2012

Complex domain structure in relaxed PbTiO₃ thick films grown on (100)cSrRuO₃/(100)SrTiO₃ substrates

Shintaro Yasui

Tokyo Institute of Technology, yasui.s.aa@m.titech.ac.jp

Yoshitaka Ehara

Tokyo Institute of Technology

Satoru Utsugi

Tokyo Institute of Technology, utsugi.s.aa@m.titech.ac.jp

Mitsumasa Nakajima

Tokyo Institute of Technology

Hiroshi Funakubo

Tokyo Institute of Technology, funakubo@mte.biglobe.ne.jp

See next page for additional authors

Follow this and additional works at: <https://digitalcommons.unl.edu/physicsgruverman>

Part of the [Physics Commons](#)

Yasui, Shintaro; Ehara, Yoshitaka; Utsugi, Satoru; Nakajima, Mitsumasa; Funakubo, Hiroshi; and Gruverman, Alexei, "Complex domain structure in relaxed PbTiO₃ thick films grown on (100)cSrRuO₃/(100)SrTiO₃ substrates" (2012). *Alexei Gruverman Publications*. 59.
<https://digitalcommons.unl.edu/physicsgruverman/59>

This Article is brought to you for free and open access by the Research Papers in Physics and Astronomy at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Alexei Gruverman Publications by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

Authors

Shintaro Yasui, Yoshitaka Ehara, Satoru Utsugi, Mitsumasa Nakajima, Hiroshi Funakubo, and Alexei Gruverman

Complex domain structure in relaxed PbTiO₃ thick films grown on (100)_cSrRuO₃/(100)SrTiO₃ substrates

Shintaro Yasui,^{1,a)} Yoshitaka Ehara,¹ Satoru Utsugi,¹ Mitsumasa Nakajima,¹ Hiroshi Funakubo,^{1,a)} and Alexei Gruverman²

¹Department of Innovative and Engineered Materials, Tokyo Institute of Technology, 4259 J2-43 Nagatsuta-cho, Midori-ku, Yokohama 226-8502, Japan

²Department of Physics and Astronomy, University of Nebraska, Lincoln, Nebraska 68588, USA

(Received 31 December 2011; accepted 4 June 2012; published online 4 September 2012)

Domain structures of epitaxial PbTiO₃ films grown on (100)_cSrRuO₃/(100)SrTiO₃ substrates by metalorganic chemical vapor deposition were investigated by x-ray diffraction (XRD) and piezoresponse force microscopy (PFM) techniques. It was found that with increasing film thickness, the domain structure changed from simple (001) polarization orientation to a complicated mixture of (001) and (100) orientations. PFM mappings showed that in the thicker films (~1100 nm), the zigzag (001)/(100) domain boundaries made an angle of approximately 87° instead of 90° typically observed in (001)/(100) domain patterns in thinner (<300 nm) films. Full-relaxed tilting angle $\theta_1 + \theta_2 + \theta_3 = 3.4^\circ$ obtained from cross-sectional profile analysis of topological step-terrace structure was in good agreement with 3.4° and 3.6° angle values obtained from XRD measurements and theoretical prediction, respectively. © 2012 American Institute of Physics.

[<http://dx.doi.org/10.1063/1.4746078>]

I. INTRODUCTION

Pb(Zr, Ti)O₃ films are actively investigated for nonvolatile ferroelectric random access memory (FeRAM)¹ and piezoelectric actuators in microelectromechanical system (MEMS).² To understand their ferroelectric and piezoelectric properties, a large number of studies focus on domain structure of these films.^{3–6} It is well known that domain structures in epitaxial Pb(Zr,Ti)O₃ films change with film thickness due to strain caused by lattice mismatch and difference in thermal expansion coefficient of the films and the substrates.^{7–10} In PbTiO₃ films of up to ~100 nm in thickness grown on SrTiO₃ substrates, only 180° domains (or *c*-domains) exist.^{11,12} This structure changes to a mixture of 180° domains and 90° domains (or *a*-domains) for the film thickness range from ~100 to ~1000 nm.^{13–16} Epitaxial PbTiO₃ films with the thickness above ~1000 nm possess even more complex domain structure consisting of *c*-domains and three different types of *a*-domains (*a*₁, *a*₂, and *a*₃). This thickness-related transformations of the domain structures are in good agreement with the theoretical model put forward by Roytburd *et al.*^{17,18} Previously, we presented a model describing the experimentally observed domain arrangements in thick (above ~1000 nm) films.^{19–21} In this model, the constituent angles between *c*-/*a*₁-domain and *a*₂-/*a*₃-domain regions of this complex structure were 90°, however, piezoresponse force microscopy (PFM) results showed that this angle was not 90°.^{20,21} In the present study, the detail analysis of domain structures in epitaxial PbTiO₃ films grown on (100)SrRuO₃/(100)SrTiO₃ substrates by metal organic chemical vapor deposition are investigated by x-ray diffraction reciprocal space mappings (XRD-RSMs) and PFM. Based on these results, a modified

model of *c*-/*a*₁-/*a*₂-/*a*₃-domain structure in thicker epitaxial PbTiO₃ films is represented.

