperature that has been used in the PbTiO$_3$ temperature cycles, results in some sample damage, comparable to what is observed in PbTiO$_3$. However, the transition temperature and tetragonality are not affected. This strongly indicates that although sample damage due to Pb loss does occur, it is not the direct origin of the observations of figure 4.3.

Comparison of the experimental data on both PbTiO$_3$ and Pb$_x$Sr$_{1-x}$TiO$_3$ thin films shows that the sample history has a clear influence on the film properties. Ferroelectric films that have been in the paraelectric phase show reproducible behavior upon heating and cooling, whereas films that have not been in the paraelectric phase undergo an irreversible change when cooled from the paraelectric phase for the first time. The Landau-Ginzburg theory simulations show that an increase of the depolarization field can explain these observations reasonably well.

The results from the truncation rod simulations suggest that the direction of the total polarization changes, and the charge compensation through domains improves, after visiting the paraelectric phase. The presence of RHEED electrons during growth can have an important influence on the polarization and domain structure of the growing film. The observation that the direction of the polarization switches from down polarized to up polarized may be a result of an electric field caused by the RHEED electrons. As ferroelectric thin films can be ferroelectric from a thickness of 3 unit cells [31], a domain structure will form during growth
when the film becomes ferroelectric, this thickness will be much lower than the fi-
nal thickness. A Kittel like scaling law [14, 15, 22] will then give a short domain
period. This domain pattern will then act as a template for the rest of the growing
film and can give rise to a non-equilibrium domain structure. Upon cooling from
the paraelectric phase the equilibrium $180^\circ$ domain structure can form providing
better charge compensation.

As the change in domain structure can not explain the conclusion from the
Landau-Ginzburg simulations, there must be a different mechanism responsible
for the increase of the effective depolarization field. The depolarization field orig-
inates in surface charges, thus a change in the (top) surface is likely to affect the
screening. The formation of a more insulating surface may lead to a larger depolar-
ization field. From the experimental results it is clear that some surface degrada-
tion, due to lead loss, occurs when heating the film to the paraelectric phase. Layers
of lead poor species such as TiO$_2$ or pyrochlore, or just the loss of the top PbO layer,
may be able to provide a more insulating surface. Such a mechanism would affect
Pb$_x$Sr$_{1-x}$TiO$_3$ films heated to a temperature high enough for sample damage in a
similar way. However, experimental results show no tetragonality and $T_C$ change,
for the Pb$_x$Sr$_{1-x}$TiO$_3$ samples heated up to 800$^\circ$C, which do show signs of sample
damage.

Conduction through the film is another pathway to get rid of surface charges.
If the conductivity of the film decreases upon cooling from the paraelectric phase,
this could also be the origin of the increased depolarization field. Leakage in thin
films typically takes place due to structural defects and is, thus, more likely in the
very thin films. Figure 4.14 shows: a) a piezoresponse microscopy image of a 9
ML thick PbTiO$_3$ film grown by MBE on SrTiO$_3$, with a SrRuO$_3$ electrode layer
and b) a conductive AFM image of the same area.$^1$ The effect of the polarization
on the resistance is due to the tunneling electro resistance effect. [120, 121] In the
conductivity map also some low resistance spots can be seen. These are most likely
due to structural defects and responsible for most of the leakage. If the density of

$^1$Measurements conducted at 1Unit Mixte de Physique CNRS/Thales (Paris, France) by Arnaud
Crassous, Vincent Garcia and Manuel Bibes
such defects decreases by heating to the paraelectric phase, this could explain the increase in effective depolarization field.

### 4.6 Conclusion

PbTiO$_3$ films and Pb$_x$Sr$_{1-x}$TiO$_3$ films were grown on SrTiO$_3$ using MBE. Under the growth conditions used, pure PbTiO$_3$ grows in the ferroelectric phase, whereas Pb$_x$Sr$_{1-x}$TiO$_3$ of the studied compositions grows in the paraelectric phase. The quality of the films was verified using XRD and AFM. Reciprocal space maps at elevated temperatures were used to confirm the epitaxial coherency.

Following the tetragonality as a function of temperature for the PbTiO$_3$ films grown in the ferroelectric phase, led to the observation that there is an irreversible change in $T_C$ and tetragonality when the films are heated to temperatures above the growth temperature for the first time. The absence of this irreversible change in the case of Pb$_x$Sr$_{1-x}$TiO$_3$ shows that this change occurs because to the PbTiO$_3$ films are grown in the ferroelectric phase and after heating they cross $T_C$ for the first time. An increase in the depolarization field when cooling from the paraelectric phase can explain the observations.

Landau theory modeling is used to show in a more quantitative manner, that
the hypothesis of an increased depolarization field holds. Simulation of the CTR profiles of PbTiO$_3$ films before and after cooling from the paraelectric phase reveals that, although a significant change in domain structure seems to occur, this cannot directly explain the increased depolarization field.

As leakage can also decrease the effective depolarization field, a decrease in the leakage after heating the films to the paraelectric phase can explain the increased depolarization field. Conductive AFM measurements show that leakage paths are indeed present in ultra-thin PbTiO$_3$ films. A decrease in the defects responsible for the leakage during heating would lead to a higher resistance and a higher depolarization field.