Structural domains in thin films of ferroelectrics and multiferroics
Venkatesan, Sriram

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

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

Publication date:
2010

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
CHAPTER 5

Nanoscale domain evolution in thin films of multiferroic TbMnO$_3$

Control of the domain structure in multiferroic thin films is of crucial importance in order to gain access to their functional properties. This chapter presents a detailed investigation of the nano-domain evolution in thin films of multiferroic TbMnO$_3$ grown on (001)-SrTiO$_3$ substrates. Thin films with thickness ranging from 2 to 140 nm were grown at 0.25 mbar and 0.9 mbar oxygen partial pressures. Transmission electron microscopy is used as the main tool to characterize these domains with supportive information obtained from X-ray diffraction.

5.1. INTRODUCTION

Perovskite manganites with a strong coupling between spontaneous electrical (P) and magnetic (M) polarizations are a topic of current interest because of their fundamental scientific importance and prospective technological applications in magnetoelectric (ME) devices [1,2]. Bulk multiferroics of rare earth substituted manganites, RMnO$_3$ (R= Rare Earth element), display two crystal structures depending on the size of the R ion: orthorhombic for R=La-Dy and hexagonal for Ho-Lu. The orthorhombic TbMnO$_3$ (TMO) is receiving much attention because of its coupling between the magnetic spin structure and electrical degrees of freedom resulting in a strong ME effect [3]. At room temperature, bulk TMO has a perovskite crystal structure (space group Pbmn) with lattice parameters $a = 5.2931$ Å, $b = 5.8384$ Å, $c = 7.4025$ Å [4]. Below $T_N \cong 42$ K, TbMnO$_3$ shows a sinusoidal antiferromagnetic order, which appears from a subtle balance between ferromagnetic (FM) and antiferromagnetic (AFM) exchange constants between different Mn neighbours. Additionally, below $T_{FE} \cong 28$ K the spin arrangement changes into a

This chapter is published as
spiral structure, which breaks inversion symmetry, and ferroelectricity comes into play
with a polarization parallel to the c axis. Thus, even though TMO does not exhibit net
magnetization, it has been considered an interesting candidate for multiferroic devices
based on exchange-bias [3,5,6].

However, recently, an interesting development has taken place: TbMnO$_3$ and other
manganites in thin film form exhibit a net magnetic moment when strained on a cubic
substrate [7-9]. Different origins have been proposed for the net magnetization; two of
these are the most prominent ones: 1) epitaxial strain changes the balance between AFM
and FM interactions, inducing a net magnetization [8] and 2) ferromagnetism originates
at the domain walls, which give rise to a different structure than that of the domains
themselves and are present in large quantities in the thin films [10]. To discriminate
between these two mechanisms is not easy because of the difficulty to image magnetism
at such small length scales and because of the direct relationship between the density of
domain walls and the epitaxial strain [11]. These developments indicate that, for a proper
understanding of the properties of the thin films, knowledge of the domain structures is a
prerequisite.

Depending on the difference between the substrate’s and film’s lattice parameters,
tensile and/or compressive strains can be imposed onto the film. This situation holds true
only upto a specific critical thickness, which varies per system depending on the misfit
strain accommodation mechanisms and of the substrate-film combination [12]. A further
increase of the film thickness will result in loss of coherency strains of the film and
relaxation starts, for instance, by formation of misfit (and/or threading) dislocations, or by
breaking into different (mutually relaxing) domains. Domain boundaries break inversion
symmetry and thus, in ferroic systems, they show different properties than the domains
themselves. Accumulation of defects, or the particular local structure of the walls, can
also give rise to different transport properties [13]. Therefore, the control of the domain
structures in thin films is of crucial importance to increase and tune the functionality of
ferroic thin films. In the present work we investigate the nanoscale evolution of domain
structures present in TMO films grown on SrTiO$_3$ substrates with increasing thickness.
and we show that it is possible to rationalize the observed structures and their evolution as a direct result of the epitaxial strain.

