

University of Groningen

Periodic Nanodomains in PbTiO₃ Films Under Tensile Strain

Noheda, B.; Vlooswijk, A.; Janssens, A.; Catalan, G.; Rijnders, G.; Blank, D.H.A.

Published in:

17th IEEE International Symposium on the Applications of Ferroelectrics, 2008. ISAF 2008

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:

2008

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Noheda, B., Vlooswijk, A., Janssens, A., Catalan, G., Rijnders, G., & Blank, D. H. A. (2008). Periodic Nanodomains in PbTiO₃ Films Under Tensile Strain. In *17th IEEE International Symposium on the Applications of Ferroelectrics, 2008. ISAF 2008* (Vol. 3, pp. 472-473). (IEEE International Symposium on Applications of Ferroelectrics). University of Groningen, The Zernike Institute for Advanced Materials.

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

Periodic Nanodomains in PbTiO₃ Films Under Tensile Strain

B. Noheda¹, A. Vlooswijk¹, A. Janssens², G. Catalan³, G. Rijnders², D. H. A. Blank²

¹Zernike Institute for Advanced Materials, University of Groningen, Groningen 9747AG, The Netherlands

²MESA+ Institute for Nanotechnology, Twente University, Enschede 7500 AE, The Netherlands

³Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, United Kingdom

Abstract – In epitaxial ferroelectric thin films under tensile strain, a transition from 180° domains to 90° domains can be achieved by increasing the film thickness. In many cases, the 90° a/c domains appear in the form of wide c-domains separated by narrow a-stripes. We have deposited thin films of PbTiO₃ on DyScO₃ substrates and show that the condition of horizontal coherence forces the a-domains to adopt discrete sizes, the smallest of which is substrate-independent and depends only on the tetragonality of the ferroelectric film. Growing PbTiO₃ on DyScO₃, we have achieved the narrowest (6 nm) possible a-domains, as well as the shortest periodicity that allows to maintain the lateral coherence in the film.

INTRODUCTION

In recent years, research in ferroelectric thin films has taken a more fundamental turn[1-5]. Nowadays, novel materials, in particular ferroelectrics, can be grown as very thin layers under strain, on an appropriate substrate. The strain can confer them artificial symmetries and, potentially, new physical properties, as well as determine the domain configuration and/or the critical temperature[6–10]. Recent results indicate that there is essentially no lower bound to the thickness at which a film can be ferroelectric, even when the polarization is perpendicular to the plane of the film[2, 3]. This is thanks to the appearance of antiparallel (180°) stripe domains, which minimize the ferroelectricity-suppressing effect of depolarization fields[11, 12]. Kittel’s law[13] also dictates that the domain size decreases as the square root of the film thickness, so the density of domains and their relative impact increases for very thin films.

Since domains determine everything from coercive fields to switching kinetics, electromechanical properties or dielectric response, the structure and behaviour of ferroelectric domains in the nanoscale is rapidly becoming a very active area of research; proper understanding of domains in very thin films is essential for harnessing the functional properties of ferroelectrics at the nanoscale and continue to reduce the size of ferroelectric devices[1].

In the simplest and most common case of tetragonal thin films grown on cubic substrates, the orientation of the polarization in the ferroelectric film depends on the relationship between the lattice parameters of the film (a ,

c) and the substrate (a_s). If $a_s \leq a$, the film will grow with c and, thus, the polarization, out-of-plane (c-phase). Such films would (if no or bad electrodes are present) split into 180° domains in order to decrease the depolarizing fields[11, 12], as mentioned above. These domains will form periodic stripe patterns[3], similar to those found on ferromagnetic thin films[13]. In this scenario, the electrostatic energy is the sole responsible for domain formation. Conversely, if $a_s \approx c$, the film will grow with c in-plane (a-phase) and in-plane a_1/a_2 domains can form. Here only elastic considerations dictate the domain scaling[14, 15].

For intermediate situations ($a < a_s < c$) the film will usually consist of domains of c- and a-phase in a ratio such as to fit the substrate and both elastic and depolarization effects compete with each other, as a function of thickness, temperature or electrode material[14–20]. These c/a/c patterns are more difficult to engineer since they involve crystallographic tilts[21] and since the strain required to stabilize them can also be accommodated by misfit dislocations and other defects, which themselves interfere with the domain pattern. Finding a right choice of film and substrate, which imposes enough strain without causing misfit dislocations is quite important but it was, until recently, difficult. Here we show that this is now possible by combining ferroelectric PbTiO₃ (PTO) with the recently introduced DyScO₃ (DSO), as a substrate[7, 9, 22].

PTO is an archetype of tetragonal perovskite ferroelectrics ($a = 3.90 \text{ \AA}$, $c = 4.14 \text{ \AA}$), and also an end member of the technologically important PZT. DyScO₃ (DSO) is an orthorhombic perovskite with a pseudocubic lattice parameter of $a_s \approx b_s = 3.95 \text{ \AA}$ [22]. There is, however, a near perfect lattice match of the two at the growth temperature, where PTO is in its cubic phase. This means that thin films of PTO can be grown with essentially zero strain, thus minimizing the appearance of defects. Only as the films cool down, strains develop and increase. At room temperature, the strain between tetragonal PTO and pseudocubic DSO is such that the elastic energy lies near the critical boundary for the appearance of a/c domains[15], and thus competition effects between depolarization and elastic energy are also easily observed. Indeed, as a function of thickness (d) we have observed a transition from depolarization-dominated, 180°-domains ($d = 5 \text{ nm}$) to strain-dominated, 90°-domains ($d = 15, 30, 45, 60 \text{ nm}$). We report that in

these latter films, the width of the a-domains is the minimum needed to keep the film horizontal coherence. Since this width decreases with increasing tetragonality and the c/a ratio of PTO is one of the largest, the observed width of periodic a-domains is one the smallest possible in ferroelectrics[23].

