FULL PAPER

Epitaxial growth mechanism of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ thin films on SrTiO_3 by chemical solution deposition via self-organized seed layerTakanori KIGUCHI^{1,†}, Takumi SHIMIZU², Takahisa SHIRAISHI¹ and Toyohiko J. KONNO¹¹Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan²Graduate School of Engineering, Tohoku University, 6-6-04 Aramaki Aza Aoba, Aoba-ku, Sendai 980-8579, Japan

Using scanning transmission electron microscopy and electron energy loss spectroscopy, we have elucidated the local structure and the crystallization mechanism of amorphous phase $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT) ($x = 0.3$) thin films deposited on SrTiO_3 (STO) (001) single-crystal substrates by chemical solution deposition. The amorphous phase involves the short-range order of $(\text{Ti/Zr})\text{O}_6$ octahedra and Pb-O , and then, they are connected with the residual carbon. During the pyrolysis process, the first unit cells of the film has already crystallized with cube-on-cube epitaxial relationship with the STO substrate. The film-substrate interface is coherent and atomically sharp between the first Pb-O layer and the substrate. In the crystallization process, this layer seems to act as a seed layer for PZT epitaxial film growth. It accelerates crystal growth as a nucleation site and simultaneously shrinks the film by combustion of the residual carbon and subsequent densification, affecting the local coordination structure in the amorphous phase. The self-organized seed layer in the pyrolyzed film appears to play an important role in the epitaxial growth.

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1. Introduction

With increasing importance of the control of electronic devices via the internet, the internet of things (IoT) is emphasized as infrastructure. Miniaturization of ferroelectrics for mobile devices is a necessary task to achieve the IoT society.¹⁾ Ferroelectric oxides have important potential for application for IoT devices because of their excellent ferroelectric and related ferroic, pyroelectric, and piezoelectric properties. Novel effects such as flexoelectric and electrocaloric effects are also emphasized as new functionalities of ferroelectric materials.²⁾⁻¹⁰⁾ A representative material that is widely used for various applications is $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ($x = 0-1$) (PZT). It is used for nonvolatile memory, ultrasonic devices, and gyroscope sensors because it shows a morphotropic phase boundary (MPB) in which the phase stability is sensitive to external fields. Moreover, its metastable monoclinic phases are believed to induce free rotation of spontaneous polarization.¹¹⁾⁻²¹⁾

The PZT thin films are prepared using various processing techniques: mainly gas-phase processes and liquid-phase processes. The former include molecular beam epi-

taxy, sputtering, pulsed-laser deposition, and metal organic chemical vapor deposition. The latter are hydrothermal deposition and chemical solution deposition (CSD) using sol-gel or metalloorganic decomposition (MOD) solutions.²²⁾⁻²⁵⁾ Here, the CSD processing presents many benefits against gas-phase processes: excellent composition transferability from mixed-raw materials to thin films, simple facilities, and low cost. We have specifically studied MOD processing as the simplest CSD.²⁶⁾⁻²⁸⁾

The crystal growth mechanism on the substrate of the CSD processing differs from that of gas-phase processes because of large differences of the concentrations of raw materials. In the gas-phase process, the crystal growth process involves adsorption of atoms onto a heated substrate surface, migration of atoms on the surface, incorporation into the kink of the substrate or already grown crystals of the film. On the other hand, CSD processing involves following four steps: metal-organic precursors with long-chain organic ligands, dissolved in an organic solution, are coated by spraying, dipping, or spin-coating. They are then dried to remove solvents, followed by decomposition into an amorphous oxide thin film as a precursor; and are finally heated to be crystallized.²⁴⁾ Consequently, for CSD processing, it is important that the structure and the bonding state of amorphous oxide thin film and the interface structure between the film and substrate are established immediately after decomposition.

[†] Corresponding author: T. Kiguchi; E-mail: tkiguchi@imr.tohoku.ac.jp[‡] Preface for this article: DOI <http://doi.org/10.2109/jcersj2.128.P8-1>

However, the initial stage of the crystal growth mechanism in CSD processing using chemical solvent has not been elucidated because the crystal growth cannot be monitored in real time.