II. EXPERIMENTAL

Epitaxial PbTiO₃ films with the thickness in the range from 50 nm to over 1000 nm have been grown on (100)_cSrRuO₃/(100)SrTiO₃ substrates at 600 °C by pulsed metalorganic chemical vapor deposition (pulsed-MOCVD). SrRuO₃ electrodes have been deposited by RF magnetron sputtering method. Details of the film deposition can be found elsewhere.²² Structural characterization of the deposited films was carried out by high resolution XRD (X'pert MRD, PANalytical) analysis using a four-axis diffractometer with CuK_α radiation. Surface morphology and domain structure of the films have been studied by using a commercial atomic force microscope (SII, SPI3800N). Detail visualization of domain configuration was carried out by PFM using vertical (out-of-plane) and lateral (in-plane) modes using AC bias of 10 V_{p-p} at frequency of 13 kHz for the thicker films above 1000 nm. In the case of thinner films below 100 nm, small voltage below coercive field of 1 V was used for PFM measurement at frequency of 13 kHz. Rh-coated conductive cantilevers were used for all PFM measurements.

III. RESULTS AND DISCUSSION

XRD-RSMs around SrTiO₃ 200 diffraction for epitaxial PbTiO₃ films of various thicknesses are shown in Figs. 1(a)–1(c). Only a 002 diffraction peak attributed to *c*-domain is detected in 50 nm thick PbTiO₃ films. This structure in Fig. 1(a) is characterized as only *c*-domain structure. In the films with the thickness range from ~100 up to ~1000 nm, PbTiO₃ 200 diffraction peaks due to the tilting from the substrate normal direction appear in addition to the PbTiO₃ 002 peaks giving rise to a structure labeled as *c*-/*a*₁-domain

^{a)}Authors to whom correspondence should be addressed. Electronic addresses: yasui.s.aa@m.titech.ac.jp and funakubo.h.aa@m.titech.ac.jp.

FIG. 1. (a)-(c) XRD-RSMs measured around SrTiO_3 200, (d)-(f) vertical piezoresponse images, and (g)-(i) schematic drawings of constituent domain structures of c -domain, c/a_1 -domain, and $c/a_1/a_2/a_3$ -domain observed in epitaxial PbTiO_3 films grown on $(100)_c\text{SrRuO}_3/(100)\text{SrTiO}_3$ substrates. Film thickness: ((a), (d), (g)) 50 nm, ((b), (e), (h)) 300 nm, ((c), (f), (i)) 1100 nm. Arrows in (g)-(i) correspond to polarization directions.

structure (Fig. 1(b)). Finally, Fig. 1(c) shows that for the films thicker than 1000 nm both PbTiO_3 002 and 200 diffraction spots are tilted from substrate normal. Note that c - and a -domain spots in this $c/a_1/a_2/a_3$ -domain structure are split along the in-plane direction due to the existence of three kinds of a -domains and one kind of c -domain (see below).¹⁹⁻²¹ Systematical crystallographic analysis as a function of film thickness has been previously reported for the epitaxial PbTiO_3 films grown on SrTiO_3 substrates.¹⁹

Typical vertical PFM amplitude images of the same films are shown in Figs. 1(d)–1(f). Homogeneous PFM contrast is observed for c -domain structure in Fig. 1(d) where the central square represents an area subjected to DC voltage poling. PFM pattern consisting of c/a_1 -domains (with the dark stripes corresponding to a -domains) is shown in Fig. 1(e). A small width of a_1 domains reduces their contribution to the PFM amplitude signal averaged over the film thickness, which explains their rather faint contrast. On the other hand, a ladder-like $c/a_1/a_2/a_3$ -domain structure is shown in Fig. 1(f), which is different from c/a -domain structure. Note that there are 2 types of a -domains in $c/a_1/a_2/a_3$ -domain structure: approximately 50-nm-wide a -domains set in c -domain band (ladder-like yellow color band) and 300-nm-wide a -domains (brown color band) parallel to the c -domain band. The a_2 - and a_3 -domains in a -domain band are indistinguishable in the vertical PFM image because the polarization directions of these domains are in-plane. Figures 1(g)–1(i) present schematic

