University of Groningen

Domain formation in lead titanate ferroelectric thin films

Venkatesan, Sriram; Kooi, B.J.; Hosson, J.Th.M. De; Vlooswijk, A.H.G.; Noheda, B.

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):

Venkatesan, S., Kooi, B. J., Hosson, J. T. M. D., Vlooswijk, A. H. G., & Noheda, B. (2008). Domain formation in lead titanate ferroelectric thin films. In *17th IEEE International Symposium on the Applications of Ferroelectrics, 2008. ISAF 2008* (Vol. 17, pp. 105-108). (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.

Domain formation in lead titanate ferroelectric thin films

Sriram Venkatesan¹, B.J. Kooi¹, J.Th.M. De Hosson¹, A.H.G. Vlooswijk², B. Noheda²
Zernike institute for advanced materials, ¹*Department of Applied Physics*, ²*Department of Chemical physics*,
University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.

Abstract — Epitaxial lead titanate ferroelectric thin films were grown on strontium titanate(001) and dysprosium scandate(110) substrates by RHEED controlled pulsed laser deposition. We used high resolution transmission electron microscope to investigate the structure of the films. The clear difference in the shape of the *a*-domains were observed in films on the two different substrates. Films on strontium titanate substrates were found to have wedge shaped *a*-domains whereas, *a*-domains in the films on the dysprosium scandate substrates were found to have nearly uniform width. The difference in the shape of *a*-domains is attributed to the difference in stiffness of the two substrates. Nanoindentations on the substrates were performed to quantify their the stiffness. In another set of experiment we have successfully grown completely *c*-oriented lead titanate thin films with various thicknesses ranging from 22-340 nm on strontium titanate substrates. Laser pulse frequency (growth rate) is the critical parameter for the formation of *a*-domain free lead titanate films. The strontium titanate substrate surface termination is also important at higher growth rates.

INTRODUCTION

Ferroelectrics have been widely studied, because of their potential application in various memory devices, sensors and actuators, MEMS etc.. The last few decades research has focussed mainly on PbTiO_3 , BaTiO_3 , $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$, $\text{BaSr}_{1-x}\text{Ti}_x\text{O}_3$. Particularly thin films of PbTiO_3 have been studied after growing them on different substrates like MgO , SrTiO_3 , KTaO_3 , LaAlO_3 . Although a lot of progress has been made, 90° domain formation is still a persistent problem at least for thicker films due to the difference in film-substrate lattice mismatch, and also cubic paraelectric to tetragonal ferroelectric phase transition [1-3]. In this work we have focussed our attention mainly on the shape of the *a*-domains in the PbTiO_3 thin films grown on two different substrates namely SrTiO_3 and DyScO_3 . There is no previous literature available on this topic. From an application point of view it is generally desired to have films with their *c*-axis oriented normal to the substrate surface, so that the spontaneous polarization is normal to the surface. Completely *c*-oriented single crystal PbTiO_3 thin films on SrTiO_3 grown by the PLD have not been reported yet, at least not for thicker films of a few hundred nanometers. By sputtering [4] and CVD [5] completely *c*-oriented films could be grown, but in the former case only for (0.9° - 1.7°) miscut substrates and in the latter case only below 150 nm thickness. Here, we show that we can grown 340 nm thick completely *c*-oriented films on 0.2°

miscut substrates. We have employed AFM, XRD and TEM for investigating the shape of *a*-domains and also to analyse completely *c*-oriented films.

EXPERIMENTAL

Pulsed-Laser Deposition was used to grow PbTiO_3 films (with various thickness) on (001) SrTiO_3 and two 30 nm films on (110) DyScO_3 with 5 nm and 30 nm SrRuO_3 conductive perovskite as intermediate layer. The SrTiO_3 substrates were treated chemically in order to induce a TiO_2 termination. AFM measurements were performed to determine mixed or single SrO/TiO_2 termination occurred. DyScO_3 substrates were only treated thermally before deposition. PbTiO_3 films were deposited on SrTiO_3 at a temperature of 570°C using a pulsed KrF excimer laser at a wavelength of 248 nm (Lambda physik COMPex pro 205) in a default ambient oxygen pressure of 0.13 mbar with a repetition rate between 0.5 and 15 Hz. The substrates were kept at a distance of 51 mm from the target. An energy density of 2.5 J/cm^2 with a laser spot of $\sim 3\text{ mm}^2$ was used. After deposition the films were annealed within oxygen of 0.5 bar and cooled generally at a rate of 5°C/min . The films on DyScO_3 were deposited with a slightly less energy density of 2 J/cm^2 and a substrate target distance of 45 mm with a repetition rate of 1 Hz; the other parameters were identical as for PbTiO_3 growth on SrTiO_3 . The intermediate SrRuO_3 layer was grown at a temperature of 600°C with 2 Hz repetition rate.

