Structure and domain formation in ferroelectric thin films
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Ferroelectric thin films under “large” anisotropic strain: PbTiO$_3$ on DyScO$_3$(110)

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5.1 Introduction

In the previous chapter we have shown that PbTiO$_3$ under isotropic compressive biaxial strain, can be grown in the single $c$-domain phase. Figure 2.4 shows undoubtedly that this should be the case. Whereas for PbTiO$_3$ on DyScO$_3$, the case treated in this chapter, several phase transitions are expected. This makes this system more complex but also potentially more interesting. Fortunately, one aspect simplifies the growth of PbTiO$_3$ on DyScO$_3$. This is the nearly perfectly lattice-matched heteroepitaxy at the growth temperature which makes the growth structurally similar to homoepitaxy. On the other hand, this means that differences in chemistry and thermal expansion coefficient that can strongly influence the substrate-film interface, may be more noticeable.

Whereas the SrTiO$_3$ substrate gives rise to a compressive (isotropic) misfit strain $u_{m,cub}$ at room temperature, DyScO$_3$ substrates induce a very small ($\sim 10^{-3}$) compressive anisotropic misfit strain at this temperature. Based on the cubic misfit strain between PbTiO$_3$ and DyScO$_3$ extrapolated to room temperature, the PbTiO$_3$ is expected to be very close to the $r$-phase. As can be seen in Figure 2.4(b), a small increase in temperature gives rise to a small tensile misfit strain. A more realistic phase diagram also includes the strain anisotropy as shown in Figure 2.5. This shows that the $c$-phase is expected
at room temperature, but a small increase in tensile strain, leads to the $r$-phase. As discussed in chapter 2, this $r$-phase, which is predicted in epitaxial $\text{PbTiO}_3$, does not exist in bulk, and has not been confirmed experimentally.

Because of the important role of the $\text{DyScO}_3$ surface, we will first treat several aspects of the $\text{DyScO}_3$ substrate in detail, like the substrate treatment and its structural and electrostatic properties. We logically move on to the thin film growth on $\text{DyScO}_3$, first treating the growth of $\text{SrRuO}_3$ electrode layers and then the growth of $\text{PbTiO}_3$. Subsequently, we will describe the periodic 90° domains with a large registry that we have observed in these films by XRD, AFM, p-AFM and TEM. We will start describing the relaxed thin films with 90° domains at relatively large thicknesses. Then we will discuss the energy balance from which the critical thickness for 90° domain formation can be calculated. These relaxed films will be treated in some more detail, calculating the stress field as a function of thickness and domain sizes. This is done by using the model of Pertsev and Zembilgotov [5], which describes the film/substrate and domain/domain interfaces by fictitious dislocations. The rich reciprocal space maps (RSMs) measured by X-ray diffraction of these relaxed films, in combination with TEM measurements, have revealed a gradient in lattice parameters, which is explained by a model describing the domains as rigid bodies. The consequences of these strain gradients are especially meaningful to increase understanding of the coupling between tetragonality and polarization.

This will be followed by a description of the 180° domains observed below the critical thickness for strain relaxation. In this case, $\text{PbTiO}_3$ is strained and we show that this strain possibly leads to the novel $r$-phase or other rotational symmetries which do not exist in the bulk material. By monitoring the 180° domains in these thin films as a function of thickness, the 180° domain wall formation energy has been determined. Finally, we have investigated the influence of the electrical boundary conditions on relaxed thin films, which is thought to be minimal. We show that the electrical boundary conditions do not alter the thickness scaling of the domain size noticeably, but they do influence the domain orientations. Moreover, we will show some preliminary piezoresponse-AFM measurements on $\text{PbTiO}_3$ thin films on $\text{SrRuO}_3$ electroded $\text{DyScO}_3$. 
5.2 Experimental considerations

5.2.1 Substrate treatment

Substrates of the perovskite $DyScO_3$ have only become available commercially a few years ago [72] and are not widely used yet. One of the large advantages of $DyScO_3$ over $SrTiO_3$ substrates is the crystal quality. This is due to the way the crystals are grown. Whereas $SrTiO_3$ crystals are mainly produced by flux growth, $DyScO_3$ is usually grown using the Czochralski process. This leads to much higher crystallinity and less mosaicity, as can be observed by the XRD rocking curves shown in Figure 5.1(a). But due to the recent introduction of $DyScO_3$ substrates, no proper treatment procedure, like that for $SrTiO_3$, to obtain single terminated substrate surfaces with unit cell steps, is available yet [59]. This is not surprising, since a similar procedure will also require more effort as the difference in chemical reactivity between $DyO$ and $ScO_2$ is very small compared to that between $SrO$ and $TiO_2$ [78].

A short report of a treatment [79] is present in literature, and although similar procedures have been performed successfully, reproducibility is known to be difficult. Therefore, we have chosen to use a thermal treatment which results in substrates with, at least locally, a single termination and unit cell steps.

A thermal treatment of 24 hours at 1020°C with an oxygen flow upon heating up and cooling down, results in substrate surfaces as depicted in figure 3.7(e). We have not determined any relationship between substrate miscut and the timing or temperature, instead we have always used substrates with miscuts between 0.1 and 0.2°. The thermal treatment functions well in a temperature range of 1000-1030°C, the cleaning seems more critical: Water has a detrimental effect leading to etch pits and recrystallization. Proper cleaning is performed by at least 2 cleaning cycles of 30 minutes in acetone with ultrasound and 30 minutes in ethanol with ultrasound, separated by mechanical polishing (rubbing) with optical tissue and ethanol.

Whereas the in-plane structure of $DyScO_3(110)_o$ is not perfectly square [40, 125], the magnitude of its lattice parameters ($a_{pc}$=3.952Å; $b_{pc}$=3.957Å)

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1Private communication with A. Molag and A. Janssens from the Inorganic Materials Science group at the University of Twente, Enschede, The Netherlands.

2At room temperature all rare-earth scandates have the orthorhombic $Pnma$ (space group 62) crystal structure, equivalent to the pseudocubic perovskites $Pbnm$ settings. The conver-
Figure 5.1: (a) XRD rocking curves around the (pseudo)cubic (002) Bragg peaks of SrTiO$_3$ and DyScO$_3$. The latter shows a FWHM of nearly an order of magnitude smaller than the former. (b) The cubic in-plane structure as we have observed it by LEED on treated DyScO$_3$ substrates. (c) In-plane atomic structure of bulk DyScO$_3$(110)$_o$ using the crystal structure as reported in literature [125].

