Effect of Ti concentration on the growth of chemically-ordered regions of Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}–PbTiO\textsubscript{3} epitaxial thin films

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(1 – x)Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}–xPbTiO\textsubscript{3} (PMN–PT) (x = 0–1) epitaxial thin films with high crystallinity have been prepared by using metallo-organic decomposition (MOD) processes at a temperature half of the crystallization temperature of the corresponding bulk crystals. X-ray diffraction patterns show that Ti-poor and Ti-rich PMN–PT thin films have perovskite-type structure with a single phase of pseudocubic and/or tetragonal phase, respectively. The morphotropic phase boundary (MPB) is located around x = 0.6. Chemically-ordered regions (CORs), where Mg and Nb ions at B-sites show 1:1 ordered structure in the STEM) images taken along the direction fi

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1. Introduction

Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}–PbTiO\textsubscript{3} (PMN–PT) is a typical relaxor ferroelectric material owing to excellent electric properties. An end component Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3} (PMN) is a typical relaxor ferroelectric material that has high dielectric and piezoelectric constants, where the dielectric constant has a broad peak as a function of temperature and frequency.\textsuperscript{1–2} It is well known that the ferroelectric properties of PMN can be improved by substitution of Mg and/or Nb at B-sites with Ti up to the composition of the morphotropic phase boundary (MPB).\textsuperscript{3–6} Thus, it is important to clarify the influence of Ti doping in PMN–PT in order to elucidate the microstructure and the electrical properties for the improvement of the properties.

By now, relaxor phenomena have not been understood completely. Various models have been proposed in the last decades.\textsuperscript{7–10} Among the models, the “random field model” can explain the phenomena comparatively. The model is based on a heterogeneous structure composed of two sub-structures, i.e. “Polar Nano Region (PNR)”, where the configuration of Mg and Nb ions is disordered and the polarization fluctuates, and “Chemically-Ordered Region (COR)”, where the configuration of Mg and Nb ions is ordered and the polarization does not fluctuate such as a normal ferroelectrics.\textsuperscript{11–15}

It is believed that PNRs are the origin of relaxor properties, and large volume fraction of PNRs is thus desirable at used temperature. PNRs begin to grow when the temperature falls below the Burns temperature T\textsubscript{B}. However, the growth of PNRs is obstructed by pre-existing CORs. This means that CORs play a critical role in controlling the microstructure and the properties of the relaxor in an indirect manner, and it is suggested that final relaxor properties become better by decreasing the volume fraction of CORs.

One of the powerful methods to analyze COR is transmission electron microscopy (TEM). Several studies based on TEM had been reported to understand the behaviors of CORs from \textsuperscript{1990s, 16–18} The focal length of TEM is on the order of \(\mu m\), so that the images show the completely overlapped structure in the projected direction. Then, most of the early researches could not image the correct structure of CORs since the sizes of both PNR and COR are of the order of a few nanometers.

Recently, there have been remarkable developments in aberration-corrected scanning transmission electron microscopy (STEM) in terms of the point resolution and the focal depth. The focal depth of aberration-corrected STEM is \(\approx 5\) nm under the convergent semi-angle 30 mrad, as compared with \(\approx 45\) nm of conventional STEM under the convergent semi-angle 10 mrad. Thus, it becomes possible to image the nano-size CORs using aberration-corrected STEM with more precision.

It should also be mentioned that most of the early researches on CORs employed bulk PMN crystals prepared with high temperature processings (1273–1573 K), which accelerates the growth of CORs. Lowering the processing temperature is one of the effective ways to suppress the growth of CORs, and therefore we focused on thin films that are usually prepared under the much lower processing temperature than that of bulk crystals.\textsuperscript{19–24} For example, by using metallo-organic decomposition (MOD) process, which is one of the chemical solution deposition (CSD) processes that use the MOD solution, PMN–PT thin film can be prepared at a temperature half of bulk crystals (\(\approx 923\) K). According to the literature, growth of PMN at a lower temperature has been reported to suppress COR.\textsuperscript{25–28}

In the present study, it is investigated that the effect of Ti concentration in the Pb(Mg\textsubscript{1/3}Nb\textsubscript{2/3})O\textsubscript{3}–PbTiO\textsubscript{3} solid solution epitaxial thin films grown at a relatively low temperature by
MOD processes. We also discussed the influence of B-site replacement qualitatively with a simple calculation based on Pauling’s rule for bond strength.

