Complex domain structure in relaxed PbTiO$_3$ thick films grown on (100)cSrRuO$_3$//(100)SrTiO$_3$ substrates

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Complex domain structure in relaxed PbTiO₃ thick films grown on (100)ₐSrRuO₃//(100)SrTiO₃ substrates

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Domain structures of epitaxial PbTiO₃ films grown on (100)ₐSrRuO₃//(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.

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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 (a₁, a₂, and a₃). 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-a₁-domain and a₂-a₃-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 metalorganic 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-a₁-a₂-a₃-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)SrRuO₃//(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 CuKα 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 Vp-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)–(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-a₁-domain.
spots are tilted from substrate normal. Note that domain spots in this (brown color band) parallel to the c-domain band. The thicker than 1000 nm both PbTiO$_3$ which is different from are 2 types of a-domains in PbTiO$_3$ films grown on SrTiO$_3$ substrates. Systematical crystallographic analysis as a function of film thickness has been previously reported for the epitaxial PbTiO$_3$ films grown on SrTiO$_3$ substrates.

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-/$a_1$-domain structure. Note that there are 2 types of a-domains in c-/$a_1$/$a_2$-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. In Fig. 1(f), c-/$a_1$/$a_2$/-$a_3$-domain structure is shown as a simplified old model. However, in contrast with orthogonal a-domains observed in c-/$a_1$-domain structure, an angle different from 90$^\circ$ 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 Omega-Psi 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$^\circ$. 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-/$a_2$-domains, $a_2$/$a_3$-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
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 \( \theta_1 = 2.7^\circ \), \( \theta_2 = 0.7^\circ \), 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 and \( a_2/a_3 \)-domain 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 \( 3.6^\circ \), 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 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 \( \alpha \) value of \( 87^\circ \) which is in good agreement with the value of \( 86.6^\circ \) estimated from XRD measurements. It must be noted that this is different from the angle of \( 90^\circ \) in conventional \( c/a_1 \)-domain structure observed in epitaxial PbTiO\(_3\) films with the thickness below 1000 nm.

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**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 \( \Psi \) direction.

**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.
A 3 x 3 μm² topographical image of epitaxial PbTiO₃ films with c-/a₁-/a₂-/a₃-domain structure is shown in Fig. 5(a). Typical step-terrace structures with broad and narrow widths along SrTiO₃ [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-/a₂-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 mage across P-Q line and R-S line corresponding to c-/a₁-domains (see Fig. 3(a)) and a₂-/a₃-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 a₂-/a₃-domains exhibit only in-plane tilting. Thus, the topographic image in Fig. 5 is in good agreement with the schematic model of c-/a₁-/a₂-/a₃-domain structure in Fig. 3. It was already confirmed by the cross sectional TEM images showing that the interface between SrTiO₃ and PbTiO₃ is c-domain structure (several nm in thickness), i.e., a-domain dose not directly contact to the substrate.²⁴,²⁵ Thus, it could be assumed that the there could be a c-/a₁-domain structure.
between $c$-domain and $a_1/a_2/a_3$-domain layers along film thickness direction. These $c$-$a_1$- and $c$-$a_2/a_3$-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 PbTiO$_3$ 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 $87^\circ$, 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.

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