XRD measurements (X'Pert Panalytical, Cu anode $\lambda=1.540598\text{\AA}$) were used to study the phase, presence, amount and tilting of *a*-domains. By performing measurements on both the θ - 2θ ($K_\parallel$) and ω ($K_\perp$) axes, reciprocal space maps were obtained.

TEM samples were prepared by the conventional method involving cutting, grinding, polishing, dimpling and ion milling. A precision ion polishing system (Gatan model 691) with 4kV Ar+ beams having incident angle of 8° on both sides was used. The observations were performed with a JEOL 2010F electron microscope operating at an accelerating voltage of 200 kV. Nanoindentations experiments were performed with a calibrated MTS Nano Indenter® XP with a Continuous Stiffness Module (CSM).

At room temperature the following lattice parameters hold. The bulk lattice parameters of PbTiO_3 are $a = b = 3.894\text{ \AA}$, $c = 4.140\text{ \AA}$ [6], i.e. with a tetragonal structure. SrTiO_3 has a cubic structure and its lattice constant is $a = 3.905\text{ \AA}$. The DyScO_3 has an orthorhombic structure with the following lattice constants: $a = 5.440\text{ \AA}$, $b = 5.713\text{ \AA}$,

$c = 7.887 \text{ \AA}$ [7]. (110)-oriented DyScO_3 has nearly a square in-plane lattice with $a_{\parallel} = 3.944 \text{ \AA}$.

RESULTS AND DISCUSSION

Fig.1. Bright-field TEM images of PbTiO_3 films (top) 110 nm film on SrTiO_3 showing the presence of wedge-shaped a -domains (bottom) 30 nm PbTiO_3 film on DyScO_3 (with 5 nm intermediate SrRuO_3 layer) showing the presence of a nearly regularly spaced array of a -domains within the PbTiO_3 film.

A cross-sectional bright field TEM image of a 110 nm PbTiO_3 film on SrTiO_3 is shown in Fig.1a. The presence of wedge shaped a -domains, with decreasing widths when approaching the substrate, can be observed clearly in the image. A bright-field TEM image of the sample with the 30 nm PbTiO_3 and 5 nm intermediate SrRuO_3 layer is shown in Fig1b. High resolution TEM images of the films on both substrates also indicate differences; see Fig 2. In general, the domain walls of the a -domain tend to be quite parallel for PbTiO_3 on DyScO_3 . The domains have clearly less wedge shape than in case of the SrTiO_3 substrate. We observed that, in case of only 5 nm intermediate SrRuO_3 layer, steps in the domain wall are present, whereas such steps were not detected in case of the 30 nm SrRuO_3 layer (Fig.2b). The c/a ratio within the PbTiO_3 derived from HRTEM images of c -domains is $1.07 (\pm 0.01)$ which is in agreement with the theoretical value of 1.063. We obtained 3.8° for the tilt between the unit cells in the a - and c -domains which is also close to the theoretical value of 3.5° . For the c -domains the (001) plane is parallel to the interface, but for the a -domains in

principle the tilt of 3.5° holds between the substrate surface and the (100) (or (010)) plane. The ‘defect’ accounting for this local misorientation can in analogy be called a misfit disclination [8-10].

