Control of periodic ferroelastic domains in ferroelectric Pb$_{1-x}$Sr$_x$TiO$_3$ thin films for nano-scaled memory devices

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Chapter 3

Thickness scaling of ferroelastic domains in PbTiO$_3$ films on DyScO$_3$

3.1 Abstract

In this chapter we investigated the thickness dependence of the ferroelastic domains of PbTiO$_3$ films grown on (110)-DyScO$_3$ with low thicknesses (up to 240 nm), which fall outside the validity range of the square root law proposed by Roytburd [1]. For slow-grown films, the data revealed the linear thickness dependence predicted by Pertsev & Zembilgotov (using a complete elastic description) [2]; while a 2/3 scaling exponent found for fast-grown films. Extremely long domains running all through the samples was observed in the latter case, compared to the short domains observed in slow-grown films. These differences were ascribed to the in-plane anisotropy for domain wall nucleation, which was likely caused by the anisotropic elastic modulus of the substrate.

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3.2 Introduction

The response of domains and domain walls crucially affects (and often determines) the dielectric properties and switching behavior of ferroelectrics. This is particularly important in thin films where the ferroelectric (180°) and ferroelastic (non-180°) domains walls are formed in order to comply with the stringent electrical (large depolarizing field) and mechanical (substrate mismatch strain and clamping) boundary conditions.

The size of the domains increases with increasing film thickness as a result of the balance between the depolarizing field energy (for 180° domains) [3], or elastic strain energy (for non-180° domains) [1], and the domain wall formation energy. Thus, the thinner the films the larger the domain wall density and the greater the influence of the walls on the ferroelectric properties. Moreover, domain walls break spatial symmetry and could add new functionalities to the films when present in large amounts [4]. It is therefore most relevant to have good control of the domain formation and the density of domain walls [5].

Domain formation in ferroelectrics has been largely studied [1, 2, 4, 6–15]. In order to adapt to the substrate and to locally minimize the mismatch strain or the depolarizing field, the domains form in a periodic manner [7,8]. It is known that there is a quadratic dependence, $W \propto d^{1/2}$, of the domain width ($W$) with the crystal thickness ($d$). In ferroelastic domains (typically 90° domains), this $d^{1/2}$ dependence is an approximation in the regime of $d \gg W$ [1]. For smaller thicknesses, a linear dependence has been predicted by Pertsev and Zembilgotov (P&Z) [2] but, to the best of our knowledge, it has not been experimentally confirmed yet.

In this chapter we investigated the thickness dependence of the width of ferroelastic 90° domains (a/c twins) in the lower thickness regime using PbTiO$_3$ films grown on DyScO$_3$ substrates. This combination has chosen because there is a very small lattice mismatch between film and substrate at the growth temperature. This minimizes the formation of defects during growth. As the films are cooled down strain develops and can be relaxed by forming a/c domain walls. The absence of defects allows these domains to form in a very periodic fashion [13,16]. Interestingly, when the films are grown by pulsed laser deposition at high laser frequencies (10Hz), extremely long domains are formed along one of the in-plane crystallographic directions, despite the very small difference in lattice parameters and thermal expansion coefficient of both in-plane lattice parameters of (110)-DyScO$_3$. 
3.3 Experimental

The thin films were grown on (110)-oriented DyScO$_3$ substrates [17] by Pulsed Laser Deposition (PLD) from PbTiO$_3$ targets with 4 atomic % excess lead. Orthorhombic (110)-DyScO$_3$ substrates were obtained from CrysTec GmbH. The two in-plane lattice directions were then [1-10] and [001], named as a-axis and b-axis, respectively. The substrates exhibit double-terminated surfaces (with both DyO and ScO$_2$ surface layers) and they were chemically and thermally treated to get a single ScO$_2$ termination [18]. This allows growing high quality SrRuO$_3$ layers, since SrRuO$_3$ preferentially nucleates in that surface [19]. An 8 nm-thick SrRuO$_3$ layer was grown between the film and the substrate. The SrRuO$_3$ layer is fully strained and acquires the lattice parameters of the substrate. The growth was monitored by Reflection High-Energy Electron Diffraction (RHEED). The RHEED intensity oscillations, together with X-ray reflectivity, were used to determine the thickness of the films. Two series of films were grown at two different growth rates, using laser frequencies of 1Hz and 10 Hz. The rest of the growth parameters were tuned to minimize the film roughness and maximize the RHEED intensity oscillations: the laser fluence, spot size at the target, substrate temperature, substrate-target distance and O$_2$ pressure in the chamber were 1.5 J/cm$^2$, 0.8 mm$^2$, 570°C, 48 mm and 0.13 mbar, respectively, for the 1 Hz series, and 2.0 J/cm$^2$, 0.8 mm$^2$, 580°C, 50 mm and 0.06 mbar, respectively, for the 10 Hz series. These have resulted in deposition rates of about 1 unit cell per 55 sec and 7 sec. We will refer to these series as slow-grown and fast-grown, respectively. Scanning Transmission Electron Microscopy (STEM) experiments in High Angle Annular Dark Field (HAADF) were carried out in a probe-corrected FEI Titan 60-300 microscope operated at 300 kV with a probe size of 1Å. Atomic Force Microscopy (AFM) was performed using a VEECO (now Bruker) Dimension V microscope. AFM images of sample preparation are shown on Figure 3.1.