illustrations of the c -, c/a_1 -, and $c/a_1/a_2/a_3$ -domain configurations in the areas marked by the dashed line squares in Figs. 1(d)–1(f) reconstructed based on the results of XRD and PFM.¹⁹⁻²¹ In Fig. 1(f), $c/a_1/a_2/a_3$ -domain structure is shown as a simplified old model.¹⁹⁻²¹ However, in contrast with orthogonal a -domains observed in c/a_1 -domain structure, an angle different from 90° is observed between a_1 -domains and a_2/a_3 -domain bands. Detail analysis of $c/a_1/a_2/a_3$ -domain structure has been performed by means of XRD-RSMs, topographic AFM, and PFM measurements.

Figure 2 shows in-plane XRD Ω - Ψ plan-view maps of the films with c/a_1 - and $c/a_1/a_2/a_3$ -domain structures. For the films with c/a_1 -domain structure, the peaks corresponding to c - and a_1 -domains in 200 and 002 mappings are observed as shown in Fig. 2(a) and 2(b). PbTiO_3 200 diffraction peaks appear in addition to PbTiO_3 002 peaks. In this case, the angle between c - and a_1 -domains is 90° . On the other hand, tilted peaks attributed to a_2 - and a_3 -domains are observed in Figs. 2(c) and 2(d) for the thicker films with $c/a_1/a_2/a_3$ -domain structure.

The schematic illustrations of c/a_1 -domains, $c/a_2/a_3$ -domains, and a_1/a_3 -domains junctions in the $c/a_1/a_2/a_3$ -domain structure are shown in Figs. 3(a)–3(h), respectively, based on the out-of-plane and in-plane XRD results. Note that the results of plan-view XRD measurement (not shown here) are also taken into account for this model. Constituent angle between domains along the out-of-plane and

FIG. 2. In-plane XRD plan-view images measured at ((a), (c)) PbTiO_3 200 and ((b), (d)) 002 reflections in the PbTiO_3 films with c - a_1 -domain structure ((a), (b)) and c - a_1 - a_2 - a_3 -domain structure ((c), (d)). Incident direction of x-ray is parallel to Ψ direction.

in-plane directions is determined based on this XRD results (see Fig. 2 and Ref. 20). Tilting angles between c - a_1 -, c - a_2 -, a_1 - a_3 -, and a_2 - a_3 -domain boundaries are found to be 0° , $\theta_1 + \theta_3 = 2.7^\circ$, $\theta_2 = 0.7^\circ$, and $\theta_1 + \theta_2 + \theta_3 = 3.4^\circ$, respectively. Based on the XRD results, it can be expected that the domain boundaries between c - a_1 -domain band and a_2 - a_3 -domain band form a zigzag structure, which is schematically illustrated in Fig. 3(i). In case of c - a_1 - and a_2 - a_3 -domain boundaries, tilting angles are almost 3.6° , which corresponds to fully relaxed domain structures found in bulk crystals. On the other hand, in case of c - a_2 - and a_1 - a_3 -domain boundaries, imperfect relaxed angles were observed as shown in Figs. 3(c), 3(d), 3(g), and 3(h). Formation of a zigzag structure in c - a_1 - a_2 - a_3 -domain structure for fully relaxing residual strain in the film are expected by XRD results.

To study c - a_1 - a_2 - a_3 -domain structure in detail, high resolution PFM imaging has been performed. Figure 4 shows vertical and lateral PFM amplitude and phase images of the films with the thickness of 1100 nm. Two kinds of domain stripes can be seen in *region i* and *region ii* in Fig. 4(a). Periodic variations in vertical PFM amplitude are observed in *region i*, while only a very weak vertical piezoresponse

FIG. 3. Schematic models of ((a), (c), (e), (g)) Cross-sectional and ((b), (d), (f), (h)) plan-view domain configurations in c - a_1 - a_2 - a_3 -domain structure. Domain boundary: ((a), (b)) c - a_1 -, ((c), (d)) c - a_2 -, ((e), (f)) a_2 - a_3 -, and ((g), (h)) a_1 - a_3 -domain boundaries together with tilting angles. (i) Schematic illustration of revised c - a_1 - a_2 - a_3 -domain structure.

signal is detected in *region ii*. On the other hand, in the lateral PFM maps, *region ii* exhibits a strong lateral piezoresponse (Fig. 4(c)). Lateral PFM images also include a weak response from c -domains due to a small tilt angle detected by XRD analysis. Therefore, there is a small cross-talk between lateral and vertical PFM maps. From the analysis of the vertical and lateral PFM phase images in Fig. 4, it can be concluded that *region i* and *region ii* represent c - a_1 -domain and a_2 - a_3 -domain structures, respectively, schematically illustrated in Fig. 3(i). In Fig. 4(a), an internal angle can be found as $\alpha = 90^\circ - (\theta_1 + \theta_2 + \theta_3)$, yielding α value of 87° which is in good agreement with the value of 86.6° estimated from XRD measurements. It must be noted that this is different from the angle of 90° in conventional c - a_1 -domain structure observed in epitaxial PbTiO_3 films with the thickness below 1000 nm.