Perovskite TMO thin films with orthorhombic structure have been investigated scarcely until now. Figs.5.1a-b show the atomic model of the unit cell of bulk orthorhombic TbMnO$_3$ and its projection along the $c$ axis, respectively.

![Figure 5.1: Atomic structure model showing (a) unit cell of (bulk) orthorhombic TbMnO$_3$ (b) projection of the (bulk) orthorhombic TbMnO$_3$ crystal along its $c$ axis and (c) the top view of cubic SrTiO$_3$, representing the surface on which the TbMnO$_3$ thin films grow.](image)

Fig.5.1c shows the atomic model of the (001) plane of cubic SrTiO$_3$; this is the surface on which the TbMnO$_3$ thin films grow. Detailed x-ray diffraction (XRD) and magnetization measurements have been reported elsewhere [7,9,10]. The structural investigation by XRD provides macroscopic volume-averaged information. On the contrary, Transmission Electron Microscopy (TEM) has the advantage of high spatial resolution which can provide information on structure, symmetry, domain sizes, domain shapes and domain-wall orientations on a local scale. Such a report on the detailed domain structure evolution at nanoscale of TMO was lacking and is the present focus of this work.

### 1.2. EXPERIMENTAL PROCEDURE

Phase pure orthorhombic TMO thin films of different thicknesses were grown using pulsed laser deposition (KrF excimer laser $\lambda=248$ nm) assisted by Reflection High Energy Electron Diffraction (RHEED) from stoichiometric targets. Epitaxial growth occurred on properly treated (001)-oriented STO substrates with atomically flat terraces of one unit cell step height. The films were grown at 750 °C and at 1 Hz laser pulse
frequency with laser fluence of 2 J/cm$^2$. The films were cooled to room temperature at -3 °C per minute under a 100 mbar of O$_2$. One set of films with various thicknesses (17 nm, 34 nm, 67 nm and 140 nm) were grown at 0.25 mbar oxygen partial pressure and another set of films (15 nm, 30 nm and 60 nm) were grown at 0.9 mbar oxygen partial pressures, keeping the other growth parameters constant [10].

The plane-view and cross-sectional TEM observations of the thin films were performed using a JEOL 2010F electron microscope operating at 200 kV. The plane view TEM sample preparation steps are not much different and relatively simpler than the cross section TEM sample preparation procedure explained in the previous chapters. The specimen preparation for TEM observation involves a conventional procedure of cutting, grinding, polishing, dimpling, and ion milling. The samples were thinned down to electron transparency using a precision ion polishing system (Gatan model 491) with two ion guns of 4 kV Ar$^+$ beams at an angle of 8°. For plane-view specimens both ion guns are focused at the bottom side of the substrate. The other side of the film is covered with a piece of glass to avoid any contamination by redeposition from the sputtered backside. For cross section specimens both sides were ion milled.

5.3 RESULTS AND DISCUSSION

5.3.1 Nanodomain structures in thin TMO films

The microstructure analysis of the thin films grown at different thickness can explain the strain accommodation of orthorhombic TMO on cubic STO, including the evolution of the domain structures and the film-substrate orientation relationships. When compared to the length of the STO[110] vector, the orthorhombic lattice parameter $b$ is under compressive strain with a lattice mismatch of about 5.7% and the lattice parameter $a$ is under tensile strain with a mismatch of about 4.1%. From the TEM images and XRD patterns [10], we infer that TMO always grows with its $c$-axis perpendicular to the STO (001) surface and, therefore, the projections shown in Fig.5.1b and c are relevant. TEM analysis of plane-view bright-field images and selected-area electron diffraction patterns as depicted in Figs.5.2a and 5.3a show that the 17 nm TMO film is epitaxially strained.
Figure 5.2: Bright field plane-view TEM micrographs of TbMnO$_3$ thin films on SrTiO$_3$ substrates grown at 0.25 mbar oxygen partial pressure with thickness (a) 17 nm (b) 34 nm (c) 67 nm (d) 140 nm. Micrographs show the evolution of domain structures with increasing film thicknesses.