3.4 Results and Discussion

(110)-DyScO$_3$ does not have a totally squared in-plane lattice, however, the difference between the two in-plane parameters is typically considered too small to give rise to anisotropic domain formation. In agreement with this, for the slow-grown samples, we found domain walls along both in-plane dir-
Figure 3.1: Sample preparation stages. Atomic Force Microscopy (AFM) images of a) single terminated (110)-DyScO$_3$ substrate, b) an 8 nm-thick SrRuO$_3$ layer grown on the top of the substrate and c) a 200 nm PbTiO$_3$ thin film grown on the top of SrRuO$_3$ layer.

The domains organize in bundles with perpendicular domain walls forming four-fold symmetric patterns [13, 20](see Figure 3.2a). However, for the fast-grown samples, extremely long domain walls were observed along the a-axis of the substrate, as shown in Figure 3.2b; while shorter, less straight and less periodic domain walls were observed perpendicularly, along the b-axis. The length of the long domain walls (||a) seems to mainly be limited by the length of the sample and only in rare cases a domain wall starts or ends at one of the perpendicular (||b) walls. STEM revealed that, despite the apparent differences between the sets of perpendicular walls in the AFM images of the fast-grown samples, both cross-sections consist of a/c twins (Figures 3.2c-3.2d).

In order to clarify the origin of the observed anisotropy, we have looked
at the effect of the substrates terraces on the domain formation. PbTiO$_3$ thin films were grown on DyScO$_3$ substrates with different direction of miscut, that is different orientation of the substrate steps: forming $0^\circ$, $45^\circ$ and $90^\circ$ with respect to the in-plane crystallographic directions. The domain structures created on two substrates with differently-oriented terraces are shown in Figure 3.3. It is observed that the a/c domain walls form along the a-axis of (110)-DyScO$_3$, independent on the orientation of the substrate terraces.

Therefore, the long domain walls $||a$ must form in response to the lattice strain experienced along the b-axis. At the growth temperature the
misfit strain along the a-axis is close to zero (well below 0.1%); while the misfit strain along the b-axis is slightly tensile (0.12%). Lattice parameters were taken from [27] and [17] and are shown in Figure 3.4. The difference between the fast-grown and slow-grown samples can be explained if we
assume that the bulk phase transition is shifted upwards, already under such relative small strain values, such that the material grows in the ferroelectric phase [21, 22]. Then, differences in nucleation of the domain walls along both in-plane directions could explain the observed differences in domain formation. Because during fast growth the sample is far from thermodynamic equilibrium (higher supersaturation), if the energy barrier for nucleation of domain walls \( ||b \) was larger than that of the walls \( ||a \), the formation of the former walls would be hampered. Different energy barriers for domain wall nucleation can originate in the anisotropic elastic properties of DyScO\(_3\) substrates, recently reported [23]. Slow-growth conditions will better reflect the equilibrium phase diagram of the system and its quite small misfit strain anisotropy.

Figure 3.4: Lattice parameters as a function of temperature of bulk PbTiO\(_3\) [27] and DyScO\(_3\) [17].

That also implies that, during fast growth, the critical thickness for nucleation of domain walls would depend largely on the in-plane direction. This is, indeed, consistent with our observations: AFM pictures of PbTiO\(_3\)
films with different thicknesses are reproduced in Figure 3.5. It shows that for a given film, the density of walls \( \parallel b \) is smaller than the density of walls \( \parallel a \). In addition, while the walls \( \parallel a \) are visible for thicknesses above 15 \( nm \), the walls \( \parallel b \) are only observed above 50 \( nm \).