The structure without long-range order, amorphous phase, and local interface structure are difficult to detect using macroscopic diffractometry or spectroscopy. Over the last decade, electron microscopy and related electronic spectroscopy methods have improved, providing atomic resolution.²⁹⁾ Recently, we elucidated the early growth mode in the Stranski–Krastanov mode of PZT/MgO interface, which affects the epitaxial thin film structure and orientation.³⁰⁾

In this study, we investigated the CSD-processed amorphous PZT/SrTiO₃ (STO) (001) thin film structure after pyrolysis of the coated and dried PZT film. Particularly, the local structure of the amorphous film and the interface structure between the film and the substrate were investigated using aberration-corrected scanning transmission electron microscopy (STEM) and the related energy-loss near-edge structure elucidated using electron energy loss spectroscopy (EELS).

2. Experiment procedures

Using MOD processing, PZT thin films were prepared on STO(001) substrates. The nominal composition of the raw materials was Pb_{1.1}ZrO₃ and Pb_{1.1}TiO₃, both including 10 at % Pb-rich as starting chemicals. These MOD solutions involve the mixture of lead(II) 2-ethylhexanoate in 2-ethylhexanoic acid, zirconium n-butoxide in 1-butanol, titanium n-butoxide, dissolved in the mixture of the solvents of 1-methoxy-2-propanol and 2-ethylhexanoic acid.

Required excess Pb ratio in the MOD solution was determined to be 10 at % by considering the loss by evaporation in the form of PbO and the formation of the pyrochlore phase.^{26)–28)} The MOD solutions were prepared by mixing of the raw MOD solutions of Pb_{1.1}ZrO₃ and Pb_{1.1}TiO₃ (Toshiba Manufacturing Co. Ltd., Japan). The nominal composition of the mixture is PbZr_xTi_{1-x}O₃ ($x = \text{Zr/Ti} = 0.3/0.7$). This Zr/Ti ratio was adopted to the MPB shift in the Pb-based ferroelectrics solid solutions. As stated later in Fig. 9, the composition of Zr/Ti = 0.3/0.7 was in the MPB composition of PZT epitaxial thin films on the STO(001) substrate in our research. The substrates were STO(001) single crystals (Shinkosha Co. Ltd., Japan).

First, all substrates were chemically cleaned in ethanol using ultrasonic cleaner with subsequent drying at 120 °C for 5 min in atmosphere on a hot plate. Subsequently the mixed-MOD solutions were spin-coated at 500 rpm for 5 s followed by 4000 rpm for 35 s using a spin coater (MS-A100; Mikasa Co. Ltd., Japan) at room temperature. The films were then dried at 120 °C for 5 min and annealed at 350 °C for 10 min in atmosphere on a hot plate for pyrolysis of the MOD solution. The films were then crystallized at 650 °C for 10 min in O₂ gas flow with rapid thermal annealing using an infrared lamp image furnace (MILA-3000; ULVAC-RIKO Inc.). The apparent heating rate was

about 20 °C/s. The O₂ gas flow rate was 300 ml/min. These processes were conducted once. The substrate was put on a SiC-coated carbon susceptor that effectively absorbs the infrared energy since the absorption coefficient of infrared ray for oxide is low. Consequently, the amorphous film and the substrate after pyrolysis are mainly heated from the susceptor by thermal conduction. This situation is preferable to epitaxial growth of the film.

Thin foils for electron microscopy were prepared using a conventional method including mechanical polishing and Ar ion milling at 0.3–5.0 kV (PIPS models 691 and 695; Gatan Inc.). Microstructures of the prepared PZT thin films were observed using STEM (JEM-ARM200F; JEOL) operating at 200 kV. High-angle annular dark field (HAADF) images were obtained under conditions whereby the convergent semi-angle (α) was 20 mrad and the collection semi-angle range (β) was 90–175 mrad to observe mainly heavier atoms. Annular bright field (ABF) images were obtained under conditions $\beta = 11$ –22 mrad to image the light atoms and heavier atoms. The obtained images were processed using the maximum entropy method (DeconvHAADF; HREM Research Inc.) to remove blurring of the images by the electron probe function.^{31),32)}

Local strain analysis was conducted using geometric phase analysis (GPA Phase; HREM Research Inc.).^{33),34)} Here, the word “strain” was used to designate the relative strain between PZT thin films and STO substrates as a reference. In this study, the linearly independent 101 and $10\bar{1}$ spots were used. The mask size in the reciprocal space was set as 0.5 nm of the estimated spatial resolution in order to detect daringly the strain state from the layer of thickness of 0.5 nm. This mask is too large for the intervals between the origin and 100/001 spots. Instead, we used the 101 and $10\bar{1}$ spots because the neighboring two masks do not overlap.³⁵⁾

