FULL PAPER

Interface reaction between PbTiO₃ epitaxial thin films and La-doped SrTiO₃ (001) substrates through edge dislocations induced by 90° domain formation

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The interface structure change between PbTiO₃ (PTO) thin films with various thickness grown on La-doped SrTiO₃(001) (La:STO) single crystal substrates by chemical solution deposition method was elucidated by (scanning) transmission electron microscopy ((S)TEM). The films were comprised of perovskite single phase and cube-on-cube orientation relationship with the substrate. STEM images revealed that the twin deformation precedes the nucleation of edge dislocations away from the coherent interface between the film and the substrate. Diffusion of Pb ions into the substrate was also observed through edge dislocations away from the interface. Edge dislocations climbs downward into the substrate with further diffusion of Pb ions increasing the film thickness. This phenomenon was not observed in the PTO film deposited on the non-doped STO substrate. Therefore, lattice defects in the La:STO substrate, the misfit dislocation induced by 90° domain formation as well as similar ionic radius between Pb and Sr ions appeared to facilitate the local interdiffusion of the constituent elements between the film and the substrate.

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1. Introduction

Ferroelectric thin films have attracted much attention as promising material for applications including nonvolatile ferroelectric random access memories, sensors and actuators in microelectromechanical systems.^{1)–5)} The ferroelectric and piezoelectric properties of these films are affected by microstructure. Therefore, it is important to understand the process of domain structure formation to control the electrical properties.

Among ferroelectric materials, PbTiO₃ (PTO) is the representative one and often used as solid solutions such as Pb(Zr,Ti)O₃ (PZT). PTO has a large spontaneous polarization and a high ferroelectric phase transition temperature $T_c = 490^\circ\text{C}$. Generally, 90° domain structure, involving (100)/(001)-oriented a/c-domains, were formed to relax strain induced by phase transition from cubic to tetragonal phase at T_c in the cooling process of film deposition.^{6),7)} Negative thermal expansion coefficient of PTO is large in the *c*-axis leading to large tetragonality. These factors generate anisotropic strain in the epitaxial films in the cooling

process after crystallization because the crystallization temperature is generally higher than the phase transition temperature from cubic to tetragonal phase.

Some models of the nucleation site of a-domains in the PTO/STO 001 epitaxial thin films have been proposed: atomic steps,⁷⁾ misfit dislocations^{8),9)} Most of the basic studies on the domain structure were focused on the ferroelectric thin films deposited on insulators, such as STO, LaAlO₃, KTaO₃, and MgO, and so on.^{9)–17)} These results showed that the interface between the film and substrate was atomically sharp, and that, segregation or interdiffusion of the film element, highly reactive Pb, did not take place at the interface.

Conductive or semi-conductive substrate or buffer layer were needed for the bottom electrode to measure electrical properties. Si substrate mostly used for ferroelectric thin films in the stacking of Pt/Ti/SiO₂/Si.¹⁸⁾ However, thin films could not grow epitaxially on the substrate.

Instead, the conductive oxides like SrRuO₃ (SRO) deposited on STO substrate have been used for the bottom electrode for PZT epitaxial films. Pb diffused into the misfit dislocation cores, and a Cottrell atmosphere was formed around it.²¹⁾ However, the effect of the Pb-diffusion on the domain structure has not been understood.

La or Nb-doped STO (La/Nb:STO) shows semi-conductivity,^{19),20)} and were used as a substrate as well

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as a bottom electrode for epitaxial growth. These substrate differ from the SRO is the existence of extrinsic A-site vacancies and valence of Ti ions change to keep charge neutrality, thus making Pb ions diffuse more easily than non-doped STO and SRO substrates. However, the effect of doping and conductivity of the doped STO substrates on the interface structure and domain formation of PTO thin films.

In this paper, we have focused on the most simple system of PTO on La:STO (001) epitaxial thin films, and investigated the inter-diffusion of Pb at the film/substrate interface, and elucidated its effect on the growth mechanism of 90° domain structure around the interface.