FIG. 4. ((a), (b)) Vertical and ((c), (d)) lateral PFM images of the 1100-nm-thick PbTiO_3 film with c -/ a_1 -/ a_2 -/ a_3 -domain structure; ((a), (c)) amplitude and ((b), (d)) phase images, and c -domain internal angle is indicated in (a) middle left.

A $3 \times 3 \mu\text{m}^2$ topographical image of epitaxial PbTiO_3 films with c -/ a_1 -/ a_2 -/ a_3 -domain structure is shown in Fig. 5(a). Typical step-terrace structures with broad and narrow widths along SrTiO_3 [100] and [010] directions are observed. Cross-sectional profile of topographical image across the X-Y line in Fig. 5(a) is shown in Fig. 5(b). Steps and terrace correspond to c -/ a_2 -domains illustrated in Fig. 3(c), and constituent angles of $\theta_1 = 2.2^\circ$ and $\theta_2 = 0.7^\circ$ have been calculated using step and terrace length. Furthermore, cross-sectional profiles of topographical image across P-Q line and R-S line corresponding to c -/ a_1 -domains (see Fig. 3(a)) and a_2 -/ a_3 -domains (see Fig. 3(e)) are shown in Fig. 5(c), respectively. Step-terrace structure was also analyzed along P-Q and X-Y lines. Constituent angles obtained from Fig. 5(c) are $\theta_1 + \theta_3 = 2.7^\circ$ and $\theta_2 = 0.7^\circ$. Therefore, evidence of full-relaxed domain structure is obtained from analysis of the topographic map which gives $\theta_1 + \theta_2 + \theta_3 = 3.4^\circ$. This result is in good agreement with the XRD experimental value of 3.4° and a strain relaxed value of 3.6° .^{4,23} A cross-sectional profile along the R-S line is almost flat due to the fact that a_2 -/ a_3 -domains exhibit only in-plane tilting. Thus, the topographic image in Fig. 5 is in good agreement with the schematic model of c -/ a_1 -/ a_2 -/ a_3 -domain structure in Fig. 3. It was already confirmed by the cross sectional TEM images showing that the interface between SrTiO_3 and PbTiO_3 is c -domain structure (several nm in thickness), i.e., a -domain does not directly contact to the substrate.^{24,25} Thus, it could be assumed that there could be a c -/ a_1 -domain structure

FIG. 5. (a) 3D topographic image of the c -/ a_1 -/ a_2 -/ a_3 -domain structure in the 1100-nm-thick PbTiO_3 film. (b) Cross-sectional profiles across the X-Y line and (c) P-Q and R-S lines.

between c -domain and $c/a_1/a_2/a_3$ -domain layers along film thickness direction. These c/a -domain and $c/a_1/a_2/a_3$ -domain structures cannot be easily distinguished by cross sectional TEM analysis, but could be inferred from the XRD analysis. It must be emphasized that the main part of the films consists of $c/a_1/a_2/a_3$ -domain structure that is ascertained by XRD as PFM can get the information mainly from the topmost layers of the films. More details of the 3-dimensional domain arrangement using asymmetric XRD-RSM, TEM, and PFM is underway.

IV. CONCLUSION

Domain structures of epitaxial PbTiO₃ films of various thicknesses have been studied by a combination of XRD and PFM. PFM measurements reveal a zigzag shape of $c/a_1/a_2/a_3$ -domain structures which forms due to relaxation of residual strain in the films. An angle between the c/a_1 - and a_2/a_3 -domain bands in $c/a_1/a_2/a_3$ -domain structure is about 87°, which is in good agreement with XRD data and theoretical prediction. In addition, angles in the c/a_1 - and c/a_2 -domain configurations estimated from the topographical surface profile variations are also in good agreement with XRD data. This study presents a good example of the advantage of synergistic approach based on a combination of structural and functional characterization of ferroelectric thin films, which can be extended to other complex oxide materials.

ACKNOWLEDGMENTS

This research was partially supported by Grant-in-Aid for JSPS Fellows (S.Y.) and Grant-in-Aid for Scientific Research.