and partially coherent with the STO substrate. The TMO has a (distorted) orthorhombic structure. The film consists of rectangular nanodomains with a relatively large aspect ratio (5:1), forming two sets of perpendicular twins. A combination of images and diffraction patterns indicates that the domain walls parallel to the long (in-plane) axis of the domains, correspond to TMO (110) or (1\bar{1}0) planes. The orientation relation with the substrate is such that these TMO planes are parallel to the STO (100) and (010). Since the TMO (110) and (1\bar{1}0) planes are not orthogonal (their mutual angle is 84.4° in the bulk structure, whereas for STO (100) and (010) it is of course 90°), four domain variants develop in the form of the two sets of twins [10] (see Fig 5.4a and 5.4b). The superposition of four diffuse diffraction spots, centered around the substrate diffraction
spots, forms a cross pattern in the electron diffraction pattern and confirms the presence of four domain variants. The diffuse (not sharp) contrast of the domain walls in the

![Figure 5.3: Selected area electron diffraction pattern of TbMnO$_3$ thin films on SrTiO$_3$ substrates with thickness of (a) 17 nm, showing cross patterns confirming the presence of the four domain variants determined by x-ray diffraction (b) 67 nm, showing arcs that confirm the in-plane rotations present between domains.](image)

plane-view TEM image is caused by the influence of the strain fields, largely associated with the coherency strains, on the TEM diffraction contrast. From plane-view images it is measured that the average domain area of this 17 nm thick film corresponds to 105±10 nm$^2$. The cross section high resolution TEM image of the film shows a sharp substrate-film interface which is free from (an array of) misfit dislocations. This confirms the epitaxial and coherent growth of the film, where coherency strain field contrast is for instance visible at the right side of the interface in Fig.5.5a.

Compared to the 17 nm film, the domains in the 34 nm film have grown to an average area of about 205±15 nm$^2$, have become less elongated (reduced aspect ratio) and also the coherency strains as deduced from the TEM diffraction contrast images are slightly reduced. The enhanced sharpness of the domain walls in the image shown in Fig.5.2b is due to the reduced strain fields. This indicates that the elastic strain in the film is lower than the strain present in the 17 nm film. The presence of four domain variants is still valid, even for the doubled thickness.
**(i) Transition from tetragonal to distorted orthorhombic structure**

In case of ultra-thin TMO films with a thickness of 2 nm, XRD reveals that the TMO structure is tetragonal with the $c$-axis perpendicular to the film surface and in-plane orientations and distances fully coherent with the STO substrate [10]. This can be regarded as orthorhombic TMO with a tensile strain of 4.1% along the $a$-axis (parallel to [110]STO) and a compressive strain of 5.7% along the $b$-axis (parallel to [1̅10]STO). As explained in the previous section, for thicker films an (partially strained and distorted) orthorhombic structure is observed, where the film breaks up in nanodomains. Intuitively one would expect that a checkerboard domain pattern would develop with domain walls parallel to the TMO(100) and (010) and where alternating the short $a$- and the long $b$-axes (perpendicular to the walls) would compensate each other; see Fig.5.6a, where the vectors...

**Figure 5.4:** Sketch of orthorhombic domains in TMO thin films and their coherence with STO (001) substrate.
Figure 5.5: Bright field cross section TEM micrographs of TbMnO$_3$ thin films on SrTiO$_3$ substrates grown at 0.25 mbar oxygen partial pressure with thickness (a) 17 nm, showing a high resolution image of the substrate-film interface with a strain field contrast on the right hand side of the interface; (b) 67 nm, showing columnar growth along with long range strain fields at the substrate film interface; (c) 140 nm, showing open columnar structure with relatively deep cusps at the column boundaries.

indicate the orientation of the (in-plane) $a$-axis of orthorhombic TMO. However, this situation is not observed. Instead, the domain walls are parallel to TMO(110) and (110) with one clearly longer than the other, resulting in rectangular nanodomains with relatively large aspect ratio, as described previously.

