Diffraction contrast analysis of 90° and 180° ferroelectric domain structures of PbTiO₃ thin films

Kenta Aoyagi¹, Takanori Kiguchi², Yoshitaka Ehara³, Tomoaki Yamada⁴, Hiroshi Funakubo³ and Toyohiko J Konno²

¹ Department of Materials Science, Tohoku University, Sendai, Miyagi 980-8579, Japan
² Institute for Materials Research, Tohoku University, Sendai, Miyagi 980-8577, Japan
³ Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama, Kanagawa 226-8503, Japan
⁴ Department of Materials, Physics and Energy Engineering, Nagoya University, Nagoya, Aichi 464-8603, Japan

E-mail: k-aoyagi@imr.tohoku.ac.jp

Received 7 January 2011
Accepted for publication 28 February 2011
Published 3 May 2011
Online at stacks.iop.org/STAM/12/034403

Abstract
The ferroelectric domain structure of a PbTiO₃ thin film on (100) SrTiO₃ has been investigated by transmission electron microscopy (TEM). Two types of a-domain were found: one extended through the film to the surface and another comprised small a-domains confined within the film. Dark-field TEM (DFTEM) observation revealed that 180° domains formed near the substrate and stopped their growth 100 nm away from the substrate. The DFTEM observation also revealed that 90° domain boundaries had head-to-tail structures. To confirm the polarization direction obtained by experiments, diffracted intensities under a two-beam condition were simulated using the extended Darwin–Howie–Whelan equations. On the basis of the obtained results, a ferroelectric domain structure model of PbTiO₃ thin films on SrTiO₃ is proposed.

Keywords: ferroelectric thin film, PbTiO₃, TEM

1. Introduction
In recent years, ferroelectric films have been extensively investigated for various applications including those in nonvolatile ferroelectric random access memories (FeRAMs), sensors and actuators in micro-electro-mechanical systems [1–3]. The ferroelectric and piezoelectric properties of these films are affected by the domain structure. Therefore, control of the domain structure of ferroelectric films is important.

PbTiO₃ (PTO) is a representative ferroelectric material, which also forms solid solutions such as Pb(Zr,Ti)O₃ (PZT). PTO has a very large spontaneous polarization [4–6] and a high ferroelectric phase transition temperature \( T_c = 490°C \) [4, 5]. The domain structure of PTO films has been studied by x-ray diffraction (XRD) analysis, transmission electron microscopy (TEM) and piezoresponse force microscopy (PFM) [7–11]. The domain structure of PTO films depends on the film thickness and the type of fabrication method. Very thin films show the epitaxial relationship PTO(100) || SrTiO₃ (STO) (100) [12, 13] and contain 180° domains [14–16] whose formation reduces the depolarizing field. When the film thickness reaches a critical value, which varies between 50 and 300 nm depending on the type of fabrication method [7], the films show a characteristic pattern consisting of alternating c-domains aligned to the surface normal and a-domains with the c-axis aligned along either the [100], [100], [010], or [010] crystal axis of the STO substrate [12, 13]. a-Domains form to relax the strain associated with the phase transition [13]. In films thicker than 1100 nm, c-domains tilt along the fourfold degenerate [110], [110], [010], and [110] STO axes [9–11]. The domain...
structure model of such thick films has been proposed on the basis of XRD and PFM results [9–11].

Despite the aforementioned studies, details of ferroelectric domain structure, including the polarity of domain walls and the polarization direction, have not been reported yet. In particular, local domain structures at the interface between the film and the substrate, need to be analyzed. TEM is an efficient technique for nanoscale material characterization. In addition, the failure of Friedel’s law in electron diffraction can be used to clarify the polarization direction. Friedel’s law can be expressed as \( I_g = I_{-g} \), where \( I_g \) and \( I_{-g} \) are the intensities of two reflections with reciprocal lattice vectors of \( g \) and \( -g \), respectively; this law is valid even in crystals lacking a symmetry center, within the kinematical theory of diffraction. However, this law fails owing to the dynamical effect [17]. Therefore, in ferroelectric crystals, ferroelectric regions with the polarization \( \mathbf{P} \) appear as bright areas in dark-field images taken by selecting reflections with \( g \cdot \mathbf{P} > 0 \) under the two-beam condition [18–20]. This technique is applied in this study to analyze the ferroelectric domain structure and polarization vector of PTO films at the nanoscale.