...make it an interesting substrate for crystalline materials with a $\sim4$ Å lattice parameter, like many perovskite metal-oxides. Figure 3.6, in chapter 3, shows the temperature dependence of the in-plane lattice parameters of, amongst others, DyScO$_3$ and the $a$- and $c$-lattice parameters of PbTiO$_3$. This clearly shows the excellent lattice match between DyScO$_3$ and PbTiO$_3$ at the growth temperature that we have employed (570$^\circ$C). Besides, the lattice parameters of the cubic PbTiO$_3$ extrapolated into the tetragonal region [13] are plotted, confirming the excellent lattice match between cubic PbTiO$_3$ and DyScO$_3$. But not only the bulk lattice parameters should be taken into account, the in-plane structure of the terminating DyScO$_3$ surface layer also depends heavily on its termination. A top view of the bulk atomic structure (Figure 5.1(c)) reveals that the scandium is clearly ordered in a nearly square in-plane structure, while the dysprosium and the oxygen octahedra show a...
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zig-zag in-plane ordering. Of course the actual reconstruction of the different terminations, is what matters, but with the limited resolution of our LEED setup, we could not detect any deviation from a cubic surface structure (see Figure 5.1(b)).

5.2.2 The DyScO$_3$ surface

The atomic structure of DyScO$_3$ is somewhat more complicated than the previously treated case of SrTiO$_3$. The in-plane lattice of DyScO$_3$ is not perfectly square, but rectangular. However, the anisotropy is only small and can be taken into account in strain calculations. The electronic structure of DyScO$_3$ can give rise to more complicated effects. Along the [110]$_o$ direction, DyScO$_3$ can be thought to be built up by alternating layers of DyO$^+$ and ScO$_2^-$. For a single-terminated DyScO$_3$ substrate, this would give rise to a macroscopically charged surface and the so-called polar catastrophe [126], which will be avoided by electronic reconstruction. On the other hand, when the surface has two terminations, it will not only be chemically, but also electronically inhomogeneous.

The different and, even more important, uncontrolled electrostatic boundary conditions are undesired. To circumvent this problem, we have usually employed SrRuO$_3$ bottom electrodes of considerable thickness. Figure 5.2 shows characteristic AFM images of SrRuO$_3$ grown on DyScO$_3$, indicating the strong thickness-dependence of the SrRuO$_3$ morphology. While films with thicknesses below 10-20 nm are non-wetting and form islands, films with thicknesses above 25 nm form a wetting layer with unit cell terrace steps. This thickness dependence of the morphology of SrRuO$_3$ on substrates with a polar surface, seems to be more general, as it is also observed on SrTiO$_3$(111) [127].

For the thin film growth of PbTiO$_3$ on these SrRuO$_3$-electroded DyScO$_3$ surfaces, we have used the same settings as for growth on SrTiO$_3$, the only difference being the spot size which was only $\sim$0.8 mm$^2$. By using a 1Hz laser frequency, this resulted in a $\sim$1 u.c./55 sec deposition rate. In several instances, we have also deposited PbTiO$_3$ on DyScO$_3$ without SrRuO$_3$-electrode layer. In line with the morphology described in the previous paragraph, we have observed, using time-resolved RHEED, both for SrRuO$_3$ as for PbTiO$_3$, an initial surface roughening or a lattice reconstruction, followed
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Figure 5.2: AFM images of $SrRuO_3$ layers of different thickness (H) on $DyScO_3$ illustrating the thickness-dependence of the morphology. (a) $H \sim 4$ nm; full z-scale $\Delta z = 10$ nm, RMS roughness = 2.0 nm; (b) $H \sim 6$ nm; $\Delta z = 15$ nm, RMS roughness = 0.88 nm; (c) $H \sim 11$ nm; $\Delta z = 15$ nm, RMS roughness = 2.3 nm; (d) $H \sim 28$ nm; $\Delta z = 2.5$ and 1.5 nm, RMS roughness = 0.2 nm; and (e) $H \sim 32$ nm; $\Delta z = 2.5$ nm, RMS roughness = 0.32 nm.

by layer-by-layer or step-flow growth.

Since the lattice match of both $PbTiO_3$ and $SrRuO_3$ with $DyScO_3$ is nearly perfect, there are very little driving forces for a structural reconstruction. A surface roughening or a reconstruction driven by electrostatics, is the most logical scenario [128] for the initial behavior. A representative RHEED intensity profile and electron diffraction image of the growth of $PbTiO_3$ on $SrRuO_3$-electroded $DyScO_3$ are shown in Figure 5.3. In this case, there is an initial, very short reconstruction, as observed frequently in heteroepitaxial growth [128].

While the $SrRuO_3$ electrode layer ensures controlled electrical boundary conditions, it leads to a complication because of the initial growth morphology: Often, “wedding-cake” surface morphologies are observed. Moreover, the $SrRuO_3$ forms in-plane twins with a twin angle of only 0.2$^\circ$ (as explained below). Since at 10K, this only modifies the in-plane lattice parameters from 3.949 ($DyScO_3$) to values between 3.937 to 3.957 Å, we will assume that the strain is that imposed by the substrate and that we can safely use the $DyScO_3$ in-plane lattice parameters in all our calculations. But especially close to the critical thickness, the $SrRuO_3$ twinning can have some effect on the thin film.
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Figure 5.3: Characteristic RHEED pattern and RHEED intensity versus time of PbTiO$_3$ grown on SrRuO$_3$ on DyScO$_3$. The intensity change in the oscillating RHEED signal around t=1500sec is due to manual adjustment of the RHEED current.

Figure 5.4(a) shows the AFM images of an 11.2 nm PbTiO$_3$ film grown directly on DyScO$_3$; exactly the same thin film (grown simultaneously), but with an intermediate 20 nm SrRuO$_3$ electrode layer, is shown in Figure 5.4(b). While the film on DyScO$_3$ shows a stepped terrace morphology, that on SrRuO$_3$/DyScO$_3$ shows a wedding-cake morphology, similar to that of the SrRuO$_3$ layer beneath. Interestingly, while the film in Figure 5.4(b) shows a/c-domains, that in 5.4(a) shows 180° domains. If this is due to the different surface morphology, the different electrical boundary conditions or the twinning of the SrRuO$_3$ layer (see Figure 5.5), is still unclear to us. For this reason, we have both grown PbTiO$_3$ thin films directly on DyScO$_3$ and with a SrRuO$_3$ electrode buffer layer. Throughout this chapter the presence or absence of an electrode layer will always be indicated.
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Figure 5.4: AFM images of 11.2 nm $\text{PbTiO}_3$ a) directly on $\text{DyScO}_3$ and b) on 20 nm $\text{SrRuO}_3$ on $\text{DyScO}_3$. The full $z$-scale of image (a) is 1.6 nm(I) and 3 nm (II) and the RMS roughness 1.9 Å(I) and 2.9 Å(II). For image (b) the corresponding values are 5 nm(I) and 10 nm(II) and 5.5 Å(I) and 9.6 Å(II).