Initially, for film thicknesses around 15 nm, coherency is fully maintained parallel to the long (in-plane) [110] or [110] axes of the rectangular domains; [110]TMO=[200]STO, or [110]TMO=[020]STO. With respect to bulk TMO,
Nanoscale domain evolution in thin films of multiferroic TbMnO$_3$

Figure 5.6: Schematic diagram for domain structure in TbMnO$_3$ film showing (a) (not observed) checkerboard pattern indicating the orientation of the $a$ (or $b$) vector in the various domains separated by (100) and (010) domain walls (b) (observed) twin structure with four sets of zigzag patterns; the orientation of the $a$ vectors in the various domains separated by (110) and (1$\bar{1}$0) domain walls is indicated (c) explanation of the twinning process, where the shear vector $\delta$ operates on the initially tetragonal TMO fully coherent with the STO substrate (shown on the top) in order to form the distorted orthorhombic TMO partially coherent with the STO (shown at the bottom).

A compressive strain of 0.9% is required to maintain this coherency, i.e. already much lower than the $\sim$ 5% required to maintain the tetragonal structure. If the [110] axis is the fully coherent direction, then the [1$\bar{1}$0], which deviates about 6 degrees from the perpendicular direction, stays over longer distances in registry with the cubic substrate by alternating short segments with plus and minus 6 degrees deviations; see Fig.5.6b. So, if full coherence is maintained along the [110]TMO=[200]STO, the [1$\bar{1}$0] is slightly longer (less compressively strained) since adding up one plus and one minus 6 degrees [1$\bar{1}$0]
vector of the zig-zag corresponds to [040]STO. Effectively, this means that there is a coherency strain of about 0.4% in this [040] direction.

The principal reasons why the checkerboard pattern in Fig.5.6a is not observed, but the pattern in Fig.5.6b is observed are the following: (i) the domains in Fig.5.6a cannot be associated with a partial coherence with the substrate, whereas the domains in Fig.5.6b can and (ii) the domains in Fig.5.6a cannot be associated with a tiling that fulfills the compatibility requirement, where the original surface area is fully covered by the domains without the formation of gaps (or overlaps) between them, whereas the domains in Fig.5.6b can.

The transition in the TMO film from the tetragonal to the orthorhombic structure and the breaking up in domains clearly indicates a twinning operation. The shear displacements associated with the twinning process are schematically indicated in Fig.5.6c. This shearing process and the coherency conditions followed during this twinning operation results in a distortion of the orthorhombic TMO such that the principal lattice vectors $a$ and $b$ do not become orthogonal. Taking $a_{\text{STO}}\sqrt{2}$ as starting condition, the decrease of the $a$ lattice parameter of TMO and the increase of the $b$ lattice parameter are nearly identical, such that the $b$ lattice parameter will always deviate stronger from its bulk value than the $a$ lattice parameter (see Fig.5.7). The observed nanodomain structures strongly suggest a twinning mechanism, but proof for this mechanism comes from the excellent quantitative agreement between predicted and measured XRD data [10](see Fig.5.7). The only unknown parameter in the twinning process is the relative length of the shear vector $\delta$ (cf. Fig.5.6c). This single parameter fully determines the distorted orthorhombic structure, i.e. the deviations from the bulk values [14]. Based on the value for the pseudocubic angle $\gamma$, [7] we derive the value for $\delta$ and then we calculate, without any adjustable parameter, the lattice parameters $a$ and $b$, [14] leading for the various film thicknesses to the excellent agreement shown in Fig.5.7. This analysis shows that the shear vector $\delta$ increases with film thickness such that the pseudocubic angle $\gamma$ and the lattice parameters $a$ and $b$ approach bulk values and thus indicates a reduced distortion and therefore a structural relaxation behaviour.
Figure 5.7: Graph showing an excellent agreement between experimentally determined and predicted [14] lattice parameters of orthorhombic TbMnO$_3$ thin films plotted as a function of film thickness.