2. Experimental details

PTO films were grown on (100) STO substrates at 600 °C by pulsed metalorganic chemical vapor deposition (pulsed-MOCVD), as described elsewhere [21, 22]. Their ferroelectric domain structure was studied by TEM and their polarization direction was determined using the failure of Friedel’s law.

TEM samples were prepared as follows. Two cross-sectional slabs were glued with Gatan G2 epoxy and the other side was polished until the sample thickness was reduced to below 50 μm. This polished side was then dimpled with a Gatan dimple grinder and ion-milled with a Fischione low-angle milling and polishing system (model 1010). A similar thinning procedure was applied to the preparation of plan-view specimens. JEOL JEM-2000FX, JEM-3010 and Topcon EM-002B microscopes were used for TEM.

3. Results

3.1. Ferroelectric domain structure of PbTiO\(_3\) films on (100) SrTiO\(_3\)

Figures 1(a)–(d) show bright-field TEM (BFTEM) images and selected area electron diffraction (SAED) patterns of a PTO film on a (100) STO substrate. Two types of a-domain were identified in a cross-sectional image of the film (figure 1(a)): one grew through the film to the surface and the other stopped its growth within the film. Small a-domains exist within 300 nm from the nearest a-domains. The small a-domains along [101] axis are 50–100 nm in size. The projected domain width of longer a-domains and the distance between them are 30–50 nm and 450–700 nm, respectively. Two adjacent a-domains merged in the magnified image in figure 1(b). Note that a-domains form a line contact with the substrate. The SAED pattern (figure 1(c)) taken with an incident beam parallel to the [010] direction reveals that the angle between the surface normal and the [001] axis of c-domains or the [100] axis of a-domains was 3.6°, which is larger than that reported previously (2.4°) [9, 12, 13] because our TEM specimen is very thin and its strain was released during the sample preparation. A plan-view observation (figure 1(d)) reveals that a-domains intersect at a right angle.

Dark-field TEM (DFTEM) images of the PTO film on the (100) STO substrate were taken to clarify the ferroelectric domain structure. Figures 2(a) and (b) were obtained using 002 and 002 reflections, respectively, for the [010] electron incidence. SAED patterns were recorded from areas where contrast inversion was observed (marked by circles). A domain with a polarization vector \( \mathbf{P} \) gives rise to a bright contrast for \( g \cdot \mathbf{P} > 0 \). Therefore, the contrast in circled areas indicates that 180° domains form near the PTO/STO interface. These 180° domains have a projected width of 10–20 nm, i.e., a period of 20–40 nm. Domain boundaries are perpendicular to the PTO/STO interface and the domain length in the [001] direction is 100 nm. The images in figures 3(a) and (b) were taken from an area more than 100 nm away from the PTO/STO interface using 002 and 002 reflections, respectively, for the [010] electron incidence. Contrast inversion was observed in c-domains. This result indicates that the polarization direction in c-domains is...
parallel to the [001] axis. There is a fine spotty contrast in figures 3(a) and (b) within c-domains. This contrast showed no inversion upon changing the observation parameters and therefore is likely an artifact introduced during the sample preparation. The polarization direction in a-domains can be determined from DFTEM images taken using 002 and 002 reflections. However, it is very difficult to set the required diffraction condition for a-domains because of their small size. Hence, the polarization direction of a-domains was determined indirectly by investigating the polarity of 90° domain boundaries.