5.3 Results and discussion

5.3.1 $90^\circ$ domains

Even though the misfit strain at increased temperatures (and thus the misfit between $\text{DyScO}_3$ and cubic $\text{PbTiO}_3$) is only of the order of $10^{-3}$, misfit strain certainly plays an important role in this system due to the (tetragonal) misfit at room temperature. In the next section, we will show that for thicknesses above 12 nm, the $90^\circ$ domains in $\text{PbTiO}_3$ on $\text{DyScO}_3$ are well described by a model reported by Pertsev and Zembilgotov and based on that of Speck et al. [4], who calculated the stress fields due to the domains considering fictitious dislocations [5]. Here we show how these domains and their periodicities can be observed by AFM, p-AFM, XRD and TEM. Moreover, we
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Figure 5.5: RSM of the in-plane (HK0)-plane around the (100) Bragg peak of a 30 nm PbTiO$_3$ / 30 nm SrRuO$_3$ / DyScO$_3$ sample, measured at 10K in GID setup at DESY-beamline W1 ($\alpha_i = 0.3^\circ$). The SrRuO$_3$ is twinned in-plane with a twin angle below $0.2^\circ$. The PbTiO$_3$ is periodically $a/c$ twinned out-of-plane and is therefore observed as an $a$-domain with $c=4.15$ Å and a $c$-domain with $a=3.90$ Å. On top of that the domain periodicity can be observed as a superstructure along the (H00)-direction with $\lambda=28$ nm.

will describe how the small cubic lattice misfit can lead to highly periodic 90$^\circ$ domain structures.

Figure 5.5 shows an area of the reciprocal space contained in the (HK0)-plane around the (100) Bragg peak of a 30 nm PbTiO$_3$ thin film on SrRuO$_3$ on DyScO$_3$, which indicates the presence of $a$-domains ($c$ lattice parameter in-plane) and $c$-domains ($a$ lattice parameter in-plane). This domain structure is confirmed by out-of-plane RSMs and AFM images as presented in Figure 5.11. These RSMs show that the $a$ domains are a minority fraction and the $c$ domains a majority fraction. The domains twin with a characteristic twin angle $\alpha \approx 3^\circ$ and both domains tilt with respect to the DyScO$_3$ substrate. Superimposed is an in-plane superlattice which reflects the domain periodicity and can be observed by X-ray diffraction due to the large registry of the twinning. The AFM images confirm the periodicity of the domains and the domain volume fractions qualitatively. Since the narrow ridges are thinner than the wider stripes, they can be assigned to be the $a$-domains (with the smaller out-of-plane ($a$) lattice parameter).

In Figure 5.7 we show a typical analysis to obtain quantitative data from these AFM images: the periodicity can be obtained from the Fourier trans-
Figure 5.6: RSM of the out-of-plane (H0L)-plane around the (001) Bragg peak of a 30 nm PbTiO$_3$/30 nm SrRuO$_3$/DyScO$_3$ sample, measured at room temperature at DESY-beamline W1. The PbTiO$_3$ is periodically $a/c$ twinned out-of-plane and consists of $a$- and $c$-domains both tilted with respect to the substrate normal. On top of that the domain periodicity can be observed as a superstructure along the (H00)-direction with $\lambda$=28 nm.

form of an AFM image. As will be shown at the end of this chapter, the contrast due to the different domains is even more clearly observed by p-AFM, for which especially the phase contrast between the two differently oriented domains is evident.

The domain structure and periodicity is further confirmed by TEM as shown in Figure 5.8. All in all, we have three independent measurement techniques to determine the 90° domain periodicities, which have shown to be in good agreement with each other. Generally we have observed 90° domain periodicities along the pseudocubic axes. For thin films without any electrode or with only bottom electrode, the domain walls orient in similar fractions along the $[H00]_c$ and $[0K0]_c$ in-plane orientations. For thin films sandwiched between top and bottom electrodes (short-circuited), we observe a preferential domain wall orientation along the shortest pseudocubic $DyScO_3$ in-plane axis.

Based on the observation of these domain periodicities and domain frac-
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Figure 5.7: AFM topography images (full z-scale $\Delta z = 3$ nm) of a 28 nm $PbTiO_3$ film on (a) $SrRuO_3$ on $DyScO_3$ and (b) bare $DyScO_3$. (c) The Fast Fourier Transform of image (a) and a horizontal section in this image (d) show three repetitive features with different length scales can be distinguished and linked to the topography: 1 is the footprint of the terrace steps of the substrate, 2 represents the size uniformity of the wedding-cake islands. 3 represents a 31 nm unidirectional periodicity associated to the periodic $a/c$ stripe pattern. These directly observed $a/c$ domains at the surface have the same periodicity as that observed with XRD. Image (b) shows this domain pattern is superimposed onto the island morphology, suggesting that the pattern is not related to the growth mode. Careful analysis by AFM and XRD has shown that the domains order along the crystallographic axes, particularly with the 90° domain walls parallel to the short in-plane axis of $DyScO_3$. In combination with Figure 5.11 this can be assigned to $a/c$ domain formation.

...tions, in combination with the very good cubic lattice match, we have studied the 90° domain formation by a simple geometrical model [130]. Still, it should be kept in mind that 90° domains are considerably harder to analyze than their 180° counterpart, because the $a/c$-domains bring to bear the subtle problem of how to join the different crystal orientations across the domain wall while simultaneously maintaining some lattice relation along the film/substrate interface. Therefore, the presence of misfit dislocations and
other defects, which interfere with the domain pattern, can not be completely ruled out.

First, we have stepped over these problems and as a first approach, we have assumed that the 30 nm thin film of $PbTiO_3$ is coherent at the growth temperature and completely relaxed at room temperature. The fraction of $a$-domains needed to compensate the mismatch upon cooling down, can be estimated by imposing (Figure 5.9)

$$N_a c + N_c a = Nb$$ (5.1)
where $N_a$ and $N_c$ are the number of unit cells in the $a$-domain and $c$-domain respectively and $N$ is the total number of unit cells in one period. This is valid because $a < b < c$ and leads to an $a$-domain volume fraction of $\frac{N_a}{N} = \frac{b-a}{c-a} = 0.16$, in reasonable agreement with the experimentally observed ratio ($\sim 0.2$). This ratio was defined by Pompe and co-workers [131] as the coherence strain and is a key parameter to many calculations of equilibrium domain sizes (for example in the next section).

The TEM images (Figure 5.8; of films with thicknesses around 30 nm)

![Figure 5.9: Schematic of the $a/c$-domain formation. (a) shows the incorrect image of twin domains which do not share a twinning angle. This simple picture is an aid to understand equation 5.1. (b) is a similar picture, showing the twin angle between $a$- and $c$-domain and the requirement of lateral coherence.](image)

also reveal another interesting feature: all periodic $a$-domains have approximately the same width, regardless of the domain periodicity ($a + c$ domain). With AFM we have only been able to measure their size is below 9 nm (limited by the tip size), but TEM consistently shows an $a$-domain size of $\sim 7$ nm (we observe smaller and larger domain sizes, but not in periodic domains). A crucial step in our geometrical twinning model, is to assume lateral coherence between adjacent $c$-domains (see Figure 5.9). There is no clear-cut reason for this lateral coherence, but it is justified first, by the fact that there is perfect coherence at the growth temperature. And second, by the relatively low stiffness of $DyScO_3$, which allows both types of domains in $PbTiO_3$ to be tilted with respect to the $DyScO_3$ lattice, as observed in XRD. To accommodate the tilting at the substrate interface elastically, the domains will form as if they mainly share their (101) stress-free plane and are not so strongly clamped to the substrate. Still, the strain energy associated with the substrate-tilted domains interfaces will be minimized when the separate domains are as small as possible, which implies a minimum possible $a$-domain size $u^{\min}_a$ to match
two subsequent atomic rows of two contiguous \(c\)-domains, being

\[
 w_{a}^{\text{min}} = \frac{c}{\tan(\alpha)}
\]  