2. Experimental procedures

PTO thin films were prepared by chemical solution deposition (CSD) method using metal organic decomposition (MOD) solution of Pb10 at %-rich composition, $\text{Pb}_{1.1}\text{TiO}_3$ (Toshima Manufacturing) as starting chemicals estimated by considering empirically the expected reduction of Pb in the film due to the evaporation in the form of PbO .^{22)–24)} The film deposition procedure is as follows; The MOD solution was dropped onto 5 at % La:STO single crystal substrates (Furuuchi Co.) cleaned by ethanol in ultrasonic cleaner. Then, the solution was spin-coated at 500 rpm for 5 s followed by 4000 rpm for 35 s using a spin coater (Mikasa MS-A100) at room temperature (step1). Then the film was heated at 120 °C for 5 min in the atmosphere to dry the solvent (step 2), and at 350 °C for 10 min in the atmosphere to obtain the oxide precursor (step 3). Finally, the oxide precursor was crystalized at 650 °C under O_2 gas flow condition by rapid thermal annealing method using an infrared gold image furnace (ULVAC-RIKO MILA-3000) (step 4). Film thickness was controlled by changing the times of repeating the procedures between spin-coating (step1) and crystallization (step4). These steps 1–4 were repeated 1, 5, 10 times.

The analyses of crystalline structure, phase, orientation, and macro strain analysis were conducted by X-ray diffractometer (XRD; PANalytical X'pert Pro MRD). An asymmetric Ge 220 two-bounce monochromator with an X-ray mirror was used for the diffracted beam optics to collimate the X-ray ($\text{Cu K}\alpha_1$; $\lambda = 0.15405$ nm). A parallel plate collimator was used as the diffracted beam optics to control the divergence of the diffracted beam.

The microstructure was examined with the (scanning) transmission electron microscopy ((S)TEM). Thin foils were prepared by low-energy Ar ion milling at 5.0–0.2 kV (Gatan PIPS model 691). Selected-area electron diffraction (SAED) patterns and high-angle annular dark field (HAADF)-STEM images were obtained using an electron microscope (JEOL JEM-ARM200F Cold FEG) operating at 200 kV. In STEM experiments, the convergence semi-angle α was estimated as 20 mrad for imaging and the acceptance semi-angle $\beta_{\text{in}}\text{--}\beta_{\text{out}}$ was 90–175 mrad. The electron microscopy images were analyzed with an image processing software (Gatan Digital Micrograph). Elemental mapping was conducted using a silicon drift detector-

type energy-dispersive X-ray spectrometer (EDS) equipped with STEM (JEOL JED-2300). Pb-M, Sr-L, Ti-K characteristic X-ray lines were used. The convergence semi-angle α for STEM-EDS analysis was estimated as 27 mrad.

Local strain analysis was conducted by geometric phase analysis (GPA; HREM Research GPA Phase).^{9),24)–26)} This method analyzes the periodicity in high-resolution TEM and STEM images using selected spots in diffractograms, which is the Fourier transformation of the images. The image intensity $I(\mathbf{r})$ is obtained by Fourier transformation with the local Fourier component $I_g(\mathbf{r})$:

$$I(\mathbf{r}) = \sum_g I_g(\mathbf{r}) e^{2\pi g \cdot \mathbf{r}}.$$

The local Fourier component $I_g(\mathbf{r})$ is described by the amplitude $A_g(\mathbf{r})$ and geometric phase $P_{gi}(\mathbf{r})$ using the displacement field as

$$I_g(\mathbf{r}) = A_g(\mathbf{r}) e^{P_{gi}(\mathbf{r})}.$$

Here, the phase is calibrated using that in the reference region. Then, the displacement field $\mathbf{u}(\mathbf{r})$ is described by the equation using two noncollinear geometric phases, $P_{gi}(\mathbf{r})$ ($i = 1, 2$) and lattice vectors, $\mathbf{a}_i$ ($i = 1, 2$), in real space as

$$\mathbf{u}(\mathbf{r}) = -\frac{1}{2\pi} [P_{g1}(\mathbf{r})\mathbf{a}_1 + P_{g2}(\mathbf{r})\mathbf{a}_2].$$