RESULTS AND DISCUSSION

The films of PTO were grown by pulsed laser deposition with thicknesses of 5, 15, 30, 45 and 60nm on (110)-oriented DyScO₃ substrates at a temperature of 570°C[24]. Some of the films were grown with an electrode SrRuO₃ buffer layer between the film and the substrate. Films with $d=5$ nm were previously shown to be fully coherent and displayed 180° domains with the polarization tilted due to the epitaxial strain[24]. Here we show that at larger thicknesses, ($d \geq 15$ nm), the elastic energy developed during cooling is sufficient to induce a-domains. The reduced amount of defects allows the self-organization of these domains in very regular $c/a/c$ patterns.

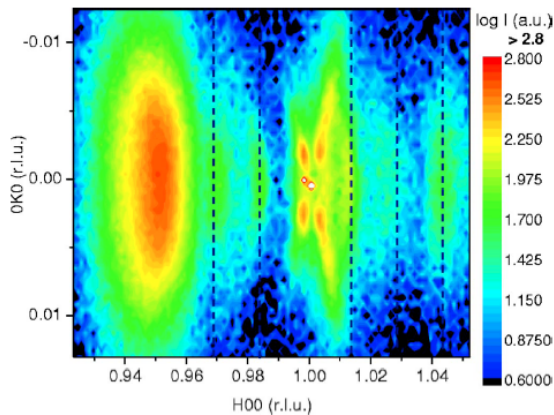


FIG. 1. Reciprocal space area scans in the in-plane (HK0) scattering plane, around the (100)_c reflection. In this particular sample, a SrRuO₃ electrode layer was deposited and the orthorhombic four-fold twinning of this buffer layer can be observed. The axes units are reciprocal lattice units of the substrate ($2\pi/3.95\text{\AA}$) in pseudo-cubic notation. The wavelength is $\lambda=1.26515\text{\AA}$.

Figure 1 shows a synchrotron x-ray diffraction (XRD) area scan around the (100)_c reflection of the substrate. XRD was performed in standard reflection geometry and in grazing incidence geometry (GID) at the wiggler W1 beamline in Hasylab (DESY-Hamburg). The intensity modulation along the [H00]_c direction is clearly visible. Scans around other reflections, both in plane and out of plane, have shown that the modulation is present throughout reciprocal space with a spacing of $\Delta H=0.014$, corresponding to a real-space wavelength of $\Lambda=0.395\text{ nm}/\Delta H=28\text{ nm}$. Similar satellites, with periodicities of $29\pm 2\text{ nm}$, were observed in all 30 nm thick films, with and without electrode bottom layer. The Bragg peak corresponding to the relaxed (bulk) c lattice parameter of

PbTiO₃ can be observed in the in-plane scan at $H=0.952$, showing the presence of a-domains.

Atomic Force Microscopy and Transmission Electric Microscopy in similar samples show the same periodicity and have revealed that it originates from the $a/c/a$ domain patterns. These are induced by the misfit strain developed during cooling after growth. Further details are found in ref. [25]

We have been able to show that the condition of horizontal coherence that allows periodic domain patterns to form, forces the a-domains to adopt discrete sizes. In the case of PbTiO₃ on DyScO₃, we have achieved the narrowest (6 nm) possible a-domains, as well as the shortest periodicity that keeps the lateral coherence in the film. The small periodicity and large coherence makes these films potentially interesting for applications such as ferroelectric memories.

REFERENCES

- [1] Scott, J. F. , Science 315, 954 (2007).
- [2] Tybell, T., Ahn, C. H. and Triscone, J. M. , Appl. Phys. Lett. 75, 856-858 (1999); Ahn, C. H., Rabe, K. M. and Triscone, J-M., Science 303, 488 (2004); Lichtensteiger, C. et al., Appl. Phys. Lett. 90 (2007).
- [3] Streiffer, S. K. et al. , Physical Review Letters 89 (2002); Fong, D. D. et al., Science 304, 1650 (2004).
- [4] Naumov, I.I., Bellaiche, L., Fu, H.X., Nature 432, 737(2004).
- [5] Schilling, A., et al. , Appl. Phys. Lett. 89 (2006).
- [6] Bungaro, C. and Rabe, K. M. , Phys. Rev. B 69 (2004); Dieguez, O. et al. , Philosophical Magazine a-Physics of Condensed Matter Structure Defects and Mechanical Properties 71, 713 (1995).
- [7] Foster, C. et al., J. of App. Phys. 79, 1405 (1996).
- [8] Roelofs, A., et al., Applied Physics Letters 81, 5231 (2002); 80, 1424 (2002).
- [9] Nagarajan, V. et al., App. Phys. Lett. 79, 2805 (2001).
- [10] Pertsev, N. A. Zembilgotov, A. G., J. of Appl. Phys. 80, 6401 (1996).
- [11] Shilo, D. et al., Nature Materials 3, 453 (2004).
- [12] Biegalski, M.D. et al., Journal of Materials Research 20, 952 (2005).
- [13] L.W. Martin et al., Appl. Phys. Lett. 90, 062903 (2007)
- [14] Catalan, G. et al., Phys. Rev. Lett. 96, 127602 (2006).
- [15] Vlooswijk A.H.G., et al. Appl. Phys. Lett. 91, 112901 (2007)

Corresponding author:

Beatriz Noheda
 Assistant Professor
 Zernike Institute for Advanced Materials,
 University of Groningen,
 Groningen 9747AG, The Netherlands

Email: b.noheda@rug.nl