(5.2)

(see Figure 5.9). This gives, for fully relaxed values, \(w_{a}^{\text{min}} \approx 6.6\) nm, in excellent agreement with our experimentally observed values of \(\sim 7\) nm. This model is only a first approximation and a more advanced model is needed to understand the dependence of the domain periodicity with thickness. This has been proposed by Pertsev and Zembilgotov [5] and will be treated in the next section. It shows a critical thickness for \(90^\circ\) domain formation and postulates a minimum domain wall periodicity. The model is based on the free energy of a strained thin film, including the stress fields due to interface incompatibilities. This means that one of the missing factors of our first approximation is included: the stress field energy due to the coherency/incoherency of the different crystal orientations.

A different approach to the domain wall scaling between 12 and 30 nm, should not be left unmentioned. If one assumes that a mechanical model can be used to calculate a correct critical thickness, then a competition between electrostatic and mechanical energy for thicknesses between 12 and 30 nm, could give rise to more complex domain structures. In close correspondence with ferromagnetic closure domains, u-shaped domains are an obvious solution in the intermediate regime between clear \(180^\circ\) and clear \(90^\circ\) domains. In some theoretical papers, these kinds of domain configurations are proposed [132, 133], but it is very unlikely that these form. Distinction should also be made between the closure
domains described in these theoretical works and our observations, since in our case, unlike in the magnetic case, closure domains would imply lattice deformations with the $c$-axis in-plane at the interface (see Figure 5.10).

The formation of $u$-domains (see Figure 5.10) in thin films with $12 \leq H \leq 30$ nm is unlikely for two main reasons. First of all for a geometrical reason: dislocations usually start forming at the free surface which is impossible for the small 90° wedge. And second for an energetical reason: probably the energy barrier to form this 90° wedge at the film/substrate interface is too high. Although XRD and AFM do not rule out the existence of these 90° closure domains, we do not observe them in X-TEM. Instead we have observed an increase in 90° domains periodicity for low thicknesses with all techniques. This leads to the conclusion that Pertsev’s model (see section 2.6.3) is the most appropriate model to described the critical thickness and domain size scaling in this case.

5.3.2 Critical thickness for strain relaxation

Figure 5.11 and 5.12 show the difficulty in determining the critical thickness from our measurement data. For thicknesses below 12 nm we observe 180° domains and above 30 nm 90° domains are observed; for $12 \leq H \leq 30$ nm, the situation is unclear. At a thickness of 12 nm the domain pattern still depends strongly on the electrical boundary conditions (see Figure 5.4) but the first signs of 90° domain formation appear. Up to 30 nm the 90° domain periodicities show no clear relation with the film thickness, which they do above 30 nm. Qualitatively, this behavior is reproduced by the model by Pertsev and Zembilgotov as described in section 2.6.3. To our knowledge, this is the only account in literature that correctly treats domain patterns in thin films over a large range of thicknesses. They have shown that, especially for low thicknesses, the domain width does not scale monotonically with the film thickness, as reported for free crystals and films with $H \gg D$ by Roitburd [49] and verified experimentally [52, 134]. Moreover, the model by Pertsev and Zembilgotov predicts a thickness interval in which the domain size scales linear with the thickness and a minimum periodicity (an upturn in domain size with decreasing thickness). Qualitatively, our observations seem to be in good agreement with this model.
The core of this approach is to describe the stress fields associated with the domains by fictitious dislocations. Besides the domain wall formation energy and the misfit strain energy, this adds two more terms to the free energy expression. These are a fictitious dislocation ensemble representing the film/substrate interface stress field, and arrays of wedge disclinations modeling the stress fields due to the domain walls. Since the internal stresses are
calculated by summation over infinite arrays of fictitious dislocations and disclinations, numerical integration is required to calculate the free energy. The free energy can then be expressed as a function of two dimensionless parameters: the $c$-domain fraction $\phi$ and the periodicity-to-thickness ratio $\chi$. The shape of the energy landscape is determined by only 2 materials parameters, the normalized film thickness

$$H_n = \frac{HG(s_a - s_c)^2}{\sigma(1 - \nu)}$$

and, for small misfit strains, thus $s_a, s_c << 1$, the strain ratio $(1 + \nu)s_r$ with

$$s_r = \frac{b - a}{c - a}$$

also called coherency strain [131]. In the above equations, $G$ is the shear modulus of the thin film, $s_a = \frac{b-a}{a}$, $s_c = \frac{b-c}{c}$, $\sigma$ is the 90° domain wall energy and $\nu$ the Poisson’s ratio. With these formulae, the equilibrium values $\phi^*$ and $\chi^*$ can be determined by calculating the simultaneous energy minima $\frac{\partial F}{\partial \phi} = 0$ and $\frac{\partial F}{\partial \chi} = 0$ of the free energy expression $F$. Since we are only investigating one film/substrate system, we have applied this model only to the relative coherency strains applicable for $PbTiO_3$ on $DyScO_3$. By varying the $s_r$ values, the $c$-domain fractions we have observed (typically around 80%) are reproduced for $0.15 < s_r < 0.35$. Therefore, we have used two different values of $s_r$ corresponding to the misfit at room temperature ($\sim 0.20$) and at a high temperature of $440^\circ C$ ($\sim 0.27$), because the domain walls could “freeze in” at elevated temperatures, id est, could have an energy barrier for movement which is too high to overcome. A fixed $s_r$-value leads to a universal $\frac{D}{H}$ ratio which can be converted to real D and H values.

Pertsev and Zembilgotov have used materials parameters for which their calculations realistically model the 90° domain structure which appears due to the mechanical film/substrate interaction. The parameters are chosen such, that the electrostatic energy can be omitted. But in some limiting cases, this is not applicable, for example when $\phi \rightarrow 1$, which is equivalent to a single $c$-domain, the model is incorrect. Even more, when at the same time $\chi \rightarrow \infty$, large $\phi$-values already give rise to very large areas with out-of-plane polarization. In this case, electrostatics becomes important and 180° domains can
form within every $c$-domain. In Pertsev-Zembilgotov’s models, the absolute energy minimum is reached for large $\chi$ and $\phi = 1$, while a local minimum exists for low $\chi$ (typically around 1) and $\phi \simeq 0.75$. Since our observations as plotted in Figure 5.12 do not show this long periodicity and extremely high $c$-domain fraction, there must be an energetic penalty for domains with $\phi \to 1$ and $\chi \to \infty$, which is not included in the model. We have reproduced the calculations by Pertsev and Zembilgotov and applied them to our particular system. For relatively large thicknesses the previous problem does not play an appreciable role since the energy barrier between the local and global minimum is relatively large. But the energy landscape has an energy barrier that decreases for decreasing thickness: first a bi-stability appears and for very low thicknesses the local energy minimum has diminished. This last feature of the model is in accordance with observations of $180^\circ$ domains in very thin films, but for an appropriate description also the electrostatics for very small thicknesses should be included.