We now look at the thickness dependence of the domain width. For too thin films, \( a/c \) domains are not expected, however, at these very small thicknesses the increased depolarizing field induces 180° domains [24, 25]. A crossover from 180° to 90° domains was thus expected at a particular thickness. In this case the crossover between 180° and 90° domains is found at \( d \sim 10 \) \( nm \) but only for \( d > 15 \) \( nm \), we were able to observe well-defined, ordered \( a/c \) domains [22, 26]. Figure 3.5 shows the high degree of ordering of the \( a/c \) domains (with walls \( \parallel [a - axis] \)) in PbTiO\(_3\) on DyScO\(_3\) and the robustness of the domain size across the film, allowed us to monitor their size not only by local probe techniques, such as AFM and piezo-AFM, but also by x-ray diffraction (XRD) [13, 20]. Typically, the best sensitivity was obtained using XRD for the relatively thinner films (Figure 3.5a) and using AFM for the thicker films (Figure 3.5 b-c).

The data collected for all the samples, including slow-grown and fast-grown samples, are summarized in Figure 3.6, showing the domain size \( (W) \) as a function of the film thickness \( (d) \) in a double logarithmic scale. The slow-grown films follow the trend predicted by P&Z [2]: a minimum introducing a change of trend at the lowest thicknesses and a linear \( W(d) \) dependence for thickness \( 30 \) \( nm < d < 100 \) \( nm \). A quantitative fit was not successful and the best possible fit (using \( T = 440^\circ C \) and \( \sigma = 19 \) \( mJ/m^2 \)) was off by 41 \( nm \) (better seen in linear scale on Figure 3.7).

In Figure 3.7, the domain periodicity is plotted versus film thickness using the P&Z model applied to our slow-grown PbTiO\(_3\) films on (110)-DyScO\(_3\). The actual fitting parameters in the model are the domain wall energy density \( (\sigma) \) and the so-called relative coherency strain \( (S_r) \), which depends on the lattice mismatches of the two tetragonal axes \( (S_a \) and \( S_c) \) with the substrate. \( S_r \) is temperature dependent, as the thermal expansions of the film and substrate differ and, thus, we used the temperature of formation of the final domain configuration as the experimental input parameter, calling it freezing temperature \( (T_{fr}) \). A relatively high temperature \( (440^\circ C) \) has been chosen for the fits, based on experimental observations. For experimental temperature values please read Chapter 4.

We used \( \sigma \) as a second adjustable parameter to try to fit our slow-grown data (grey symbols) with the P&Z model [2] since this is the data set that
Figure 3.5: The top panels show AFM images (5µm × 5µm) of PbTiO$_3$ layers on DyScO$_3$ with different thicknesses, d, and average domain periods, W: a) d=50 nm, W=80 nm; b) d=80 nm, W=105 nm; c) d=180 nm, W=197 nm. The substrate b-axis is horizontal in all three images. The method used to determine the domain size is shown for each sample in the bottom panels: d) X-ray reciprocal space mapping around the (002)$_c$ reflection shows the intensity oscillations due to periodic domains. Axes are in units of $k_o = 2\pi/\lambda$, being $\lambda$ the x-ray wavelength. The color scale represents log(I). A linear scan along the dashed line (rocking curve) is plotted as a solid curve showing the intensity maxima from whose $k||$ values the domain periodicity is obtained; e)-f) AFM auto-correlation images of b)-c), respectively, and their Fast Fourier Transforms (in the insets).
Figure 3.6: Log-log plot of the observed domain period, $W$, as a function of film thickness, $d$, for $90^\circ$ domains in PbTiO$_3$ thin films grown on SrRuO$_3$-buffered DyScO$_3$ substrates. The data for the slow-grown and fast-grown samples are plotted as open and closed circles, respectively. The red line is a linear fit for the fast-grown films with $d \geq 20$ nm. The dashed blue line corresponds to the $n=1/2$ exponent [1], and uses the materials parameters at $T=480^\circ$C and a domain wall energy of 21 mJ/m$^2$. The dashed green line is obtained subtracting 41 nm from the domain period produced with the P&Z model [2] using the lattice parameters at 440$^\circ$C and a domain wall energy $\sigma=19$ mJ/m$^2$ (see Fig. 3.7 and description to it).

should show a better agreement with equilibrium models. We found that no set of realistic input parameters ($T$, $\sigma$) reproduces the experimental data, however we find a similar linear slope and a similar position for the curve minimum for $T_{fr}=440^\circ$C and $\sigma=19$ mJ/m$^2$, a value that is in agreement with the literature values for $90^\circ$ domain wall formation energies. Quantitatively, the experimental domain periodicities for slow-grown samples were 41 nm smaller than those predicted by P&Z, as it can be seen in Figure 3.7 (the thin solid line curve is exactly the thick solid line curve shifted down by 41nm).
Figure 3.7: Linear $W$ vs. $d$ plot showing the best qualitative P&Z fit to the slow-grown data (same slope and same minimum position) obtained for $T_f = 440\,^\circ$C and $\sigma = 19\, \text{mJ/m}^2$ (thick line). The experimental data can only be reproduced by an overall down-shift of the curve of 41 nm (thin line).