Elemental analysis was conducted using a silicon drift detector-type energy-dispersive X-ray spectrometer equipped with STEM (JED-2300; JEOL). This study used Sr-K α , Pb-L α , Ti-K α , and Zr-K α characteristic X-rays. The convergence semi-angle (α) for STEM-energy dispersive X-ray spectroscopy (STEM-EDS) analysis was estimated as 27 mrad. Energy-loss near edge structure (ELNES) of the O-K edge of PZT film was obtained using EELS (Enfinium ER system model 977; Gatan Inc.) to analyze the bonding state between cations and oxygen. STEM-EELS measurements were taken with the convergent semi-angle (α) of 20 mrad and the collection semi-angle range for the energy spectrometer (β) of 39 mrad.

3. Results

3.1 Structure of amorphous and crystallized PZT thin films

This subsection presents the structural difference between PZT thin films after pyrolysis and crystallization in macroscopic scale.

Figure 1 shows the selected area diffraction patterns projected from the [010]_{STO} zone axis of PZT thin films after (a) pyrolysis and (b) crystallization. Only basic

Fig. 1. Selected area diffraction patterns projected from the $[010]_{\text{STO}}$ zone axis of PZT thin films after (a) pyrolysis and (b) crystallization.

reflections from STO substrate appear in Fig. 1(a), which means that the PZT film has no long-range order, such as amorphous or nanocrystalline. The basic reflections from STO substrate as well as those from PZT film are presented in Fig. 1(b). The relation of the spots of PZT and STO show that PZT film has a cube-on-cube epitaxial relation with STO, $(001)_{\text{PZT}}// (001)_{\text{STO}}$, $[100]_{\text{PZT}}// [100]_{\text{STO}}$. No intensity was found from any second phase and the different orientation. The crystallized PZT thin film involves a perovskite-type single phase with a cube-on-cube epitaxial relation with STO(001) substrate.

Figure 2 is cross-sectional HAADF-STEM image of (a) pyrolyzed and (b) crystallized PZT thin films. Figure 2(a) shows that the film thickness before crystallization is 22 nm, whereas that after crystallization is 14 nm. This result indicates that large shrinkage and densification of the pyrolyzed film took place because of the combustion of volatile molecules in the oxygen atmosphere and the disappearance of voids.

Figure 3 shows (a) an EDS spectrum and (b) a HAADF-STEM image and qualitative elemental mapping by EDS of the pyrolyzed film using Sr- $K\alpha$, Pb- $L\alpha$, Ti- $K\alpha$, and Zr- $K\alpha$ characteristic X-ray. Although Fe, Co, and Fe are not involved in the PZT thin films, Fe- $K\alpha$, Co- $K\alpha$, and Cu- $K\alpha$ characteristic X-ray also are detected. They should be the system X-ray excited by the polepiece in the objective lens of the microscope and the supporting brass ring of the thin foil specimens.³⁶⁾

No strong segregation of elements exists in the film. However, as shown in **Fig. 4(a)**, weak compositional variation of Zr and Ti is shown in the depth profile in the elemental maps in Fig. 3(b). This phenomenon was well

Fig. 2. Cross-sectional HAADF-STEM image of (a) pyrolyzed and (b) crystallized PZT thin films.

documented in earlier studies.^{37)–39)} The average compositional ratio of Zr/Ti is 0.28/0.72 against the nominal ratio of 0.3/0.7. The compositional variation of Zr/Ti is 0.32/0.68 to 0.24/0.76. This variation is ascribed to different decomposition temperatures of the MOD solution between PbZrO_3 and PbTiO_3 .³⁹⁾ The DSC spectra of the $\text{Pb}_{1.1}\text{ZrO}_3$ and $\text{Pb}_{1.1}\text{TiO}_3$ MOD solutions, supplied from the manufacturer and used respectively in this research, show the exotherm reaction around 305 and 288 °C. This difference is expected to be the principal cause of the compositional variation.