Our measurement data shows at least an upturn in periodicity for low thicknesses and a linear thickness-to-periodicity scaling for large thicknesses. Possibly, this upturn for low thicknesses is preceded by a bump in the periodicity, but our measurement accuracy does not allow a firm conclusion on this aspect. The first two features are reflected in the curve obtained using the experimental $s_r$ at room temperature and the bump can only be reproduced by the model for increased $s_r$ values, implying freezing of the domain walls at increased temperatures. The conversion from dimensionless parameters (see equation 5.3) to observed parameters, allows us to obtain the $90^\circ$ domain wall energy $\sigma$ (since the involved lattice parameters, the shear modulus $G$ and Poisson’s ratio are well-established values). In this way the experimental data can be fitted by either assuming room temperature bulk parameters and a $90^\circ$ domain wall energy of $\sigma = 27mJ/m^2$. Or assuming “freeze in” of the domain walls at an increased temperature. For “freeze in” at $440^\circ$C, the fit to Pertsev and Zembilgotov’s model corresponds to a $90^\circ$ domain wall energy of $\sigma = 17mJ/m^2$ (fitting the $H$-value of the upturn).

In both cases the $\frac{D_H}{\Pi}$-values from the simulation are larger (by approximately a factor of 2) than the observed values. This effect can not be accounted for by a different effective lattice parameter, since this is accompanied by $c$-domain fractions which are not in line with observations. Besides, the $\frac{D_H}{\Pi}$ ratio is increased when the $s_r$-value is outside the range $0.30 < s_r < 0.40$. 
The two most sensible reasons for the discrepancy between experiment and theory are an energy penalty for 180° domain formation which is not included in the model and a different energy cost of the dislocations than accounted for. The latter effect can be due to the low stiffness of the DyScO$_3$ substrate which possibly gives rise to different stress fields in substrate and thin film (considered equal in the calculations) or due to wedge-shaped domains which will give rise to a modified stress field.

Figure 5.12: (a) Domain period $D$ as a function of film thickness $H$ for 180° (red, left) and 90° (blue, right) domains in PbTiO$_3$ on DyScO$_3$. The vertical dotted line indicates the critical thickness for strain relaxation. The dashed line is a fit to the 180° domains with Streiffer’s model [53], room temperature materials properties and a domain wall energy density of 143$mJ/m^2$. The solid line is a fit to the 90° domains with Roytburd’s model [49], room temperature materials parameters and a 100$mJ/m^2$ domain wall energy density. (b) Idem, now with the dotted line being a fit with Roytburd’s model, room temperature materials parameters and a 100$mJ/m^2$ domain wall energy density. The upper dashed line is a fit with Pertsev’s model, materials parameters at 440°C and a 17$mJ/m^2$ domain wall energy density, the lower dashed line is the same fit with 37 nm subtracted from the periodicity. No physical explanation for this subtraction is readily available, but it results in a very good fit. The upper solid line is a fit with Pertsev’s model, materials parameters at room temperature and a 27$mJ/m^2$ energy density, the lower solid curve is the same fit with 41 nm subtracted from the periodicity.

In conclusion, the 90° domain wall energy we obtain from fitting the model to our data, assuming all other parameters unchanged, is certainly
below the value one obtains with Roitburd’s model (100 mJ/m²) and most likely also smaller than, although close to, the 35 mJ/m² calculated by first principles by Meyer and Vanderbilt [31] for domain walls at 0K. This deviation can be explained qualitatively by the experimental TEM analysis by Foeth et al. [135]. They have measured the temperature dependence of 90° domain walls by TEM, and show that the 90° domain wall energy density decreases as the temperature approaches $T_c$. This implies that first principles calculations (which are valid at $T=0$K) of the 90° domain wall energy by Meyer and Vanderbilt [31], are an upper limit of the domain wall energy that will be observed at room temperature. This corresponds qualitatively to our observation and leads to an estimate of the 90° domain wall energy $\sigma = 27(+3;-13)$ mJ/m². Meyer and Vanderbilt also calculated that 90° domain walls are mobile at room temperature (the energy barrier for movement is smaller than $k_B T$). This implies that using room temperature parameter values, is most appropriate. Figure 5.12 shows that when 90° domain walls are mobile down to room temperature, the model by Pertsev can successfully reproduce both the linear thickness-to-domain-size scaling and the upturn for low thicknesses, This would imply that the solid line in Figure 5.12, with a domain wall formation energy of $27 mJ/m^2$ is most appropriate.

5.3.3 Strain gradients

The broad $a$- and $c$-domain peaks in RSMs like Figure 5.13 give rise to the question of what this peak broadening is caused by. The spread in lattice parameters is ranging from pseudocubic ($a=c=3.987 \text{ Å}$) to nearly relaxed with bulk-like lattice parameters ($a=3.905 \text{ Å}$ and $c=4.156 \text{ Å}$). Both finite size effects and strain gradients can give rise to broadening. The latter causes a gradient along the tilting direction, whereas the former leads to broadening in the direction along which the crystal has a finite size.

Measurements in different diffraction planes and a careful analysis of the peak broadening can answer this question. Since the full width half maximum (FWHM) of the peaks in Figure 5.13 is rather ill-defined due to convolution with the in-plane superlattice, we will work the other way around and use the film thickness observed by X-ray reflectivity and the domain sizes observed by TEM and AFM to estimate the broadening.
Figure 5.13: RSMs around the (a) (002), (b) (103), (c) (001), and (d) (110) Bragg peak of a 30 nm PbTiO$_3$ thin film on 30 nm SrRuO$_3$ on DyScO$_3$. Superimposed to the measurement data around the Bragg peaks with an out-of-plane component, a model including crystal size broadening and a gradient in lattice parameters is plotted. The RSM around the (110) Bragg peak is measured with a grazing angle $\alpha = 0.3^\circ$ and shows that the in-plane lattice parameters do not fully relax to the bulk values. Besides the coherent peak, the main intensity corresponds to the $c$-domain with an intermediate in-plane lattice parameter between fully coherent and fully relaxed.

We know from AFM and TEM that the $a$- and $c$-domains are nano-sized crystallographic twins with their twinning plane $\sim 45^\circ$ tilted with respect to the substrate normal, and that the $a$-domains are much narrower than the $c$-domains. We also know their sizes. The corresponding finite size peak broadening is, thus, superimposed as solid lines in Figure 5.13(a). This shows that part of the broadening is caused by the finite crystal sizes. But the peak
broadening seems to stretch further, which would mean smaller crystal sizes than those observed by AFM or TEM. This implies that the large peak width is not only due to the crystal size broadening, and this is supported by several other observations.