To determine the polarity of 90° domain boundaries, DFTEM images were taken using reflections parallel and perpendicular to the domain boundaries. Figures 4(a)–(d) were obtained using 101, 101, 101 and 101 electron incidence. A difference in background intensity is observed for diffraction vectors parallel to 90° domain boundaries but not for diffraction vectors perpendicular to 90° domain boundaries. This indicates that 90° domain boundaries have no polarity, i.e. head-to-tail coupling [23].

3.2. Simulation of diffracted intensity of PbTiO$_3$

To confirm the polarization direction in ferroelectric domains, the diffracted intensities of PTO were simulated by solving the Darwin–Howie–Whelan equations under a two-beam condition [24, 25], extended by Gevers et al [23]. The diffracted intensity, including absorption, is expressed as

$$I = e^{-2\pi\xi_0'z}/2|q_g|^2|\sigma|^2[\cosh(2\pi\sigma_t z) - \cos(2\pi\sigma_r z)],$$

$$\sigma = \sigma_r + i\sigma_i = \sqrt{s_g^2 + 1/q_g q_{-g}},$$

$$\frac{1}{q_g} = \frac{1}{\xi_g} + i\frac{e^{i\theta_g}}{\xi_g},$$

$$\beta_g = \theta_g' - \theta_g,$$

where $\xi_0'$ and $\xi_g'$ are the respective extinction distances of the transmitted and diffracted electron beams, $z$ is the distance from the beam entrance, $s_g$ is the excitation error, and $\theta_g'$ and
Figure 4. (a–d) DFTEM images taken using 10\(\bar{1}\), 10\(\bar{1}\), 101 and \(\bar{1}0\bar{1}\) reflections, respectively. The contrast of the 90° domain can be observed in (a) and (b) images, but not in the (c) or (d) image, indicating that 90° domain boundaries have head-to-tail structures.

Figure 5. Diffracted intensities calculated with the extended Darwin–Howie–Whelan equations: (a, b, c) at 200 kV when the excitation errors are +0.05, 0, and −0.05, and, (d, e, f) at 300 kV when the extinction errors are +0.05, 0, and −0.05, respectively.

\(\theta_g\) are the respective phase angles of the Fourier coefficients of the real and imaginary parts of the electrostatic lattice potential. The parameters required to calculate diffracted intensities were determined from the complex structure factor of PTO calculated by the Weickenmeier–Kohl method [26]. The polarization direction of the unit cell was set parallel to the [00\(\bar{1}\)] direction.

Figures 5(a)–(c) show the diffracted intensities of the 001, 001, 002 and 002 reflections of PTO for \(s_g = +0.05\), 0 and −0.05, respectively, and an acceleration voltage of 200 kV. The diffracted intensities and effective extinction distance \(\xi_{g,\text{eff}}\) for \(s_g \neq 0\) were smaller than those for \(s_g = 0\) (\(\xi_{g,\text{eff}}\) for \(g = 002\) or 002 is shown in figure 5). The effective extinction distances for \(s_g \pm 0.05\) and \(s_g = 0\) were 16 nm and 27 nm,
PTO thin films on STO show a typical polydomain. DFTEM revealed ferroelectric domain structures with fractions of oppositely polarized (180◦) domains obtained in this study (20–40 nm). Note that our films are 400 nm rather than 100 nm thick, and the agreement between the theoretical and experimental results is due to the experimental domain length (100 nm) being equal to the film thickness in the calculation (100 nm). We conclude that the period of 180◦ domains depends on their length.