2. Experimental procedure

\[(1 - x)\text{Pb}(x\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3 - x\text{PbTiO}_3\] (PMN–xPT) thin films were prepared on SrTiO$_3$(001) substrates by a CSD process using the mixture of MOD solutions. Here, we used the MOD solutions 10% Pb-rich composition, Pb$_3$(xMg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ and Pb$_3$TiO$_3$, as starting chemicals estimated by considering empirically expected reduction of Pb in the film due to evaporation of the film of PbO during the heating process.\(^{30-32}\) PMN–xPT (x = 0–1.0) MOD solutions were prepared by mixing Pb$_{1.1}$(xMg$_{1/3}$Nb$_{2/3}$)$_3$O$_3$ and Pb$_{1.1}$TiO$_3$ MOD solutions (Toshiba Manufacturing Co. Ltd., Japan). PMN–xPT thin films were deposited on the 5 mm × 5 mm SrTiO$_3$ (001) single crystal substrates (Shinkosha Co. Ltd., Japan) by using a spin-coat film forming. The solution was 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). The spin coated thin films were then dried at 393 K for 5 min for pyrolysis, and annealed at 623 K for 10 min in air for decomposition. The films were then crystalized at 923 K for 10 min in O$_2$ gas flow, by using a rapid thermal annealing (RTA) technique, where an infrared lamp (MILA-3000; ULVAC-RIKO. Inc.) was used. The nominal heating rate was 30 K/sec and the O$_2$ gas flow rate was 300 ml/min. These processes were repeated 5 times to achieve sufficient thickness of about 100 nm for subsequent analyses.

The phase identification and the evaluation of crystallinity were done by an X-ray diffraction (XRD) method (X’pert Pro MRD, PANalytical). The incident optics is composed of an asymmetric Ge 220 2-bounce monochromator with an X-ray mirror in order to collimate the X-ray (monochromatic X-ray Cu K$_\alpha$: λ = 0.15405 nm). The diffraction optics is equipped with a parallel plate collimator to keeping the intensity of the diffracted beam. Atomic-resolution analysis of COR microstructures was conducted by using HAADF-STEM (JEM-ARM200F; JEOL Ltd. (Topcon Corp.), Japan) operating at 200 kV. Atomic-resolution analysis of COR microstructures was conducted by using TEM [EM-002B; JEOL Ltd. (Topcon Corp.), Japan] operating at 200 kV. In our experiments, the convergent semi-angle (α) was 30 mrad in order to limit the focal depth less than 5 nm, while the acceptance semi-angle, β$_{p-e}$ was 90–175 mrad, respectively. The electron microscope images have been analyzed with DigitalMicrograph™ (Gatan Inc., U.S.A.). HAADF-STEM images were filtered by the Bragg filtering method in order to analyze COR.

3. Results

3.1 Phase and crystal structure of PMN–PT thin films

XRD patterns of the PMN–xPT thin films (x = 0–1.0) are shown in Fig. 1. The XRD patterns show that all the prepared thin films have the PMN–xPT single phase, i.e. no pyrochlore structure was observed. XRD patterns of the films with Ti concentration \(x = 0–0.6\) have peaks 00l planes (l = 1–4) of pseudocubic phase of the perovskite structure except for those of the STO substrate. These patterns show that PMN–xPT films with \(x < 0.6\) are composed of the pseudocubic single phase with 00l orientation. On the other hand, the XRD patterns of the films with \(x > 0.7\) exhibit splitting of the peaks, 000 and 00l (h, l = 1–4). This can well be explained by a tetragonal phase of perovskite structure. Some peaks are in the vicinity of the tail of STO substrate peaks. This result suggests that so-called 90° domains are formed in the PMN–xPT thin films with \(x = 0.7–1.0\).

Figure 2 shows out-of-plane lattice parameters of PMN–xPT thin films calculated from the 004 and 400 peaks in the PMN–xPT films as shown in Fig. 1. It can be seen that the lattice parameter decreases monotonically with increasing Ti concentration up to \(x = 0.6\). On the other hand, above the concentration, the unit cell parameter of \(a\)– and \(c\)-axis of the tetragonal phase decreases and increases, respectively. The tetragonality of the film increases rapidly above \(x = 0.7\). It should be pointed out here that \(a\)-axis lattice parameter of the film with \(x = 1.0\) cannot be specified because it overlaps with the STO 004 substrate peak. The gradual change of lattice parameters indicates that Ti is randomly substituted in the B-site ions, Mg or Nb.