First of all, the width of the peaks associated with the c-domains around the (002) Bragg peak, is reproduced with a lattice gradient ranging from about c=4.05 to c=4.11 Å (Figure 5.13(a), circles with dots in them are central lattice parameters; dots indicate the broadening range). The corresponding in-plane a lattice parameters observed in the (200) RSM range from 3.90 to 3.94 Å. And second, it is very unlikely for crystal size broadening that similar domains tilted in opposite directions have different peak widths, which is the case for the a-domains in our (103) scans (see Figure 5.13(b)). Using a similar model as for the SrTiO$_3$ substrate (chapter 4), this a-domain peak asymmetry is perfectly reproduced. Since the c- and a-domain are connected via their twinning plane, the array of lattice parameters in the c-domain, gives rise to an array of lattice parameters in the a-domain. But the a- and c-domain are not in the same strain state, so the a- and c-lattice parameters of the a-domain have to be verified separately. Using the (002) reflection and assuming peak broadening according to the domain sizes as observed by AFM and TEM, the a lattice parameter of the a-domain can still vary between a=3.90 and a=3.95 Å. And the (200) allows a spread of c lattice parameter from 3.97 to 4.07 Å. The overlaid model in Figure 5.13 is obtained by simply using volume conservation and gives lattice parameters of a=3.941 Å for the DyScO$_3$ substrate, from cubic (a = c =3.987 Å) to bulk (a=3.905 Å and c=4.156 Å) for the a-domains and from cubic to nearly bulk (a=3.927 Å and c=4.110 Å) for the c-domains. The twinning takes place in such a way that the a-domains tilt more than the c-domains with respect to the substrate. For the a-domains, the tilt angle ranges from 0° to 2.03° and for the c-domains from 0° to 1.12°. The twin angle α between the a- and c-domains is ~ 3°, in good agreement with the angle observed in TEM.

It should be noted that these odd-shaped satellites show some resemblance of diffuse scattering due to dislocations [136], but this effect is ruled out, first of all because of the good lattice match at the growth temperature,

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1Due to the anisotropic in-plane misfit, the in-plane lattice parameters do not have to be equal. Based on volume conservation, the observed $a_1$ and $c$ lattice parameters for the c-domain lead to an $a_2$ of approximately 3.96 Å which is within the range of observed in-plane lattice parameters. For the a-domain, this would give an in-plane $a= 3.99-4.04$ Å.
second because of the observation of $a$- and $c$-domains by AFM and TEM and finally because no dislocations are observed by TEM. All this leaves a lattice strain inhomogeneity as the main reason for the large spread in lattice parameters in both the $a$- and $c$-domains. The most likely scenarios for this inhomogeneity to be present are a strain gradients along the growth direction (vertical), or due to the $a/c$-domain structure, parallel to the substrate plane (horizontal). From XRD, this can not be resolved, but high-resolution transmission electron microscopy (HR-TEM) can provide this information.

First of all, the domain shape reveals the absence of a gradient in the vertical direction. We have shown before that wedge-shaped domains are present on very stiff substrates [137]. At the same time, this wedge-shape implies that a strain-gradient along the vertical can be present in these thin films. Since $PbTiO_3$ on $DyScO_3$ shows nearly parallel shaped domains, no clear strain gradient along the vertical is expected. Second, analysis software to map lattice deformations\(^1\), shows that a gradient is present at the obtuse ($\sim 135^\circ$) and acute ($\sim 45^\circ$) corners of the domains (Figure 5.14(a)+(b); we will call this “corner” gradients).

This “corner” gradient can be explained by a “rigid body” model of the temperature-dependent behavior of the system (see Figure 5.14(c)): The $PbTiO_3$ is grown on $DyScO_3$ in the cubic phase with zero misfit, giving no rise to dislocations whatsoever. Upon cooling down, the $PbTiO_3$ undergoes its phase transition to the tetragonal ferroelectric phase, and a misfit is developed, which has to be accommodated. Apparently, the temperature at which the misfit arises, is too low for dislocations to form and the misfit strain is accommodated by domain formation. Therefore, the system can be modeled by a simple block model, of rigid blocks attached to the substrate. When a misfit arises, this is accommodated by domain formation and the domain tilt with respect to the substrate and to each other in order to match at their interfaces. In reality, the domain walls move, but the observed stress fields can be very well explained by a model of rigid blocks of alternating sizes with fixed domain walls. The expected stress field from this model (Figure 5.14(c)) reflects very well what we observe: The stress fields upon deformation in the $a$- and $c$-domains, are compressive in the acute angle corners and tensile in the obtuse angle corners (T stands for tensile and C for compressive in Fig-

\(^1\)These images have been captured and analyzed by Etienne Snoeck using a modified version of GPA Phase 2.0 (HREM Research) and DigitalMicrograph (Gatan) software.
Figure 5.14: a+b) are out-of-plane lattice deformation maps, obtained from TEM images. Contrast corresponds to changes in the out-of-plane lattice parameter, i.e. in the direction perpendicular to the film surface. The numbers indicate the relative differences with respect to the $DyScO_3$ substrate. c) is a schematic representation of the way the inhomogeneous strain distribution comes about. At high temperatures, the $PbTiO_3$ is cubic. One can imagine virtual domain walls which are drawn by a dotted line. When the temperature is decreased, a tetragonality strain develops. When $a$ and $c$-domains form, the corners of the virtual blocks experience different strains, as if they were rigid bodies. This gives rise to an inhomogeneous strain distribution with a relatively more tensile (T) strain in the obtuse angles and a more compressive (C) strain in the corners enclosed by an acute angle.

We can observe this stress profile in the larger $c$-domains, but not in the small $a$-domains. Although this profile can not be observed in the $a$-domains, the profile in the $c$-domains and our XRD observations suggest that a similar stress profile is present in the $a$-domains.

This leads to the more general conclusion that nanometer-sized domains in this films can show rather inhomogeneous behavior because of this strain gradient. Since the tetragonality and polarization are thought to be coupled, this gives at the same time rise to a polarization gradient. And the observation of strain gradients in these nano-domains, sheds an interesting light on the recently proposed connection between the extrinsic piezoelectric effect in morphotropic PZT and the presence of nano-domains [28].

5.3.4 180° domains

For thicknesses below $\sim 12$ nm, 180° domain periodicities are observed in the RSMs. An overview of these periodicities in a 5 nm $PbTiO_3$ film on $DyScO_3$...
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Figure 5.15: Out-of-plane diffraction of a 5 nm thin film of PbTiO$_3$ on DyScO$_3$. Both images are in the same scale (and with logarithmic z-scale), so the equally spaced satellites in reciprocal space can be attributed to a superlattice.

and on SrRuO$_3$ on DyScO$_3$ is found in Figures 5.15 and 5.16.