The strains associated with this disclination create the tendency to minimize the width of the a -domains. However, for strain accommodation within the film a -domains are required. Overall, a strain-energy balance will hold. In fact, this balance will prevent the formation of a -domains below a critical thickness in accordance with theory [11] and experiments [12]. Above the critical thickness these domains can develop, but nevertheless the interface strains will tend to keep the domains in most cases thinner near the interface than in the bulk. To minimize domain-wall energy in principle thick a -domains would be expected, but these are not found due to the interfacial clamping strain. Clearly away from the interface the a -domains have the tendency to have a width corresponding to $c/\sin\alpha$ where α is the tilt mentioned above (which is $90^\circ - 2 \tan^{-1}(c/a)$). In this way the planes parallel to the interface in the c -domains on both sides of the a -domain match coherently with the slightly tilted plane in the a -domain [12]. If the clamping strain energy at the interface of an a -domain is higher than the strain energy associated with steps in the domain wall, then a wedge-shaped a -domain with smaller width near the interface will result. Apparently this situation holds in case of the SrTiO_3 substrate. In case of DyScO_3 with SrRuO_3 as intermediate layer the interface clamping strain energy is apparently less and the steps in the domain wall tend to run all the way to the interface and form domains with nearly uniform width. This difference in clamping strain energy is due to a difference in stiffness of the substrate, where a higher stiffness causes more strain energy.

Indeed, this analysis appears consistent, because with nanoindentation measurements we found the following values for the Young’s modulus: SrTiO_3 $279 \pm 2 \text{ GPa}$, DyScO_3 $250 \pm 3 \text{ GPa}$ and SrRuO_3 161 GPa [13].

Fig.2. High-Resolution TEM images of PbTiO₃ films. (top) 110 nm film on SrTiO₃ shows steps within the domain wall (bottom) Two closely spaced *a*-domains with uniform width of about 5 nm in the PbTiO₃ film on DyScO₃ with 30 nm intermediate SrRuO₃ layer.

Based on these considerations it can now be understood that the *a*-domains in the PbTiO₃ on the 30 nm SrRuO₃ showed most uniform width, because they make use of the most compliant SrRuO₃ in reducing the stress fields in PbTiO₃ and that in case of the 5 nm SrRuO₃ film a higher step density in the domain walls is found (because the *a*-domains also experiences the stiffer DyScO₃), but the domains are most clearly wedge-shaped in case of SrTiO₃ being the stiffest material of the three.

Fig3. Bright field TEM image of completely c-axis oriented PbTiO₃ film of ~340nm on SrTiO₃.

We have successfully grown completely c-axis oriented thick PbTiO₃ on SrTiO₃. These PbTiO₃ films ranged in thickness from 22-340 nm. The PbTiO₃ films were grown with changing parameters like laser pulse frequency (growth rate), cooling rate, oxygen-partial pressure and substrate (termination) treatment. At low laser pulse frequencies (≤ 5 Hz) *a*-domains did not develop up to large thickness (larger than 250-340 nm) independent of the quality of the substrate treatment (i.e. fraction of TiO₂ termination), oxygen partial pressure and cooling rate. At high laser pulse frequencies (≥ 8 Hz) *a*-domains develop above critical thickness (typically between 20-100 nm) even for perfect 100% TiO₂ terminated substrates. In these cases secondary phase

were generally detected (XRD/TEM) which are expected to act as nucleation sites for *a*-domain formation. At intermediate laser pulse frequencies (in between 5 and 8 Hz) *a*-domain formation can be avoided up to larger thicknesses (>250 nm) when the substrate has perfect TiO₂ termination; with poorly treated substrates (mixed termination) *a*-domains did occur.

According to K.Wasa et al. [4] a step flow growth mode helps to grow completely c-axis oriented PbTiO₃ films of 260 nm on SrTiO₃ substrates. Indeed this step flow growth mode was induced by a critical miscut of the SrTiO₃ substrate ranging from 0.9° - 1.7°. However, in our case all the films were grown on 0.2° miscut substrates and we obtain 340 nm thick PbTiO₃ film without formation of any *a*-domain. The reciprocal space maps from the X-ray diffraction data (not shown) and TEM (cf. Fig. 3) confirm the absence of *a*-domains. Although our deposition temperature is above the Curie temperature of bulk PbTiO₃ (i.e. the cubic paraelectric phase should grow), the absence of *a*-domains indicate that our films were directly grown in the tetragonal (ferroelectric) phase, which is in good agreement with the recent work reported by Janolin et al. [14].

CONCLUSIONS

Domain structures of *c/a/c* type in PbTiO₃ thin films have been investigated with the help of HRTEM. The *a*-domains in the films on the SrTiO₃ substrate have a clear wedge shape. The *a*-domains on the DyScO₃ substrates have uniform width. The difference in the shape of *a*-domains in the films was attributed to the difference in stiffness between SrTiO₃ and DyScO₃ substrates, which is in agreement with our nanoindentation measurement on these substrates.