However, simultaneously, the angle between the $a$- and $b$-vectors shows an increasing deviation from 90° and thus leads to an increasing, although relatively small structural distortion, which is too small to be observed in our XRD experiments [10]. The angle between $a$ and $b$ can be calculated from $\tan^{-1}(1+2\delta/3.905)+\tan^{-1}(1-2\delta/3.905)$ with the $\delta$ in Å. More importantly, this mechanism does not allow a full relaxation of the $b$ lattice parameter (cf. Fig 5.7). A further increase of $\delta$ would relax the $b$ lattice parameter, but then the $a$ lattice parameter and the pseudocubic angle $\gamma$ would decrease below their bulk values. Therefore, this mechanism of an increasing shear vector is running into a dead alley and a second structural transformation, explained in the next section, is required that can really lead to a completely relaxed orthorhombic structure.
Chapter 5

(ii) Disappearance of the distortion in the orthorhombic structure

Remarkable changes occur with respect to the domain shape and size when the film thickness is increased from 34 to 67 nm; compare Figs. 5.2b and 5.2c. In addition to the rectangular domains, now also nearly circular (coalesced) domains can be seen in the plane-view TEM image (Fig.5.2c). The domain area reaches about $320 \pm 20 \text{ nm}^2$ on average and domains have a much reduced aspect ratio. The sharp contrast of the domain walls in the image is due to the smaller magnitude of strain fields, where the top of the film for the circular coalesced grains become relaxed.

The 67 nm thick film shows an intermediate stage where the coalesced grains adopt a new orientation relationship (OR) not present in the thinner films. Due to the reduced elastic strain, the domains tend towards an energetically more stable configuration with two domain variants i.e., (100) and (010) of the orthorhombic film parallel to the (110) and (1\overline{1}0) of the cubic substrate, instead of four variants (see Fig 5.4c). Evidence of this has been also obtained by XRD [10]. In principle, the change in OR is only related to a slight in-plane rotation of about 3 degrees. The development of this new OR allows the removal of the distortion of the orthorhombic structure such that (i) the $b$ vector can relax to its bulk value and (ii) the $a$ and $b$ vectors can become orthogonal and thus allows a complete strain relaxation to the bulk orthorhombic unit cell not possible by the twinning process delineated in the previous section.

The electron diffraction pattern of the 67 nm thick film, depicted in Fig.5.3b, shows that the TMO domains/grains exhibit relatively large mutual in-plane rotations (i.e. around their common $c$-axis). Cross section bright field TEM images of the 67 nm thick film show columnar grains (see Fig.5.5b), where the top of the columns are still relatively flat. The height variation in the 67 nm thick film around the domain/column boundaries observable in Fig.5.5b are larger than in the 17 nm film (Fig.5.5a), but develop clearly to cusps in the 140 nm thick film (Fig.5.5c). For the latter thickness the column structure is clearly more developed and the top of the columns approach a dome structure. In the cross-section images shown in Figs.5.5a-c it is observable that relatively large sized strain
fields are still present at the substrate-film interface indicating that the foot of each column is always partially coherent and that arrays of misfit dislocations at the film-substrate interface are absent. Particularly in Fig.5.5b for the 67 nm thick film, the long-range strain fields, extending into the STO substrate with a similar range as the width of the columns, are clearly visible.

The bright field plane-view and cross-section TEM image of the 140 nm thick film, depicted in Figs.5.2d and 5.5c, show that the growth is completely columnar and that the shape of the domains (now grains) in plane-view are nearly circular. Relatively deep cusps are present at the column boundaries, which also appear to have a more open structure. These columns are still strained to maintain the partial coherence at the substrate-film interface. Approximately up to 30 nm, the compressive strain parallel to the film/substrate interface are transferred across the column boundaries. Above ~30 nm the columns start to grow independently and the column boundaries allow strain relaxation. In this first 30 nm also growth selection occurs, where some columns grow broader at the expense of other columns which become thinner and even can disappear. The average grain area of the 140 nm thick film as measured based on plane-view images is ~800±40 nm². The RMS surface roughness of the film increases with increasing
Figure 5.9: Plot showing number of domain walls as a function of inverse thickness of film.

thickness, from 0.45 nm for the 17 nm film to 2.4 nm for the 140 nm film, which is also clearly observable in the cross section TEM images. Moreover, the domain size increases, in a similar fashion as the surface roughness, with increasing thickness of the film (Fig.5.8).