The coherency between film and substrate is proven by the RSM around the (103) Bragg peak (Figure 5.15(b)), which shows that the in-plane lattice parameters of film and substrate are equivalent. Besides, all RSMs in Figure 5.15 and in Figure 5.16 show satellite peaks which are equally spaced in reciprocal space for all monitored diffraction orders. Therefore these satellites can be attributed to an in-plane superstructure: periodic 180° domains. The satellite spacing of the thin film of 5 nm PbTiO$_3$ in Figure 5.15 corresponds to a periodicity of 32 nm and in Figure 5.16 to a periodicity of 23 nm. Whereas the satellites around the 00L and H0L peaks only reveal the presence of an in-plane superstructure, the presence of equivalently spaced satellites around the peaks in the HK0-plane imply that the polarization has both an in-plane and out-of-plane component. This can be explained by looking at the way the structure factor determines the diffracted intensity (equation 3.9). Whereas zero in-plane displacement, as that in the 180° domains, gives rise to the absence of satellites in HK0 peaks (as observed in the previ-
ous chapter), an in-plane displacement leads to satellites around the peaks in the HK0-plane. Looking at the occurrence and orientation of these satellites in reciprocal space (see figure 5.17), two polar symmetries have found to be compatible with this result: the $r$-phase with the polar axis within the $(1\bar{1}0)$ plane and the $ac$-phase with the polar axis along the cubic [101]-direction. For PbTiO$_3$ on DyScO$_3$, both symmetries are not directly expected from theory, but are relatively close in the phase diagram (see Figure 2.4 and 2.5). Therefore, the presence of either of these two domain structures is not surprising and by looking at the phase diagram, one can conclude that the $r$-phase is most likely to be present. After all, the $r$-phase forms under a tensile misfit strain while the $ac$-phase requires a large strain anisotropy with compressive strain along one axis. However, we have no definitive proof to distinguish the $ac$- and $r$-phase from our experiments. Figure 5.17 shows the reasoning and the resulting satellite positions of both phases. This figure consequently leads to the conclusion that these thin films consist of $180^\circ$ domains of $ac$-phase or $r$-phase PbTiO$_3$, a symmetry not observed in bulk.

Independent of the crystal symmetry ($ac$ or $r$-phase), $180^\circ$ domains form in these thin films and their size scales with thickness as determined by equation 2.29. We have fitted the thickness $H$ and periodicity $D$ with this formula, assuming temperature dependence of the $180^\circ$ domain wall energy as given by 2.26. With the $180^\circ$ domain wall energy as the only adjustable parameter, we obtain $\gamma(0K) = 143mJ/m^2$ (Figure 5.12). This is is reasonable agreement with first principles calculations by Meyer and Vanderbilt [37], which give $\gamma(0K) = 132mJ/m^2$. 
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Figure 5.16: In-plane diffraction of a 5 nm thin film of PbTiO$_3$ on SrRuO$_3$ on DyScO$_3$. All images are the same scale, so the equally spaced satellites in reciprocal space can be attributed to a superlattice. Note that the spacing between the different scans is not to scale and the z-scale of all images is logarithmic.
Figure 5.17: The ac and r-phases (depicted in Figure 2.3), give rise to 180° domain patterns as depicted in this figure. The top (a) and bottom (c) rows show the real space domain patterns, split up in the top-view (HK0-plane; second column) and the side-view (H0L- or 0KL-plane; last column). The satellites in reciprocal space due to the periodicity of the domains in both the ac and the r phase are presented in the middle row (b) and can be deduced using the structure factor (equation 3.5) with the proper (hkl) and displacement components. This clarifies that the ac and r-phase cannot be distinguished with this method.

5.3.5 Electrical boundary conditions

In the previous sections, we have shown that the elastic energy and mechanical boundary conditions mainly determine the domain sizes in 90° domain patterns and the electrostatic energy and electrical boundary conditions do the same in 180° domain patterns. For this reason, most models include ei-
ther strain energy or electrostatic energy. Only recently, more complete models, like that by Nagarajan and co-workers [42], have included both. Here we will show that even for relaxed films, electrostatics is important. The electrostatic energy is not influencing domain sizes in a measurable way, but the electrostatic boundary conditions have a strong influence on the domain orientation.

As can be deduced from the free energy analysis in section 2.6, for thicknesses above the critical thickness for strain relaxation, the electrostatic energy plays a minor role on the domain size. The periodicity of the 90° domains can be fitted using the purely mechanical model by Pertsev [5]. But it is easily seen that a perfect 90° domain structure with stripe domains in open-circuit conditions is energetically unfavorable (Figure 5.18(a)): a charged surface will form and the question rises how this can be prevented. Basically, a checkerboard macroscopic structure superimposed to the microscopic stripe structure (Figure 5.18(b)) is formed. Although AFM images (Figure 5.7) show that the length scales of the micro- and macrostructure are relatively close to each other, this structure is present in PbTiO₃ on DyScO₃ and on SrRuO₃-electroded DyScO₃. Only short-circuiting with a top-electrode can prevent this structure from forming as can be seen in Figure 5.19. This figure shows that the 90° domain orientation is influenced by the electrical boundary conditions, but it also shows that the domain periodicity is not measurably

Figure 5.18: Schematic top views of thin films with 90° domain patterns. a) When the electrical boundary conditions do not play any role (e.g. in a short-circuited capacitor), the 90° domains can be ordered with all polarization up (or down). b) When the electrical boundary conditions do play a role (e.g. in an open-circuit capacitor), the 90° domains will form a macroscopic checkerboard structure 90° superimposed to the microscopic stripe pattern.
changed.

Figure 5.19: \( \phi \)-scans (as indicated in the accompanying schematic) of a 13 nm \( \text{PbTiO}_3 \)-layer sandwiched between two 10 nm \( \text{SrRuO}_3 \) electrodes on \( \text{DyScO}_3 \). While a) is in short-circuit (top and bottom electrode connected), b) is open-circuit (top and bottom electrode not connected). In the first case the periodicity has 2-fold rotational symmetry, whereas in the latter case it has 4-fold rotational symmetry.

This observation poses the interesting question of whether the anisotropy of the substrate is reflected in the crystal structure of short-circuited \( \text{PbTiO}_3 \) thin films, in their domain structure or in both. If the lattice would be strained to the substrate in one direction and relaxed in the other, this would, to our knowledge, be the first observation of so-called monotaxy. But the broad peaks and the superimposed superlattice do not allow us to determine whether the \( \text{PbTiO}_3 \) lattice has anisotropic in-plane lattice parameters and, therefore, an orthorhombic symmetry. The peak positions in Figure 5.20, indicate that the film is neither fully strained nor totally relaxed in both directions. Along the (0K0)-direction, there are two options: the \( \text{PbTiO}_3 \) relaxes but does not form a periodic pattern, or it does not relax at all (remains strained). This means that the film is partially relaxed and we can not determine the in-plane crystal symmetry of \( \text{PbTiO}_3 \) on \( \text{DyScO}_3 \) for these intermediate thicknesses.
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Figure 5.20: RSMs of a 16 nm PbTiO$_3$ layer sandwiched between a 46 nm SrRuO$_3$ bottom electrode and a 10 nm top electrode on a DyScO$_3$ substrate, around the (a) (001) and (b) (110) Bragg peaks and (c) around the (110) Bragg peak of a 13 nm PbTiO$_3$ layer sandwiched between 10 nm SrRuO$_3$ electrodes on a DyScO$_3$ substrate. In both cases, the long in-plane axis of DyScO$_3$ ([001]$_o$) is along the [H00]-direction. The misfit between PbTiO$_3$ and this axis is the largest of the two in-plane misfits, which explains why along this direction the thin film relaxes and forms a/c-domains.