The elastic theory for the small deformation shows that the displacement gradient tensor is divided into the symmetric and asymmetric tensors by

$$\begin{aligned} \frac{\partial u_i}{\partial x_j} &= \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right) + \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} - \frac{\partial u_j}{\partial x_i} \right) \\ &= \varepsilon_{ij}(\mathbf{r}) + \omega_{ij}(\mathbf{r}). \end{aligned}$$

Here, ε_{ij} is the strain tensor and ω_{ij} the rotation tensor. These tensors are two-dimensional in the projected image of the electron microscopy, so that each component is represented as

$$\begin{aligned} \varepsilon_{ij}(\mathbf{r}) &= \begin{pmatrix} \varepsilon_{xx}(\mathbf{r}) & \varepsilon_{xy}(\mathbf{r}) \\ \varepsilon_{xy}(\mathbf{r}) & \varepsilon_{yy}(\mathbf{r}) \end{pmatrix}. \\ \omega_{ij}(\mathbf{r}) &= \begin{pmatrix} 0 & \omega_{xy}(\mathbf{r}) \\ \omega_{xy}(\mathbf{r}) & 0 \end{pmatrix}. \end{aligned}$$

$\varepsilon_{xx}(\mathbf{r})$ is the normal strain component in the in-plane direction, $\varepsilon_{yy}(\mathbf{r})$ that in the out-of-plane direction, $\varepsilon_{xy}(\mathbf{r})$ the shear component, and $\omega_{xy}(\mathbf{r})$ the rigid rotation. The estimated spatial resolution is limited by the mask size for each spot in the diffractogram. The maximum mask size is determined by half of the spacing between nearest-neighbor spots. In this study, linearly independent two $\langle 101 \rangle$ vectors were used, and the mask size was determined from the estimated spatial resolution of 1 nm. Here, the strain is defined as relative value of the unit cell deformation against that of the substrate. The channeling behavior of the convergent electron beam in the PTO and STO crystal at each atomic site, Pb, Ti–O, and Sr, was simulated using the multislice method (HREM Research xHREM).^{27),28)}

3. Results

3.1 Macroscopic structure of PbTiO₃ thin films: phase and orientation

Here, the macroscopic structure of PTO thin films is analyzed to identify the orientation and phases in this subsection.

Figure 1(a) shows XRD $2\theta/\omega$ profiles of PTO thin films deposited on La:STO substrates, indicating all of the films include a single perovskite phase and no pyrochlore phase. These patterns showed all prepared PTO films had

Fig. 1. (a) XRD 2θ - ω patterns of 1-layer, 5-layer, 10-layer PTO on La:STO. (b1)–(d1) SAED patterns corresponding to 1-layer, 5-layer, 10-layer PTO on La:STO. (b2)–(d2) Blow-up in the vicinity of 002_{STO} spot in the SAED patterns corresponding to (b1)–(d1). Each film is composed of a single perovskite phase and epitaxially grown on the substrate: $\{001\}_{\text{PTO}}//\{001\}_{\text{La:STO}}$ $\langle 100 \rangle_{\text{PTO}}//\langle 100 \rangle_{\text{La:STO}}$.

a (001) orientation of a pseudocubic single phase. Figures 1(b1)–1(d1) are SAED patterns corresponding to (b2)–(d2). The SAED patterns indicated that all films had a cube-on-cube orientation relationship with the La:STO: $\{001\}_{\text{PTO}}//\{001\}_{\text{La:STO}}$ $\langle 100 \rangle_{\text{PTO}}//\langle 100 \rangle_{\text{La:STO}}$. Thus, all the films were composed of a single perovskite phase epitaxially grown with a cube-on-cube orientation relationship with the substrates.