Figures 1 and 2 mean that the morphotropic phase boundary (MPB) locates around \(x = 0.6–0.7\). This value is larger than that of bulk crystals with \(x = 0.3–0.35\). Residual stress in the thin film would be one of the main causes of the compositional difference of MPB. It should be necessary for further study using X-ray reciprocal space mapping to elucidate precise compositional
range of MPB of this film. The detail analysis will be discussed in a separate paper.

Figure 3 shows rocking curves of 002 peaks of PMN–xPT films, from which the crystallinity of these films can be estimated. Each full width at half maximum (FWHM) is shown in Fig. 4. A comparison between FWHM of PMN–xPT 002 peaks with that of STO 002 peak, i.e. 0.015°, shows that the films have the crystallinity as high as STO substrate below \( x = 0.7 \), i.e. pseudocubic or tetragonal phase with small tetragonality. High FWHM values of the films with the tetragonal phase, especially \( x > 0.7 \), indicate that the mosaicity of the films increases with the tetragonality since the 90° domain structure raises the small angle tilt of the unit cells in a-domains against the unit cells in c-domains. The tilt angle \( \theta \) of a-domain increases with the tetragonality \( c/a \) as follows: \( \theta = 2 \arctan (c/a-90°) \). The tilt of the unit cells in a-domains induces the mosaicity in c-domains. This is the principal source of the higher FWHM of the 002 peak in c-domains.

![Figure 3. Rocking curves of PMN–PT (002) peaks.](image)

![Figure 4. Profile of FWHMs of PMN–PT (002) peaks.](image)

### 3.2 Structure of CORs in PMN–PT thin films

Based on these results, analysis on CORs should focus on the compositional range of \( x < 0.5 \), in which the films have pseudocubic single phase. Figure 5 shows SAED patterns and intensity profiles along the (111) direction of PMN–xPT thin films on STO (001) substrates: (a) \( x = 0 \), (b) \( x = 0.1 \) (c) \( x = 0.2 \) (d) \( x = 0.3 \) (e) \( x = 0.5 \). Further observations show that in both SAED patterns and intensity profiles, weak \( h/2k/2l \) superlattice reflections are observed, as shown by arrows in the intensity profiles. It is widely understood that the superlattice reflections arise from the CORs, which means the CORs have the double periodicity in the (111) direction against the pseudocubic phase. The profiles also show that the intensity of superlattice reflection decreased with an increase of Ti concentration. However, it is difficult to quantify the extent of COR from the weak \( h/2k/2l \) superlattice reflections.

The atomic-resolution analysis was carried out in order to elucidate the detail structure of CORs. Figure 6 shows atomic-resolution HAADF-STEM images of (a) PMN, (b) PMN–0.4PT, and (c) PMN–0.5PT. The diffractograms of images and the magnified images of typical region marked with the white broken squares were also displayed. The diffractogram of PMN thin film shows the ordered reflections of \( h/2k/2l/2 \), that of PMN–0.4PT
thin film shows very weak ordered reflections of h/2 k/2 l/2, and that of PMN–0.5PT thin film shows no ordered reflections of h/2 k/2 l/2. These results indicate that the volume fraction of CORs decreases with Ti concentration, and that CORs completely disappear at the Ti composition between x = 0.4 and 0.5.

The magnified images show the atomic-scale structure of CORs projected along the (110) direction. The Z-contrast of the HAADF-STEM image of PMN thin film clearly shows the B-site ordering of Mg and Nb. The size of each COR is 1 to 2 nm on a side. On the other hand, at a glance, the Z contrast of the HAADF-STEM images of PMN–0.4PT and 0.5PT thin films indicate almost no ordered structure in HAADF-STEM images. However, the diffractogram of the image indicates that PMN–0.4 thin film actually show weak spots of the superlattice. Then, the regions of CORs were depend on the Bragg filtered image of the superlattice reflections. PMN–0.5PT thin films show no CORs even in the diffractogram and the Bragg filtered image. It can also be pointed out that the results of the decrease of COR agree with those of superlattice reflections in SAED patterns intensity profiles, as shown in Fig. 5. Thus, atomic-resolution HAADF-STEM images are useful in analyzing the presence of COR.

Now, it is usually known that the lattice mismatch induced-stress between the thin film and the substrate might affect the thin film structure and morphology of ferroelectrics. PMN thin film formed on SrTiO3 substrate has lattice mismatch of 3.5% at room temperature (PMN: 0.4041 nm, STO: 0.3905 nm). Figure 7 shows a HAADF-STEM image around the interface of PMN thin film and STO substrate. The growth of CORs just above the interface seems to have little correlation with the misfit dislocations that generates the residual stress. This result shows that it can be ignorable that the influence of induced-stress on COR growth in the thin films.