When PbTiO$_3$ is grown on SrRuO$_3$-electroded DyScO$_3$, macroscopic electrical characterization of the PbTiO$_3$ is hindered due to the same arguments as mentioned in section 3.6 and 4.4.3. Although resistances up to MΩ and dielectric constants of the order $10^2$ have been measured, the main problem in this case was the large variation and instabilities in the macroscopic measurements, probably due to the electrical contact quality. This problem is circumvented by piezoresponse-AFM (p-AFM). The qualitative ferroelectric properties have been determined and the 90° domains show contrast in p-AFM as expected. A very well defined periodicity is clearly observed. Imperfections in the film surface (the bright spots in Figure 5.21(b)) do not noticeably influence the piezoresponse signal. And the contrast in the phase image (Figure 5.21(a)) is due to the domain orientation. The $a$-domains are dark, while the $c$-domains are intermediate. The bright areas disappear when the contact force applied to the tip is increased. This indicates that this signal is probably
due to adsorbates like $H_2O$.

![Figure 5.21: Piezoresponse- and normal AFM images of a 31 nm $PbTiO_3$ film on 110 nm $SrRuO_3$ on $DyScO_3$. The piezoresponse images of the PR-phase (a), normal height (b) and PR-amplitude (c) show a periodicity of $\sim 34$ nm, most clearly observed in the PR-phase. The full z-scale of a) is 5 nm and since no calibration of the PR-signal has been performed, the z-scales of b) and c) are physically irrelevant. d+e) are tapping mode AFM images of the same sample with full z-scales of 3.5 and 8 nm. For these image we would like to acknowledge ScienTec France where these images have been taken on Agilent 5100 and 5500 AFM systems.](image)

5.4 Conclusions

We have found a thermal treatment for $DyScO_3(110)_o$. This results in a terrace structure with unit cell steps. The termination can not be controlled, for which a chemical treatment would be required. Efforts in this direction have remained fruitless and we stress that this will be difficult due to the small difference in chemical etchability between $DyO$ and $ScO_2$. The surface of $DyScO_3(110)_o$ is polar which leads to interface roughness, especially for very thin films. We show that $SrRuO_3$ grows in an island growth mode up to a thickness of $\sim 50$ unit cells and above this thicknesses, a terrace structure with unit cell steps reappears.

When $PbTiO_3$ is grown on $DyScO_3$ or $SrRuO_3$-electroded $DyScO_3$, $90^\circ$ domains form for thicknesses $H \gtrsim 12$ nm. Between 12 and 30 nm the scaling
between thickness and domain periodicity is non-monotonic and for thicknesses $30 \leq H \leq 100$ nm, the domain sizes scale linearly with film thickness. In literature, this thickness and domains size regime is not well accounted for: Although it is generally believed that $90^\circ$ domains scale with thickness following a $\sqrt{H}$ law, this has been shown to work only when $H \gg D$ [49]. For $D \approx H$, the only model available is that of Pertsev and Zembilgotov [5].

We show for the first time that there is a linear relationship between $D$ and $H$ in a range of thickness from 30 to at least 100 nm, which experimentally confirms the model by Pertsev and Zembilgotov. Pertsev and Zembilgotov’s model predicts an upturn in the domain size for sufficiently small thickness, which implies a minimum in the domain size vs. thickness curve. We have observed such minimum for a thickness, approximately equal to the domain period and equal to $\sim 30$ nm. Consistent with the $a/c$ domain ratio expected for the $\text{PbTiO}_3/\text{DyScO}_3$ system, the width of the $a$-domains is as small as 6-7 nm. This very small size for the $a$-domains is systematically found in all the samples with periodic domains. We have been able to explain this by a simple geometrical model that imposes lateral coherence across the domain walls and neglects the clamping at the substrate interface. The success of this too simplistic model could be explained by the low stiffness of the $\text{DyScO}_3$ substrate and the nearly-perfect lattice match at the growth temperature.

We have not grown thin films of $\text{PbTiO}_3$ on $\text{DyScO}_3$ with larger thicknesses, but the model by Pertsev predicts that for increased thicknesses, the domain size will scale Roitburd-like with $D \sim \sqrt{H}$ behavior. We have shown that the $90^\circ$ domain wall energy as deduced by fitting Roytburd’s law [49] to our data, results in very high $90^\circ$ domain wall energy densities (100 mJ/m$^2$). Fitting Pertsev’s model results in $90^\circ$ domain wall energy densities $\sigma = 27(\pm 3)\text{-}13$ mJ/m$^2$, just below theoretical predictions [31], as expected from earlier observations [135].

In addition, the crystal lattice in thin films with thicknesses $12 \leq H \leq 100$ nm is inhomogeneously strained. In XRD these thin films show a strain gradient which is confirmed by TEM. Moreover, out-of-plane lattice deformation maps, obtained from TEM, show that the inhomogeneity is caused by strain gradients in the obtuse (tensile) and acute (compressive) angles of every domain.

For $\text{PbTiO}_3$ on $\text{DyScO}_3$ with $H \leq 12$ nm, we have observed $180^\circ$ domains. The crystal symmetry of these films is corresponding to either the $ac$- or $r$-
phase. In any case the $PbTiO_3$ has a symmetry that is not observed in bulk and that can be qualified as a “bridge” phase between either the $a$ and the $c$-phase or the $aa$ and the $c$-phase. The $180^\circ$ domain size scales with film thickness and from this scaling we have deduced a $180^\circ$ domain wall energy $\gamma(0K) = 143mJ/m^2$, in very good agreement with first principles calculations [37].

Subsequently, we have studied the electrical properties and the influence of the electrical boundary conditions of thin films with $90^\circ$ domains. We have shown that the domain orientation in partially relaxed thin films with $90^\circ$ domains, is sensitive to electrical boundary conditions. For short-circuited thin films (in which there is no influence of the electrostatic energy), we have observed periodic $90^\circ$ domain ordering only along the large misfit direction (the difference in in-plane lattice parameters of the substrate is only 0.003 Å). We are unable to distinguish whether the two in-plane lattice parameters of the $PbTiO_3$ thin film are different, which would mean a lowering of the symmetry (to orthorhombic) and the first observation of so-called monotaxy (the one-dimensional equivalent of epitaxy).

Finally, we would like to point out that, especially these relaxed thin films with nanometer-sized periodical polar domains, which have the polarization alternating in-plane and out-of-the-plane, can be very suitable as a polar template to preferentially deposit materials on surfaces with different polarization and produce periodic nano-structures [138].