Figure 4(b) shows depth profiles of all cations in the film. Pb presents no compositional gradient reported in early studies.^{37)–39)} This result indicates homogeneous distribution and less evaporation of Pb. Here, the Zr- $K\alpha$ peak shows a non-zero intensity in the STO substrate. This can be ascribed to an artifact induced by the overlapping of peaks of Sr- $K\beta_{1,3}$ at 15.83 keV with Zr- $K\alpha_{1,2}$ at 15.77 keV, of which the energy difference of 60 eV is much smaller than the energy resolution of the EDS detector of 130 eV, as portrayed in Fig. 4(c).⁴⁰⁾ The causes of the artifact are seemed to be the spurious X-ray from the thin foil that are excited away from the probed region, and the re-deposition of the sputtered STO on the PZT layer in ion milling

Fig. 3. (a) EDS spectrum and (b) HAADF-STEM image and qualitative elemental mapping by EDS of the amorphous film using $\text{Sr-K}\alpha$, $\text{Pb-L}\alpha$, $\text{Ti-K}\alpha$, and $\text{Zr-K}\alpha$ characteristic X-ray.

Fig. 4. Depth profiles of (a) Zr and Ti, (b) all cations in the thin film, and (c) EDS spectra of overlapping $\text{Sr-K}\beta_{1,3}$ and $\text{Zr-K}\alpha_{1,2}$.

Fig. 5. ELNES around the energy loss around 280 eV: (a) C-K and Zr-M_{23} edges in pyrolyzed PZT thin film, (b) Sr-M_{23} edge in STO substrate, and (c) Zr-M_{23} edge in crystallized PZT film.

process. The tailing of the electron probe is well suppressed by the aberration correction of the condenser lens, then this effect can be ignored.³⁶⁾

The pyrolyzed PZT thin film was obtained by the pyrolysis of the spin-coated and dried MOD solution. The residual carbon in the film was analyzed according to ELNES. **Figure 5** shows ELNES for energy loss of around 280 eV: ELNES of the pyrolyzed PZT, the crystallized PZT, and the STO substrate. The ELNES of the pyrolyzed PZT shows a large C-K edge and a high-lying Zr-M_{23} edge. On the other hand, the crystallized PZT and the STO substrate indicate the Zr-M_{23} edge and the Sr-M_{23} edge of the complex shape with a sharp threshold and a delayed maximum.^{29),40)–42)} C-K edge is not apparent. These results suggest that residual carbon exists only in the pyrolyzed PZT thin film of the amorphous phase, and that the carbon does not derive from the contamination. Thus, the results here show that the pyrolyzed of PZT thin film has Pb, Zr, Ti, O, and C.

3.2 Interface structure between amorphous PZT thin films and STO substrate

This subsection describes the structure and the deformation state of the interface between PZT thin films and STO substrate compared with those of the crystallized PZT thin films.

Figure 6 shows (a) a cross-sectional HAADF-STEM image of the pyrolyzed PZT thin film and (b) a magnified image of (a). These images depict one or two atomic layers with brighter contrast on the substrate with steps of atomic height at two indicated positions. This contrast shows the heavier element as Z-contrast (Z: atomic number): $Z = 82$ for Pb in PZT and $Z = 38$ for Sr in STO. Then, the first layer of PZT has already nucleated epitaxially immediately after thermal decomposition of the coated and dried PZT thin film at 350°C . No second phase or contamination was found between the PZT and the STO, although the MOD solution comprises the organic solvent and the metallo-

Fig. 6. (a) Cross-sectional HAADF-STEM image of the amorphous PZT thin film after pyrolysis at 350 °C and (b) the blow-up image of (a).

organic compounds. This result reveals that PZT connected directly with the STO substrate.

Figure 7 portrays (a) HAADF-STEM and (b) ABF-STEM images of the pyrolyzed PZT thin film with higher resolution than that of Fig. 6. Black arrows indicate the interface between PZT and STO. White arrows indicate the strong Z-contrast region of the second Pb–O layer. The interface is atomically sharp between the first Pb–O layer and the substrate. No misfit dislocation is observed, and the interface is coherent with atomic steps. Compared with the first Pb–O layer, the second Pb–O layer shows weaker contrast. The Z-contrast of HAADF-STEM images also reflects the average atomic number along each atomic column: weaker contrast means a lower average atomic number. In this image, carbon atoms overlapped with the Pb atomic columns lower the average Z-contrast in the second Pb–O layer. These results correspond to a situation in which the first Pb–O layer widely covers the STO surface, whereas the second layer grows like an island, and covers it locally, which is rippling, and the interplane distance increases.