The lack of quantitative agreement between the data and the P&Z model is not surprising. Firstly, the data do not correspond to the equilibrium domain configuration and, secondly, several elements are missing in the P&Z model. This model comprises a rigorous calculation of the elastic energy of the system, considering a fictitious array of dislocations and disclinations that mimic the same strain fields as those present in domain formation. It is thus a purely mechanistic model. Important missing ingredients are the strain dependence of the order parameter and the depolarization field, which would induce ferroelectric 180° domain formation at low thicknesses instead of a monodomain state. Moreover, it is assumed in the model that the strain is fully released by formation of dislocations/disclinations (or domain walls), while the films are often not fully relaxed after domain formation.
For the fast-grown samples, the experimental domain size does not follow the predicted evolution, since it does scale neither as $d^{1/2}$ [1] nor linearly with $d$ [2]. Instead, fitting the data in Figure 3.6 for the fast-grown samples resulted in an exponent $n = 0.68 \pm 0.03$ ($n \approx 2/3$), thus experimental results exhibit a behavior in between the classic Roytburd’s square-root law and Pertsev’s linear law. One possible explanation is that we were probing the crossover between these two regimes. One can argue that, indeed, for the lowest thicknesses ($d < 40$ nm) the data are not inconsistent with a $n= 1$ exponent; however, for the large thickness regime, there is no indication of approaching $n= 1/2$. Intermediate scaling exponents $1/2 < n < 1$ have been reported before for fractal domains [28] but clearly the wall roughening mechanism cannot be invoked here, since our domains are perfectly smooth. Fractional scaling exponents have also been extracted from switching dynamics [29], and thus it may be the case that our exponent reflects the dynamics of domain nucleation. Indeed, it rather looks like we are seeing a law that differs from that predicted by equilibrium models, something unsurprising for such fast-grown films.

According to the usual description of the energy balance between domains and domain walls [12], the domain size is found by minimizing the sum of the elastic energy stored within the domains plus the energy of the domain walls. This minimization leads to the well-known Kittel formula, $W = \sqrt{\frac{\eta}{U} d}$, where $U$ is the volume energy density of the domains and $\sigma$ the energy per unit area of the walls. In the standard derivation of Kittel’s law it is assumed that $U$ and $\sigma$ are independent of the thickness $d$, but this is not a realistic assumption for very thin films where strain is only partially relaxed or when structural and compositional gradients [30], and competing relaxation mechanisms with different critical thicknesses (such as dislocations and twinning) introduce a thickness dependence on the energy densities. Within the thickness range of this study, the domain size scales as a power law, which implies that the energy densities can also be expressed as power laws: $U = u d^K$ and $\sigma = \eta d^K$ and Kittel’s law thus becomes $W = \sqrt{\frac{\eta}{u d^{(-K+L+1)/2}}}$. Comparing with the experimental result, $W \propto d^{2/3}$, we get that $L-K=1/3$.

The exponent $K$ that determines the volume energy density as a function of thickness has been amply studied by the semiconductor thin film community. The equilibrium models for strain relaxation and formation of dislocations [31–33] give rise to a residual strain that is inversely proportional to the layer thickness ($\varepsilon \propto d^{-1}$), which, given that elastic energy is
proportional to the square of the strain (Hooke’s law), implies that $K=-2$. On the other hand, it has also been shown that during epitaxial growth, the non-equilibrium kinetics of dislocation formation can lead to $\varepsilon \propto d^{-1/2}$ (or $U \propto d^{-1}$) [34]. In contrast, much less is known about the value of $L$ that determines the thickness dependence of the domain wall energy. Since the energy cost of the walls is proportional to the spontaneous strain in the domains, a thickness dependence of the residual strain must also result in a thickness dependence of the domain wall energy. If we accept $-2<K<-1$ as the two limiting cases for the volume energy density, then compliance with our empirical results requires $-5/3<L<-2/3$ for the equilibrium and non-equilibrium growth scenarios, respectively.

### 3.5 Conclusion

We investigated the thickness scaling of the domain periodicity of slow-grown and fast-grown samples. We showed that, for films grown on (110)-DyScO$_3$, working out of equilibrium with well-defined conditions allows a large degree of control of the domain width and morphology, beyond the predictions of thermodynamical models. This is enabled by the differences in domain wall nucleation along different crystal in-plane directions, which is most likely caused by the anisotropy in the elastic modulus of the substrate.
THICKNESS SCALING OF FERROELASTIC DOMAINS IN PBTIO₃ FILMS ON DYSCO₃
Bibliography