Next, we consider how to determine the domain length from published data. In the above discussion, 90◦ domains are not taken into consideration, but they are formed in PTO films to relax residual strain induced by the phase transition and the difference in thermal expansion coefficient between PTO and STO. Then, the interaction between 90◦ and 180◦ domains must be taken into account. As Li et al pointed out, the long-range Coulomb interaction promotes antiparallel dipole alignment and thus 180◦ domain walls whereas minimization of the gradient energy (interfacial energy) favors 90◦ domain walls. Meyer and Vanderbilt also pointed out that the energy is about 4 times lower for 90◦ domain walls than for 180◦ domain walls. This is one of the factors for stopping the growth of 180◦ domains because such growth increases interfacial energy. Note that the long-range elastic interaction associated with ferroelectric phase transitions cannot be neglected, and the effects of substrate constraint have to be taken into account for thin films. It is generally presumed that a long-range elastic interaction hinders domain growth. We therefore propose that such an interaction is one of the factors hindering the growth of both 180◦ and 90◦ domains (small domains in figures 1(a) and (b)). However, both interfacial energy (domain wall energy) and elastic interaction can hinder the growth of 180◦ domains and their contributions are difficult to separate experimentally.

4. Discussion

The results of this study reveal that 180◦ domains were formed near the substrate. The period and length of these 180◦ domains were 20–40 nm and 100 nm, respectively. Figure 6 shows a summary of the ferroelectric domain structure model of the PTO thin film inferred from the experimental results. 180◦ domains form near the substrate and stop their growth 100 nm away from it; 90◦ domains form a line contact with the substrate and 90◦ domain boundaries have head-to-tail structures.

The presence of nanoscale 180◦ domains is expected to have significant effects on electrical properties. 180◦ domains near the PTO/STO interface are discussed as follows. The change in the polarization across the interfaces produces an electric field that tends to oppose the polarization. This depolarizing field can be reduced in two ways: through compensation by free charges arriving at the interfaces or by the formation of equal fractions of oppositely polarized (180◦) domains. However, the former is unlikely in our case because the substrate is an insulator. Equilibrium 180◦ domains have been studied by several theoretical treatments, including analytical solutions, shell-model calculations, and Monte Carlo simulations using a first-principles-based effective Hamiltonian. Stephenson and Elder showed that the period of 180◦ domains in PTO films on STO is ∼20 nm when the film thickness is 100 nm. Zhao et al proposed a modified scaling law depending on domain wall width and film thickness. The period of 180◦ domains calculated using the scaling law was ∼35 nm when the domain wall width and film thickness were 1.2 nm and 100 nm, respectively. In their model, the domain length of 180◦ domains is equal to the film thickness. Their calculated period of 180◦ domains agrees with the period of 180◦ domains obtained in this study (20–40 nm). Note that our films are 400 nm rather than 100 nm thick, and the agreement between the theoretical and experimental results is due to the experimental domain length (100 nm) being equal to the film thickness in the calculation (100 nm). We conclude that the period of 180◦ domains depends on their length.

5. Conclusions

We have investigated the ferroelectric domain structure of PbTiO3 thin films on SrTiO3 by transmission electron microscopy and the major results can be summarized as follows.

1. PTO thin films on STO show a typical polydomain structure. Cross-sectional BFTEM images show two types of a-domain. One extends through the film to the surface and another stops its growth within the film. a-Domains make a line contact with the substrate. A plan-view observation revealed that a-domains intersect at right angles.

2. DFTEM revealed ferroelectric domain structures with 180◦ domains formed near the substrate. These 180◦ domains stop their growth 100 nm away from the substrate. It was found that 90◦ domain boundaries show head-to-tail structures.

From these results, we conclude that 180◦ domains are formed to reduce depolarizing field energy. We also suggested that the length of 180◦ domains is determined by the competition among the depolarizing field energy, domain wall energy, Coulomb interaction and elastic interaction.
Acknowledgments

This work was supported in part by the Global COE Program ‘Materials Integration International Center of Education and Research, Tohoku University’, financed by MEXT, Japan. TEM observation was carried out at the High-Voltage Electron Microscopy Center of Tohoku University and the Analytical Research Core for Advanced Materials, Institute for Materials Research, Tohoku University. We thank Mr Eiji Aoyagi, Mr Yuichiro Hayasaka and Mr Shun Itoh for assistance with the TEM observation.

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