The second layer is weakly incorporated into the interface layer. The ABF-STEM image Fig. 7(b) indicates much clear contrast around the interface layer. White arrows in Fig. 7(b) point out the incorporating atoms on the second Pb–O layer. However, these atoms are difficult to recognize in the HAADF-STEM image of Fig. 7(a), which shows a small atomic cluster in the amorphous region incorporating into the crystallized PZT. Thus, the pyrolyzed PZT film is an amorphous phase except for the

Fig. 7. (a) HAADF and (b) ABF-STEM images of the amorphous PZT thin film with high resolution. Black arrows indicate the interface between PZT and STO, and the white arrows in (a) point the strong Z-contrast region of the second Pb–O layer. White arrows in (b) point out the just incorporating atoms on the second Pb–O layer.

interface region. **Figure 8** portrays another region with a much rougher surface with a position incorporating into the second layer and just incorporated into the third layer at white arrows. After crystallization, the PZT film grows epitaxially on the STO(001) substrate, as described later in this section. From the interface layer, about one or two pairs of Pb–O and Zr/Ti–O layers of PZT have already been crystallized epitaxially after pyrolysis. This layer is expected to act as a seed layer for PZT epitaxial film growth.

Figure 9 presents a cross-sectional (a) HAADF-STEM image, strain maps of (b) the normal strain map along the out-of-plane direction, (c) a normal strain map along the in-plane direction, (d) a rigid rotation map, and (e) a pure shear strain map of the crystallized PZT thin film. Figures 9(b) and 9(c) clearly depict the 90° domain structure of tetragonal phase; the domain boundaries are parallel to $\{101\}_{\text{PZT}}$ planes. The width of each a -domain, with the a -axis oriented in the out-of-plane direction, is as narrow as about 2 nm. The domain structure appears only in the bottom side of the PZT layer, although no domain structure exists on the surface side. The two-layer morphology of the pseudocubic (rhombohedral) and the tetragonal phases was also observed in PMN-PT epitaxial thin

Fig. 8. (a) HAADF and (b) ABF-STEM images of the amorphous PZT thin film with rough interface region. Black arrows indicate the interface between PZT and STO, and the white arrows in (a) point the strong Z-contrast region of the second Pb-O layer. White arrows in (b) point out the just incorporating atoms on the second Pb-O layer.

films.^{17,28)} Then, the PZT thin films involve the rhombohedral and the tetragonal phases; PZT thin films with the compositional ratio $\text{Zr}/\text{Ti} = 0.3/0.7$ are in the MPB composition. Each domain grows from the dislocation core, which was also observed in our earlier study of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ epitaxial films.²⁸⁾

Figure 9 also exhibits misfit dislocations (small arrows). The average interval of misfit dislocations is 13.0 nm, which indicates an apparent lattice mismatch of 0.030. The (100) lattice spacing of PZT film is 0.402 nm, assuming that of STO as 0.3905 nm. This value was comparable with 0.4016 nm of the a -axis of tetragonal phase of PZT ($\text{Zr}/\text{Ti} = 0.3/0.7$) epitaxial thin film assessed using XRD measurement. Moreover, the value is comparable with 0.402 nm of the a -axis of tetragonal phase of PZT ($\text{Zr}/\text{Ti} = 0.5/0.5$) thin film reported earlier.^{43,44)}

Figure 10 shows the cross-sectional (a) HAADF-STEM image, strain maps of (b) the normal strain map along the out-of-plane direction, (c) the normal strain map along the in-plane direction, (d) the rigid rotation map, and (e) the pure shear strain map of the amorphous thin film. Figure 10 clearly illustrates no misfit dislocation in the interface layer because the interface layer is less than the unit cell thickness of 0.4 nm, which is less than the critical thickness of 1.3 nm for introducing dislocation half loops to form misfit dislocations. Critical thickness will be discussed in section 4. The elastic strain energy is small, and

Fig. 9. Cross-sectional (a) HAADF-STEM image, strain maps of (b) the normal strain map along the out-of-plane direction, (c) the normal strain map along the in-plane direction, (d) the rigid rotation map, and (e) the pure shear strain map of the crystallized PZT thin film.

Fig. 10. Cross-sectional (a) HAADF-STEM image, strain maps of (b) the normal strain map along the out-of-plane direction, (c) the normal strain map along the in-plane direction, (d) the rigid rotation map, and (e) the pure shear strain map of the amorphous thin film after pyrolysis.

then, the interface layer coherently strains to take a pseudomorphic structure. Consequently, Fig. 10(b) indicates that the out-of-plane lattice spacing of the interface layer is elongated relative to the STO substrate because of the larger lattice spacings of PZT than that of STO. Figure 10(c) shows no strain because the in-plane lattice spacings of PZT and STO are mutually coincident. Moreover, no shear strain or lattice rotation is visible. This situation corresponds to a coherent interface with no misfit dislocation.⁴⁵⁾

3.3 Local structures of amorphous and crystallized PZT thin films

This subsection is investigated the local structure of the pyrolyzed amorphous thin films in terms of the bonding state and coordination structure between the cations and oxide ions in the films.