4. Discussion

In the results section, the effects of Ti concentration in PMN–xPT thin films on the formation of CORs are shown in the light of the macro- and microscopic point of view. HAADF-STEM analysis shows that the increase of Ti concentration is effective in suppressing the growth of CORs. The nucleation of CORs is perfectly suppressed at the composition x = 0.4–0.5. These results can be understood from the viewpoints of bond strength based on Pauling’s rule for bond strength. The rule states that the charge of anions in a coordination polyhedron should be balanced by that of a cation that locates at the center of the polyhedron. Thus, a stable octahedron in the perovskite-type structure has a cation whose bond strength is similar to charge of the anions (O²⁻).

Based on the theory, the bond strength of MgO₆ octahedron is \(\Sigma_{\text{Mg}} = \Sigma_{\text{Mg}} = 1.3 < n_{\text{Mg}}\) and NbO₆ octahedron is \(\Sigma_{\text{Nb}} + \Sigma_{\text{O}} = 2.3 > n_{\text{O}}\), where \(\Sigma_{\text{Mg}} = n_{\text{Mg}}/n_{\text{C}}\) is a bond strength, \(n_{\text{C}}\) a coordination number, and \(n_{\text{O}} = 2.0\) the absolute value of the formal valence of O²⁻. This means that PMN unit cells have intrinsically unstable B–O bonds. On the other hand, the sum of the bond strength of TiO₆ octahedron is \(\Sigma_{\text{O}} + \Sigma_{\text{Ti}} = 2.00 = n_{\text{O}}\). These estimations indicate that the unit cells containing Ti have the most stable local structure in PMN–xPT. Therefore, it is suggested that the substitution of B-site by Ti is electrostatically stable, and the whole PMN–xPT becomes a homogeneous solid solution without B-site ordering of Mg and Nb. Strictly, the Pauling’s rule is valid for the pure ionic crystal without considering the covalency of bonds. However, the discussion would be qualitatively accountable for the crystalline stability of PMN–PT.

The driving force for the growth of CORs arises from the strain among the difference of B-sites cation radius, Mg²⁺:0.072 nm and Nb⁵⁺:0.067 nm, and the electrical neutrality (Mg²⁺:Nb⁵⁺ = 1:2). Overall, these considerations suggest that CORs have intrinsically structural frustration. Assuming homogeneous distribution of Ti, Ti³⁺ cations should locate in the interval of 10
unit cells in PMN–0.1PT, and 2.5 unit cells in PMN–0.4PT. Then, the cube roots of the volume of 10 unit cells and 2.5 unit cells, calculated to convert the number of unit cells to the distance between neighboring Ti$^{4+}$ cations along the [001] direction, are 0.870 nm (2–3 unit cells) and 0.544 nm (1–2 unit cells), respectively. This result indicates that Ti$^{4+}$ interrupts the frustration between Mg$^{2+}$ and Nb$^{5+}$ locally as dilute concentration as $x = 0.1$. Comparing with the result of Fig. 6, influence of the interruption of Ti$^{4+}$ is shown as rapidly decrease of COR. Therefore, it can be said that the growth of COR is strongly disturbed by Ti$^{4+}$.

Finally, Fig. 7 shows that the effect of the local strain on the growth of CORs seems little. Figure 6 shows the size of CORs is at most 2 nm, which means the COR is the short range ordered structure. Yan et al. proposed the charge balanced random-layer model as a structure of COR. According to these results and model, the local strain should be relaxed within a COR, then the residual strain would not affect the growth of the CORs in the PMN–xPT thin films.

5. Conclusion

In this study, PMN–PT epitaxial thin films with high crystallinity were prepared by the CSD process using MOD solution on STO substrates. PMN–xPT thin films with Ti composition $x < 0.6$ have pseudocubic single phase and the films with Ti composition $x > 0.6$ have tetragonal single phase, as elucidated from XRD patterns. The lattice parameter gradually decreases with the increase of Ti concentration up to $x = 0.6$, and their tetragonality gradually increases above $x = 0.7$. The SAED patterns and atomic-resolution HAADF-STEM images clearly showed that, with Ti concentration, the density of CORs decreases remaining each size. CORs vanished completely at the Ti composition $x = 0.4$–0.5, which is less than the Ti composition of MPB in this study. These results indicate that the effect of Ti concentration on the growth of CORs resembles to the bulk crystals. It is also clarified that the induced-stress around the interface between thin film and substrate indicated almost little effect on the growth of COR in PMN–PT thin films.

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