Tuning and control of these domain structures in multiferroic thin films is of crucial importance in order to gain access to their functional properties. In recent work on BiFeO$_3$ thin films, the conduction at 109° and 180° domain walls is observed, which emphasizes that the domain walls are discrete functional entities. This TEM investigation of TbMnO$_3$ thin films plays a vital role in order to understand the domain structures. Daumont et.al.[11] observe an interesting trend, that the induced net magnetization observed in the antiferromagnetic films clearly scales linearly with the reciprocal film thickness. We observed that the density of domains walls measured from the TEM images is also directly proportional to reciprocal film thickness (see Fig. 5.9). Therefore, the net magnetization observed by Daumont et al. could originate from the domain walls. However, the direct proof for this hypothesis has to come from a direct characterizing of these nano-domain structures using microscopy techniques like Magnetic Force Microscopy (MFM), Lorentz Microscopy within the TEM or Photo Electron Emission Microscopy (PEEM). An additional challenge is that these experiments have to be performed with the specimen (i.e. the TbMnO$_3$ films) in low temperature conditions.
(< 40 K), because the net magnetization is only observed within this temperature range, and preferably at $T < 27$ K where spiral spin structure appears.

### 5.3.2 Role of oxygen partial pressure

![Figure 5.10: Bright field TEM micrographs of TbMnO$_3$ thin films on SrTiO$_3$ substrates grown at 0.9 mbar oxygen partial pressure with a thickness of 60 nm: (a) Overview cross section image showing columnar growth with localized strain fields; (b) magnified cross section image showing in more detail the strain field contrast of misfit dislocations (examples indicated by arrows). (c) Plane-view TEM micrograph of a 30 nm TbMnO$_3$ thin film on SrTiO$_3$ substrate grown at 0.9 mbar oxygen partial pressure shows the absence of moiré patterns (d) Plane-view TEM micrograph of a 60 nm TbMnO$_3$ thin film on SrTiO$_3$ substrate grown at 0.9 mbar oxygen partial pressure showing high density moiré patterns resulting from mutual rotations and/or differences in lattice constants of TMO and STO. Note that these moiré patterns were not observed in plane-view TEM micrographs of TMO film on STO substrates grown at 0.25 mbar oxygen partial pressure.

The 30 nm film grown in 0.9 mbar oxygen pressure has similar structure as the thinner (17 and 34 nm) films grown in 0.25 mbar. Compared to the films grown in 0.25 mbar, the films grown at 0.9 mbar oxygen pressure relax the strains due to partial coherence at a relatively lower thickness. Fig.5.10a-b shows a cross section TEM image of a 60 nm film grown in 0.9 mbar. The film exhibits a well-developed columnar
structure with relatively deep cusps at the column boundaries. This structure does not resemble the one observed for a film of similar thickness grown in 0.25 mbar (compare Figs.5.10a-b and 5.5b). Instead, the 60 nm 0.9 mbar film has a similar structure as the 140 nm 0.25 mbar film (compare Figs.5.10a-b and 5.5c).

The columnar growth and the strain relaxation mechanism by column boundaries for a thin film is not new, and it is observed commonly in many perovskites thin films in the case of high lattice mismatch substrate-film combinations. One such an example is given in the Fig 5.11, which shows a 40 nm YbMnO$_3$ multiferroic thin film grown on (111)-SrTiO$_3$ [16].