Figure 11 shows ELNES of the amorphous PZT, the interface layer, and crystallized PZT of the rhombohedral and the tetragonal phases as references: (a) Ti-L₂₃ edge, (b) blow-up of L₃ edge in (a), (c) variation of the full width of half maximum (FWHM) of L₃-t_{2g} and L₃-e_g edges and the ligand field splitting (LFS) between them, and (d) O-K edge.

The Ti-L₂₃ edge in Fig. 11(a) shows the LFS of white lines and the high-lying satellites. The LFS of white lines reflects the coordination state of O ligands around Ti. The four white lines correspond to the electronic excitations: L₃-t_{2g}:Ti 2p_{3/2}→Ti t_{2g}, L₃-e_g:Ti 2p_{3/2}→Ti e_g, L₂-t_{2g}:Ti 2p_{1/2}→Ti t_{2g}, and L₂-e_g:Ti 2p_{1/2}→Ti t_{2g} under the ligand field with O_h symmetry.^{40),41)} Here, t_{2g} and e_g respectively denote triply degenerated d_{xy}, d_{yz}, and d_{zx} orbitals, and doubly degenerated d_{z2} and d_{x2-y2} orbitals.

Both of the pyrolyzed and the crystallized films show LFS under the O_h local symmetry. The TiO₆ octahedron coordination structure already exists in the pyrolyzed PZT thin film that is apparently of amorphous phase in STEM images. These results indicate that the amorphous PZT thin film involves short range order of TiO₆ octahedra like SiO₄ tetrahedra in silica glass. The amorphous phase intensity and the interface layer in the pyrolyzed PZT thin films are weaker than that of the crystallized PZT of the rhombohedral and the tetragonal phases used as references. Figure 5 depicts considerable amounts of residual carbon in the amorphous PZT thin film. The Ti and O density in the detected volume are expected to decrease, which engenders the weaker edge intensity of the amorphous PZT thin film.

We particularly examine the L₃-t_{2g} and L₃-e_g edges to investigate the ligand field effects on Ti because splitting of L₂ and L₃ arises from the spin-orbital interaction of Ti 2p orbitals. Figure 11(b) is a magnified image showing the area around the L₃ edge in (a). The FWHM of L₃-t_{2g}/L₃-e_g and the LFS in Fig. 11(b) are shown in Fig. 11(c). The FWHM of L₃-t_{2g}/L₃-e_g of the amorphous phase and the interface layer are, respectively, 1.19 eV/1.85 eV and 1.17 eV/1.90 eV. These results suggest that the ligand fields to lifting degeneracy of the amorphous phase and the

Fig. 11. ELNES of the amorphous PZT, the interface layer, and crystallized PZT of the rhombohedral and the tetragonal phases as references: (a) Ti-L₂₃ edge, (b) blow-up of L₃ edge in (a), (c) variation of the FWHM of L₃-t_{2g} and L₃-e_g edges and the LFS between them, and (d) O-K edge.

interface layer are comparable. However, the LFS of the interface layer of 2.00 eV is greater than that of the amorphous phase of 1.85 eV.

First, comparison of the amorphous phase and the interface layer reveals that the difference of L₃-t_{2g} edge is slight, but that of L₃-e_g stands out. Ligand field splitting is apparent between L₃-t_{2g} and L₃-e_g edges. Also, the FWHM of L₃-e_g edge of the interface layer is larger than that of the amorphous PZT. The orbitals of the e_g orbitals of Ti localized toward the 2p orbitals of Ti. The e_g edge is sensitive to the strain and experiences strong covalent interaction.^{46),47)} The interface layer is grown epitaxially on the substrate. It forms a coherent interface with no dislocation, which, and then, induces strain as presented in Fig. 10. The difference of LFS between the amorphous phase and the interface layer can be ascribed to the coherent strain. Such a difference also appears in crystallized PZT thin films. The strain in the tetragonal phase shrinks in the in-plane direction, i.e. the d_{x²-y²} orbital direction. The FWHM of L₃-e_g edge of the tetragonal phase is larger than that of the rhombohedral phase, increasing the energy of the d_{x²-y²} orbital. Such strain deforms unit cells in the interface layer tetragonally. Then the tetragonal phase is stabilized by the constraint of the substrate.²⁸⁾