Intuitively, the 2θ angle of the 00L peaks of the 1-layer PTO film is smaller than that of the 5- and 10-layer ones. Considering 004 peaks of Fig. 1(a), the length of the c -axes of 5- and 10-layer PTO films are 0.4135 nm, while that of 1-layer is 0.4164 nm. The selected area diffraction patterns in (b2), (c2), and (d2) show the peak position of H00 reflections of PTO and La:STO is coincident, which means the a -axis of PTO and La:STO appear to be same, 0.3906 nm. The tetragonality c/a of 1-layer and 5- or 10-layer PTO are 1.066 and 1.059, respectively. The length of a -, c -axis, and c/a of bulk PTO are 0.3899 nm, 0.4140 nm and 1.062, respectively.²⁹⁾ Then, the 1-layer PTO is compressively strained, while the 5- and 10-layer PTO are tensely strained, compared with the crystal structure of the bulk crystal. These differences seem to be subjected to the misfit and thermal stress by the substrate. The 1-layer PTO film should be strongly subjected to this constraint to elongate by 0.6% in the c -axis direction. While, the c -axis of the 5- and 10-layer PTO films is weakly shrunk by 0.1% close to the strain free bulk value.

3.2 a-domain configuration

In this subsection, we analyze the thickness dependence of the configuration and growth process of 90° domains. **Figure 2** shows cross-sectional TEM bright-field images of 1-, 5-, and 10-layer PTO thin films under the excitation of 002 or 200 reflection. According to the images, film thickness was about 6–14, 55–65 and 140–150 nm for 1-, 5-, and 10-layer films, respectively. The region grown in $\langle 101 \rangle$ direction corresponds to 90° domains of the tetragonal phase of PTO. The interval of each domain is about 100 nm in all the films, which indicated that domain nucleation has already finished in 1-layer film and these domains continued to grow in $\langle 101 \rangle$ direction with a larger domain width as film become thicker.

Figure 3 are histograms of domain width in number. As the film thickness increases, the maximum domain width, as well as the spread in the distribution becomes larger. For example, in 5-layer film, the domain width was larger than 1-layer film. This means that 90° domains with the boundaries on $\{101\}_{\text{PTO}}$ already nucleated in 1-layer film continues to grow. In 10-layer film, the domain width distribution was larger than 1-layer and 5-layer film.

From these observations, the effect of film thickness on domain growth process can be understood. **Figure 4** shows a schematic model of 90° domain growth process with varying film thickness. The distribution of domain width increase with the film thickness, however, the domain configuration does not change drastically.

Fig. 2. Cross-sectional TEM bright-field images of (a)(b) 1-layer (c)(d) 5-layer (e)(f) 10-layer PTO thin films deposited on La:STO (a)(c)(e) 002 reflection is excited. (b)(d)(f) 200 reflection is excited.

3.3 a-domain formation

In this section, we investigate the effect of the 90° domain formation on the interface with La:STO substrate to elucidate the interface reaction between PTO and La:STO.

Figures 5(a1)–5(c1) are cross-sectional HAADF-STEM images of 1-, 5- and 10-layer PTO films in the vicinity of the interface between films and substrates. Figures 5(a2)–5(c2) are rigid rotation maps corresponding to Figs. 5(a1)–5(c1), respectively. The rigid rotation maps were calculated from the HAADF-STEM images based on GPA.

For each film, at the bottom edge of 90° domain, an edge dislocation with the Burgers vector $\mathbf{b}=\mathbf{a}[\bar{1}00]$ is present. This dislocation should be formed accompanying domain formation, since the interface is supposed to be coherent and there is no misfit dislocations because of the low lattice mismatch as small as 0.013 between cubic phase PTO and STO at the crystallization temperature of 650 °C, higher than the Curie temperature of PTO at 490°. ^{6,7)} In contrast, the nucleation and growth of the a-domain comprising PTO unit cells with (100) orientation induces lattice mismatch of 0.026 in the in-plane direction at the Curie temperature, and increases up to 0.061 at room

Fig. 3. Histogram of 90° domain width (a) 1-layer (b) 5-layer (c) 10-layer PTO thin films.