¹J. F. Scott and C. A. Araujo, *Science* **246**, 1400 (1989).

²T. Kobayashi, J. Tsaur, and R. Maeda, *Jpn. J. Appl. Phys.*, Part 1 **44**, 7078 (2005).

- ³C. Foster, W. Pompe, A. Daykin, and J. Speck, *J. Appl. Phys.* **79**, 1405 (1996).
- ⁴C. Foster, Z. Li, M. Bucketto, D. Miiller, P. Baldo, L. Rehn, G. Bai, D. Guo, H. You, and L. Merkle, *J. Appl. Phys.* **78**, 2607 (1995).
- ⁵M. Keijser, G. Dormans, J. Cillessen, D. Leeuw, and H. Zandbergen, *Appl. Phys. Lett.* **58**, 2636 (1991).
- ⁶W. Hsu and R. Raj, *Appl. Phys. Lett.* **67**, 792 (1995).
- ⁷M. Otsu, H. Funakubo, K. Shinnozaki, and N. Mizutani, *Trans. Mater. Res. Soc. Jpn.* **14B**, 1655 (1994).
- ⁸K. S. Lee and S. Baik, *J. Appl. Phys.* **85**, 1995 (1999).
- ⁹K. S. Lee and S. Baik, *J. Appl. Phys.* **87**, 8035 (2000).
- ¹⁰K. S. Lee, J. H. Choi, J. Y. Lee, and S. Baik, *J. Appl. Phys.* **90**, 4095 (2001).
- ¹¹S. Streiffner, J. Eastman, D. Fong, C. Thompson, A. Munkholm, M. Murty, O. Auciello, G. Bai, and G. Stephenson, *Phys. Rev. Lett.* **89**, 067601 (2002).
- ¹²I. Vrejoiu, G. Le Rhun, L. Pintilie, D. Hesse, M. Alexe, and U. Gosele, *Adv. Mater.* **18**, 1657 (2006).
- ¹³B. Kwak, A. Erbil, J. Budai, M. Chisholm, L. Boatner, and B. Wilkens, *Phys. Rev. B* **49**, 14865 (1994).
- ¹⁴J. S. Speck, A. C. Dykin, A. Seifert, A. E. Romanov, and W. Pompe, *J. Appl. Phys.* **78**, 1696 (1995).
- ¹⁵A. Roytburd, S. Alpay, L. A. Bendersky, V. Nagarajan, and R. Ramesh, *J. Appl. Phys.* **89**, 553 (2001).
- ¹⁶V. Nagarajan, A. Roytburd, A. Stanishevsky, S. Prasertchoung, T. Zhao, L. Chen, J. Melngailis, O. Auciello, and R. Ramesh, *Nature Mater.* **2**, 43 (2003).
- ¹⁷A. L. Roytburd, *Phys. Status Solidi A* **37**, 329 (1976).
- ¹⁸A. L. Roytburd and Y. Yu, *Ferroelectrics* **144**, 137 (1993).
- ¹⁹H. Nakaki, Y. K. Kim, S. Yokoyama, R. Ikariyama, K. Nishida, K. Saito, and H. Funakubo, *Appl. Phys. Lett.* **91**, 112904 (2007).
- ²⁰H. Nakaki, Y. Kim, S. Yokoyama, R. Ikariyama, K. Nishida, K. Saito, S. Streiffner, A. Gruverman, and H. Funakubo, *J. Appl. Phys.* **104**, 064121 (2008).
- ²¹S. Utsugi, T. Fujisawa, R. Ikariyama, S. Yasui, H. Nakaki, T. Yamada, M. Ishikawa, M. Matsushima, H. Morioka, and H. Funakubo, *Appl. Phys. Lett.* **94**, 052906 (2009).
- ²²T. Kamo, K. Nishida, K. Akiyama, J. Sakai, T. Katoda, and H. Funakubo, *Jpn. J. Appl. Phys.*, Part 1 **46**, 6987 (2007).
- ²³B. Jiang, J. Dong, L. Bursill, and W. Zhong, *J. Appl. Phys.* **87**, 3462 (2000).
- ²⁴T. Kiguchi, K. Aoyagi, T. J. Konno, S. Utsugi, T. Yamada, and H. Funakubo, *Mater. Res. Soc. Symp. Proc.* **1199**, 1199–F09-08 (2010).
- ²⁵T. Kiguchi, K. Aoyagi, Y. Ehara, H. Funakubo, T. Yamada, N. Usami, and T. Konno, *Sci. Technol. Adv. Mater.* **12**, 034413 (2011).