The bright field TEM image of the 60 nm TMO film grown at 0.9 mbar, shown in Fig.5.10d, exhibits high density moiré patterns. The moiré fringes occur due to the interference of two crystal lattices with small mutual rotation and/or differences in lattice constants. The observation of these fringes, not present in case of the films grown in 0.25 mbar, is direct evidence for the presence of misfit dislocation at the substrate-film interface. This is corroborated by our cross section TEM images, where instead of a single long-range strain field per column, there are many more also very localized (small) strain fields present that can be associated with arrays of misfit dislocations (see Fig.5.10b). The moiré patterns were also not observed in the film with a thickness of

![Figure 5.11](image.png)

**Figure 5.11:** Bright field cross section TEM micrograph of of 40 nm YbMnO$_3$ films grown on (111) – SrTiO$_3$ substrates showing a columnar growth.
Nanoscale domain evolution in thin films of multiferroic TbMnO$_3$

30 nm (see Fig. 5.10c) grown at the same 0.9 mbar. Moreover, the domain structure has a similar appearance as observed in the 17nm or 34 nm films grown at 0.25 mbar. This is an additional proof that at these low thicknesses the films are strained.

In general, perovskite oxide films can accommodate a high concentration of oxygen vacancies without losing its perovskite structure. The possibility of a significant concentration of oxygen vacancies in the films grown at an oxygen partial pressure of 0.25 mbar cannot be totally ruled out even though our XPS measurement does not show evidence of Mn$^{2+}$[10]. Assuming that the oxygen vacancy concentration in the films grown in 0.25 mbar is clearly higher than in the ones grown in 0.9 mbar, it can also be understood that the critical thickness for strain relaxation is higher in the films grown at 0.25 mbar. The reason is that the vacancy concentration can assist in the strain relaxation such that the remaining strain is lower, so that the driving force for introduction of misfit dislocations is reduced. Moreover, in thicker films strain can be relaxed at the column boundaries. Effectively this means that the strain in the 0.25 mbar films is relaxed by the oxygen vacancies and the column boundaries such that misfit dislocations do not come into play. On the other hand, misfit dislocations appeared unavoidable for providing completely relaxed films in the films grown at the higher oxygen partial pressure of 0.9 mbar (maximum pressure we could reach in our PLD chamber allowing RHEED intensity to be monitored).

5.4 CONCLUSIONS

(001)-oriented TbMnO$_3$ thin films, grown epitaxially on (001) SrTiO$_3$ substrates with various thicknesses at different oxygen partial pressures, show a remarkable evolution of nano-domain structures. This evolution can be understood on the basis of an initial tetragonal structure, transforming into a distorted orthorhombic structure by a twinning process. This mechanism gives rise to four domain variants (with [110] or [1$\bar{1}$0] of TMO parallel to [100] or [010] of STO) above a first critical thickness of about 5 nm, transforming finally into a relaxed (undistorted) orthorhombic structure, which gives rise to two domain variants (with [100] and [010] of TMO parallel to [110] and [1$\bar{1}$0] of
STO) above a second critical thickness of about 60 nm. Knowledge of the twinning mechanism allows accurate prediction and understanding of the measured distortion of the orthorhombic structure and it shows that the symmetry of the strained films is lower than orthorhombic, since $a$ and $b$ are not exactly orthogonal.

TMO films grown at a higher oxygen partial pressure (0.9 mbar) show strain relaxation at lower thickness (60 nm) than films grown at lower pressure (0.25 mbar). This difference is attributed to a higher concentration of oxygen vacancies at lower oxygen partial pressure and therefore a reduced strain. After the first relaxation mechanism of twinning has been completed a second way of strain relaxation in the film occurs by two mechanisms: 1) Misfit dislocation formation at the substrate-film interface and 2) the formation of columnar structures with increasing relaxation at the column boundaries with increasing thickness. At 0.9 mbar the first mechanism dominates, whereas at 0.25 mbar the second one occurs.
References

[14] The value of $\delta$ is obtained by using the formula $\delta = 3.905 \tan(\theta)/2$, where 3.905 is the STO lattice parameter, $\theta$ is $(90^\circ-\gamma)$ with $\gamma$ the pseudocubic angle i.e.,
orthorhombic distortion from $90^\circ$. The lattice parameter of the film $a$ and $b$ is calculated using the formula 

\[ a = \sqrt{(3.905)^2 + (3.905 - 2\delta)^2} \]

\[ b = \sqrt{(3.905)^2 + (3.905 + 2\delta)^2} . \]