Figure 11(d) shows the O-K edge of the amorphous PZT, the interface layer, and the rhombohedral and the tetragonal phases of crystallized PZT thin films. O-K edges correspond to the electronic excitations of O1s→O2p. Generally, transition metal oxides show the pre-edge in the energy range of 530–540 eV because of hybridization between the transition metal d-orbital and the oxygen 2p-orbital.^{42),43)} Furthermore, hybridization occurs between the lead 6p-orbital and the oxygen 2p-orbital in the Pb-based perovskite ferroelectrics.^{46)–51)} Peaks A and B respectively correspond to the hybridization of Ti3d-O2p and Pb6p-O2p.^{28),48)} This result indicates that covalent bonds of Ti3d-O2p and Pb6p-O2p already formed in the amorphous state.

Figure 11(d) also shows peaks A and B as well as peak C. Generally, the region above 5–10 eV from the threshold energy reflects weak hybridization between O2p and metallic 4sp band, leading to the continuum state.⁵²⁾ The peaks in this energy range corresponds not to the electronic transition but to the interference effect by the multiple scattering of the excited electron by the surrounding oxygen coordination shells. Then, these peaks are sensitive to the structure. The useful relationship between the energy position of the peak above threshold ΔE and the distance between the excited atom and the atoms of surrounding shells R, i.e. the O-O length:^{52)–54)}

$$\Delta E \cdot R^2 = \text{const.} \quad (1)$$

Focused on the peak C, the energy positions of the crystalline and the amorphous phases are different. The width of the peak C of the amorphous phase and the interface layer is wider than that of the crystalline phases, which infers that the wider distribution of the O-O length in the amorphous and the interface layer. The difference shows

that the BO_6 octahedron of these phases are inhomogeneously deformed than that of the crystalline phases. Here, the tetragonal phase of PZT involves three kinds of the distance between oxygen ions: 0.2835 and 0.2965 nm for O1-O2, and 0.2864 nm for that of O2-O2.⁵²⁾ The ELNES in Fig. 11(d) shows averaged information of these bond length. The number of the bond of each length are 4, then the average bond length is 0.2888 nm. Using this value, the constant value of above the Eq. (1) is 1.047, which leads to the bond length ranging from 0.250 to 0.334 nm. Then, the BO_6 octahedra is drastically deformed ranging from -13% to $+16\%$ in the amorphous phase.

Figure 11(b) also shows high-lying satellites other than the white lines. The origin of the high-lying satellites of the Ti-L₂₃ edge of the perovskite-type oxide is understood by the charge-transfer effect induced between transition metal 3d orbitals and oxygen ligands 2p orbitals.^{55)–57)} The high-lying satellite of Ti-L₂₃ edge appears in the crystallized PZT thin films. However, the satellites are weak for the amorphous phase and the interface layer, which means that the charge transfer between Ti and O is slight.

Finally, the oxygen vacancy in the amorphous phase of the amorphous PZT must be described. An earlier study examined effects of the oxygen vacancy on the LFS of the Ti-L₂₃ edge of STO.⁵⁸⁾ The LFS is sensitive to the oxygen vacancy concentration. Oxygen vacancy of 10 at % greatly decreases the LFS. That of 25 at % vanishes the LFS completely. Figure 11(b) shows that the widths of the amorphous PZT and the interface layer closely resemble those of the crystallized PZT films of rhombohedral and the tetragonal phases. This result illustrates that the amorphous PZT and the interface layer include few oxygen vacancies.

4. Discussion

The preceding section showed important findings related to the local structure of the amorphous phase and the interface layer of PZT/STO thin films prepared by the CSD processing. This section describes the crystallization mechanism with the epitaxial relation between PZT and STO. **Figure 12** depicts a schematic model of the crystallizing process of the PZT/STO thin film after the pyrolysis. Figures 12 (a) and 12(b) respectively portray macroscopic and atomic scale models of the crystal growth of the present research. The nucleation site is apparently the interface layer (blue plate) grown in the pyrolysis process. Figure 11 reveals that the LFS observed in ELNES implies that $(\text{Ti}/\text{Zr})\text{O}_6$ coordination with O_h symmetry, and that the hybridization between Ti–O and Pb–O already formed in the amorphous film after pyrolysis. A short-range order of $(\text{Ti}/\text{Zr})\text{O}_6$ octahedra and Pb–O exists, but the long-range order is broken by connection with residual carbon.