Fig. 4. Schematic model of PTO domain growth depending on film thickness (a) 1-layer (6–14 nm): Nucleation of 90° domains, (b) 5-layer (55–65 nm): Growth in width and length, and (c) 10-layer (140–155 nm) films: Further growth in width and length.

temperature. Then, misfit dislocations should be introduced between the a-domain and STO. ^{6,7)}

Figures 6(a) and 6(b) are HAADF-STEM image and rotation map, showing 90° domain without edge dislocation around the interface in 5-layer film. In this case, the tilt angle, i.e. the tetragonality, decreases just near the interface to relax the lattice mismatch without edge dis-

Fig. 5. (a1)–(c1) Cross-sectional HAADF-STEM images of 1-, 5-, and 10-layer PTO on La:STO. (a2)–(c2) rigid rotation maps of (a1)–(c1), respectively.

Fig. 6. (a) Cross-sectional HAADF-STEM image and (b) rotation map of 90° domain in 5-layer PTO thin film on La:STO without edge-type dislocations.

location. In fact, this situation was rarely observed, and we may propose that the domain structure without dislocation at the interface may be metastable and a transition state. Considering the results in Figs. 5 and 6, we may further put forward that the assumption that rigid rotation precedes the emergence of dislocation.

Here, the detail of the interface structure in the vicinity of a dislocation with an a-domain of 10-layer PTO film on La:STO substrate is investigated again. **Figure 7** is (a) HAADF-STEM image of 10-layer PTO on La:STO, (b) the rotation map, (c) the in-plane normal strain map, and (d) the out-of-plane normal strain map. Figure 7 demonstrates that brighter contrast below the edge dislocation as well as the a-domain. The bright contrast at the dislocation

Fig. 7. (a) HAADF-STEM image of 10-layer PTO on La:STO, (b) the rotation map, (c) the in-plane normal strain map, and (d) the out-of-plane normal strain map.

elongated into the region of about 4 nm depth. Interestingly, the edge of a-domain connected with the dislocation intrudes into the surface region of the La:STO substrate as indicated by the broken lines. The strain maps shows that the surface region of the La:STO is strongly strained and rotated as if it transforms to a part of the a-domain. Thus, the region of La:STO in the vicinity of the Pb diffused region with edge dislocation strongly strained and to fit together with the a-domain. The strain maps in Figs. 7(b)–7(d) also shows that the center of the strain field of the dislocation core locates in the La:STO substrate. This result means that the downward climb motion of the dislocation takes place on the La:STO substrate.

For comparison, the detail of the interface structure in the vicinity of a dislocation with an a-domain of 5-layer PTO film on a non-doped STO substrate is investigated. **Figure 8** is (a) HAADF-STEM image of 5-layer PTO on the non-doped STO substrate, (b) the rotation map, (c) the in-plane normal strain map, and (d) the out-of-plane normal strain map. Figure 8 demonstrates that brighter contrast below the edge dislocation expands into the non-doped STO substrate only by 1 or 2 mono layers like atomic steps. The edge of a-domain is also connected with the dislocation, however it does not intrude into the non-doped STO substrate. The strain maps in Figs. 8(b)–8(d) also shows that the center of the strain field of the dislocation core locates in the PTO film. This result means that the climb motion of the dislocation little takes place on the non-doped STO substrate.

3.4 Interface reaction

Comparing Figs. 7 and 8, the edge dislocation induced by the a-domain formation acts as a diffusion pass and migrates itself, however, the diffusion and the migrate length strongly depends on the difference of the A-site of

Fig. 8. (a) Cross-sectional HAADF-STEM image of 5-layer PTO thin film deposited on non-doped STO and (b) rigid rotation map of (a).

STO substrates. In order to investigate the interface reaction, the elemental mapping by STEM-EDS was conducted. **Figure 9** depicts (a) overview of HAADF-STEM image (b) HAADF-STEM image around the interface and STEM-EDS elemental maps of (c) Pb-M, (d) Ti-K, and (e) Sr-L characteristic X-rays for the cross-section of 5-layer PbTiO₃ thin film deposited on La:STO substrate. The HAADF image in Fig. 9(a) shows the interface reaction took place locally. The elemental mapping in Figs. 9(c)–9(e) depict the existence of Pb just under the dislocation in the La:STO substrate, while the Sr is deficient under the dislocation. Ti is uniformly distributed. The region where Pb intrudes in the substrate corresponds to the bright contrast region in HAADF image Fig. 9(a). However, the Pb distribution in the Pb map is somewhat different from the Z^2 -contrast in the HAADF image, and the deficiency of Sr is ambiguous.