Completely c-axis oriented PbTiO₃ films of thickness up to 340 nm were grown on SrTiO₃ substrates by pulsed laser deposition under different growth conditions. Predominantly the laser pulse frequency (growth rate) but also the substrate termination clearly influence the growth of single crystalline single domain PbTiO₃ thin films on SrTiO₃ substrates. Piezo-response Force Microscopy investigations of the functional properties of these systems are in progress.

REFERENCES

- [1] B.S Kwak, A. Erbil, J.D. Budai, M.F. Chisholm, L.A. Boatner and B.J. Wilkens, "Domain formation and strain relaxation in epitaxial ferroelectric heterostructures", *Phys. Rev. B*, Vol 49, pp.14865-14879, June 1994.
- [2] S. Stemmer, S.K. Streiffer, F. Ernst, M. Ruhle, W.-Y. Hsu, R. Raj, "Domain configuration in ferroelectric PbTiO₃ thin films: The influence of substrate and film thickness", *Solid State Ionics*, Vol 75, pp. 43-48, January 1995.
- [3] W.Y. Hsu and R. Raj, "X-Ray characterization of the domain structure of epitaxial lead titanate thin films on

- (001) strontium titanate”, *Appl. Phys. Lett.*, Vol 67, pp. 792-794, August 1995.
- [4] K. Wasa et al., “Single domain /single crystal ferroelectric PbTiO₃ thin films”, Proceedings of the the IEEE Ultrasonics Symposium, pp. 619-623, October 1998.
- [5] Z. Li, C.M. Foster, D. Guo, H. Zhang, G.R. Bai, P.M. Baldo and L.E. Rehn, “Growth of high quality single domain single crystal films of PbTiO₃”, *Appl. Phys. Lett.*, Vol 65 (9), pp. 1106-1108, August 1994.
- [6] G. Shirane, S. Hoshino and K. Suzuki, “X-Ray study of phase transition in lead titanate”, *Phys. Rev.*, Vol 80, pp. 1105-1106, October 1950.
- [7] J.H. Haeni et al., “Room-temperature ferroelectricity in strained SrTiO₃”, *Nature (London)*, Vol 430, pp. 758-761, March 2004.
- [8] J.S. Speck, A.C. Daykin, A. Seifert, A.E. Romanov and W. Pompe, “Domain configurations due to multiple misfit relaxation mechanisms in epitaxial ferroelectric thin films.III. Interfacial defects and domain mis orientations”, *J. Appl. Phys.*, Vol 78(3), pp. 1696-1706, August 1995.
- [9] J.S. Speck and W. Pompe, “Domain configurations due to multiple misfit relaxation mechanisms in epitaxial ferroelectric thin films.I. Theory”, *J. Appl. Phys.*, Vol 76, pp. 466-476, July 1994.
- [10] J.S. Speck, A. Seifert, W. Pompe and R. Ramesh, “Domain configurations due to multiple misfit relaxation mechanisms in epitaxial ferroelectric thin films.II. Experimental verifications and implementations”, *J. Appl. Phys.*, Vol 76, pp. 477-483, July 1994.
- [11] W. Pompe, X. Gong, Z. Suo and J.S. Speck, “Elastic strain energy release due to domain formation in strained epitaxy of ferroelectric and ferroelastic films”, *J. Appl. Phys.*, Vol 74, pp. 6012-6019, November 1993.
- [12] A.H.G. Vlooswijk, B. Noheda, G. Catalan, A. Janssens, B. Barcones, G. Rijnders, D.H.A. Blank, S. Venkatesan, B. Kooi, J.T.M de Hosson, “Smallest 90° domains in epitaxial ferroelectric films”, *Appl. Phys. Lett.*, Vol 91, pp. 112901-1 – 112901-3, September 2007.
- [13] S. Yamanaka, T. Maekawa, H. Muta, T. Matsuda, S. Kobayashi, K. Kurosaki, “Thermophysical properties of SrHfO₃ and SrRuO₃”, *J. Solid State Chem*, Vol 177, pp. 3484-3489, August 2004.
- [14] P.E. Janolin, B. Fraisse, F. Le Marrec, B. Dkhil, “Temperature evolution of the structural properties of monodomain ferroelectric thin films”, *Appl. Phys. Lett.*, Vol 90, pp. 212904-212910, May 2007.