Generally, the nucleation site is important for orientation control, particularly with epitaxial growth. Actually, CSD-processed films require solid-state epitaxy during crystallization. Nucleation at the substrate surface is necessary for epitaxial growth. Figures 6–8 indicate that the interface layer of epitaxially crystallized PZT with about one-unit cell thickness already existed on the STO substrate in the

Fig. 12. Schematic model of the crystallizing process of the PZT/STO thin film after pyrolysis: (a) and (b) respectively show the macroscopic and the atomic scale models of the crystal growth.

pyrolysis process at 350 °C. Two types of the short-range order, $-\text{Ti}/\text{ZrO}_6-$ and $-\text{Pb}-\text{O}-$, in the amorphous phase connected with the interface layer are expected to be incorporated into the PZT crystal of the layer in the crystallization process at 650 °C. Nucleation is expected to occur at the interface layer rather than in the bulk of the amorphous PZT because heterogeneous nucleation generally lowers the energy barrier for the crystallization process. The film was heated preferentially from the substrate side by the susceptor, which is beneficial for epitaxial growth.^{24),45)} Particularly, PZT and STO take the perovskite-type structure, with the difference of the covalency of chemical bonding and the consequent atomic displacement, and the lattice mismatch. The analogy of these crystal structure also lowers the interface energy between the film and the substrate. Therefore, the interface layer formed by pyrolysis seems to act as the self-organized seed layer for PZT film growth. Earlier reports of the literature described the seed layer as having important roles to control the nucleation site and film orientation.^{59),60)} Consequently, the interface layer has important roles for epitaxial growth of PZT film on the STO substrate.

As described in subsection 3.2, the critical thickness for introducing misfit dislocations in the PZT ($\text{Zr}/\text{Ti} = 0.3/0.7$) on STO substrate was estimated as 1.3 nm from the lattice mismatch at the crystallization temperature, assuming mechanical equilibrium theory for misfit dislocation and the elastic stiffness coefficient.^{61)–66)} Consequently, misfit dislocations did not exist between the interface layer and the substrate in the pyrolysis process. Figures 7–10 show that the interface layer coherently strained to take a pseudomorphic structure before crystallization. The residual region of the amorphous phase incorporates serially into the crystallized PZT up to the surface. The misfit dislocation expected to be introduced in the very early stage of the crystallization process when the crystallized

layer thickness exceeds the critical thickness, and the coherent strain of the PZT thin film is relaxed.

The HAADF-STEM images in Figs. 7(a) and 8(a) show that the amorphous PZT film exhibits non-uniform contrast of the size as about 2 nm, which represents the local density variation of the clusters in the amorphous PZT film. Then, the high-density region of C is combusted, releasing volatile organic molecules such as CO₂ into an oxygen atmosphere, and then, the film contracts. It is densified concurrently during the crystallization process at the crystallization temperature. This situation is presented in Fig. 12(b).

5. Conclusions

The local structure and the crystallization mechanism of the amorphous phase of PZT (Zr/Ti = 0.3/0.7) thin films were elucidated using STEM and EELS. They had MPB composition of the epitaxial thin film, which had been deposited by CSD processes on STO(001) single-crystal substrates. The bottom layer of the amorphous PZT thin film contacting with STO substrate had already been crystallized. It shows a cube-on-cube epitaxial relation with the substrate. The interface layer acts as surely as a self-organized seed-layer for epitaxial growth. The amorphous phase of the pyrolyzed PZT thin film already possesses the short range order of (Ti/Zr)O₆ octahedra and Pb–O connected by the residual carbon. Consequently, the precursor state of the PZT thin film involves these ordered structures. The epitaxial growth of the PZT thin film appears to proceed by incorporating a (Ti/Zr)O₆ octahedron and Pb–O into unit cells at the seed-layer or the growth front of the epitaxial growth of the crystallized region. Therefore, the decarburization and the short range order in the amorphous phase and the self-organized interface layer appear to be the crucially important points of epitaxial growth in the CSD process, and play a crucial role in elucidating the crystal growth of the solid-state epitaxy and for lower-temperature growth using the CSD process. Our data underscore the validity of STEM-EELS analysis of a local structure without long-range order, such as that of an amorphous phase.

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