Here, the difference between Pb- and Sr-maps seems to be ascribed to 3 reasons: (i) lower intensity of signal and S/N ratio of an EDS map than a HAADF image, (ii) the difference of the channeling behavior between Pb and Sr atomic columns, and (iii) the strain effect on the HAADF image contrast. The reason (i) is trivial reason. Here, the points (ii) and (iii) are investigated.

Figure 10 depicts the electron channeling behavior at Pb or Pb_{0.5}Sr_{0.5}, Sr, Ti–O atomic columns of PTO obtained from the multislice simulation. This graph clearly shows the strong dependence of the average Z -number. Particularly, the incident beam intensity localized in the thin foil surface region less than 10 nm at the Pb columns. While, the intensity keeps up to 40 nm at the Sr columns. These differences indicate that the channeling depth drastically decreases by the existence of Pb. This result tells us the important facts: the electron probe is off the atomic column in the surface region on the Pb columns rather than on the Sr columns. Then, the characteristic X-ray of Pb is excited

Fig. 9. (a) Overview of HAADF-STEM image of the cross-section of 5-layer PTO thin film deposited on La:STO, (b) HAADF-STEM image around the interface and STEM-EDS elemental maps of (c) Pb-M, (d) Ti-K, and (e) Sr-L characteristic X-rays.

from the Pb ions in the surface region, while that of Sr from both of the surface and deep region of the thin foil. This detection volume difference also effects on the spatial resolution of Pb and Sr. This situation also leads to the dechanneling effect of the channeling electrons, which excite the characteristic X-ray of Sr from the matrix in the vicinity of the Pb-diffused region in the La:STO matrix. Therefore, the Sr map shows the ambiguous contrast at the Pb diffused region with Sr deficiency.

Then, (iii) the strain effect on the HAADF image contrast is investigated. The dislocation core is strongly strained as shown in Figs. 7 and 8, then the electron channeling seems to be easily disturbed compared with the matrix region. The thermal diffuse scattering is main contribution to the HAADF image, then the Debye-Waller factor-type strain with dislocation core increases the Z^2 -contrast.^{30)–32)} Therefore, the Z^2 -contrast around the dislocation core is stronger than that of the matrix region. Thus, the contrast of an EDS map is lower than that of the Z^2 -contrast in the HAADF image around a dislocation core.

The Pb diffusion and the climb motion of dislocations seems to depend on the annealing duration as shown in

Fig. 10. Electron channeling behavior in PTO: (a) Pb, (b) Pb_{0.5}Sr_{0.5}, (c) Sr, (d) Ti–O columns, and (e) line profile of (a)–(d).

Fig. 5. The interface was annealed 1, 5, and 10 times repeatedly for 1-, 5- and 10-layer PTO films, respectively. High reactivity of Pb at high temperature leads to Pb diffusion into the substrate, and (Pb,Sr)TiO₃ (PST) solid solution is formed.^{33),34)} This causes d-spacing variation in the solid solution in substrate side, leading to the climb motion of edge dislocations according to the change of the lattice mismatch. Then, PST forms at the region between the Pb diffused region and STO matrix. The Pb-rich PST takes the tetragonal phase, then an edge of the a-domain below the interface may be PST with the tetragonal phase and compose a part of the a-domain as stated in the section 3.3.

4. Discussion

We have described in detail the configuration and the growth mechanism of the 90° domains in PTO(001) epitaxial thin films prepared by CSD process on the La:STO substrate. The sharpness of the interface becomes locally bluer and rough at misfit dislocations induced by a-domain formation. In this section, the relationship between the interface structure change and the domain growth are discussed.

Figure 11 is the schematic model of nucleation process of a-domain in PTO (001) epitaxial films on La:STO substrates based on the results of Figs. 5, 6, 8 and 9. Each a-domain nucleates at a position in a bottom region of the PTO layer but away from the interface. The strained region

Fig. 11. Schematic model of 90° domain nucleation and growth and interface reaction at the dislocation induced by the 90° domain: Step 1: lattice rotation induced by a-domain nucleation, Step 2: a-domain growth and formation of edge-type dislocation, Step 3: growth of the a-domain and the climb motion of the dislocation, Step 4: intrusion of a-domain into La:STO substrate induced by climb motion of edge-type dislocation.

in a c-domain changes its orientation into an a-domain if the domain nucleation takes place in the PTO film. The growth front of the a-domain moves closer to the interface between PTO and La:STO. The interface inhibits the further growth of the a-domain because STO does not make domain structure, and then, the misfit dislocation is induced instead of the twin deformation by the domain re-orientation. Therefore, the front of the a-domain and the edge dislocation are initially away from the interface.

HAADF-STEM images reflect the Z^2 -contrast, where Z means averaged atomic number, then a brighter contrast corresponding to higher concentration of Pb atomic columns.^{35),36)} The strain effect of dislocations also affects on the Z^2 -contrast as stated in the section 3.4.^{30)–32)} In the 1-layer PTO film in Fig. 5(a), Z^2 -contrast reveals that the film/substrate interface is atomically sharp. On the other hand, in the 5-layer PTO in Fig. 5(b), the interface

becomes blurrier, and the bright contrast region intrudes into the substrate side just at the bottom edge of 90° domain. This result means that the Pb diffusion took place at the edge dislocation introduced by the 90° domain formation. The diffusion depth is larger in the 10-layer film than 5-layer film. Edge dislocations also climb downward into the substrate as film thickness becomes larger.

Figure 8 hardly shows the Pb diffusion into the STO substrate, even though Pb shows intrinsically high chemical activity at the elevated temperature. The migration of Pb should be facilitated in the presence of the diffusion sites and the diffusion pass. Generally, the concentration of thermally induced intrinsic vacancies is ppm order or less even at the melting point. On the other hand, the concentration of 5 at%La:STO involves the extrinsic vacancies of % order to keep the charge-neutrality between Sr^{2+} and La^{3+} . Furthermore, the formation of 90° domains induces misfit dislocations to compensate the lattice mismatch between the c -axis of PTO and a -axis of PTO or STO by the phase transition as stated above. Figures 5, 7, and 9 indicate that Pb diffusion takes place at the edge dislocations with open space in their core. The ionic radius of Sr^{2+} and Pb^{2+} under the 12-coordination environment are 0.144 and 0.149 nm, respectively, so that the local strain induced by the substitution of these ions is small.³⁷⁾ Therefore, high density of the A-site vacancies, dislocation core as the diffusion pass, and small strain accompanying with the migration of Pb^{2+} ions facilitate the interdiffusion of A-site ions along the dislocation. The diffusion forms the region of PST solid solution around the dislocation, the lattice parameter and the lattice mismatch vary according to the Pb/Sr composition along the dislocation. Thus, the PST was locally formed around the dislocation in the La:STO and relax the lattice mismatch between the PTO intruded and the La:STO without misfit dislocation.

5. Conclusion

This study elucidated that nucleation and growth process of 90° domains in PTO thin films deposited on La:STO (001) substrates with various film thickness. The coherent interface was formed in the film because of the small lattice mismatch at the crystallization temperature. Then, 90° domains of tetragonal phase were formed away from the interface between the film and substrate at the phase transition temperature, and then, the edge dislocations were induced by the rigid rotation caused by the domain formation during the cooling process. A-site vacancy in La:STO appeared to facilitate the interdiffusion of A-site cations between PTO and La:STO through the dislocation core. Therefore, dislocation induced by 90° domain formation as well as similar ionic radius between Pb and Sr ions appeared to facilitate the local interdiffusion of the constituent elements between the film and the substrate. The interface reaction seems to deteriorate the electrical property at the interface between the ferroelectric material and the electrodes of the thin film devices. Thus, the defect control at the interface is important for crystal growth as well as the electrical properties.

These results suggest that another semiconductive substrate like Nb doped STO must show a different type interface reaction. We are now investigating the PTO thin films on the Nb:STO and will report findings in the near future.

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