Atomic-resolution analysis for the effects of heat treatment on the growth of chemically-ordered regions in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ thin films

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This paper describes growth behaviors of chemically-ordered regions (CORs) in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) epitaxial thin films. The films are crystalized at 650°C, which corresponds to about half of the crystallization temperature of bulk crystals. We obtained PMN epitaxial thin films with high crystallinity by using a metallo-organic decomposition (MOD) process. According to our atomic-resolution analysis using HAADF-STEM images, it is shown that CORs in PMN epitaxial thin films grow by nucleation of small clusters whose sizes are 1 to 2 nm on each side of habit plane, (100) and (110). In addition, post-annealing process at 700 or 800°C causes growth of CORs. The growth mechanism of CORs is not by the expansion of each cluster but by the nucleation of new clusters. After post-annealing at high temperatures, CORs join with each other on their habit plane and made a network along (100), (110) and (112) direction.

Key-words: PMN, Thin film, Chemically ordered region (COR), Chemical solution deposition (CSD), HAADF-STEM

1. Introduction

Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) is a typical relaxor ferroelectric material that has giant dielectric and piezoelectric constants, where the dielectric constant has a broad peak as a function of temperature and frequency.1,2 These unique properties of relaxor ferroelectrics were discovered by Smolenskii et al. in 1950s.3 Since then, a number of researches have been conducted, though relaxor phenomena have not been understood completely yet.4–10 To elucidate the origin of relaxor phenomena, various models have been proposed in the last decades.7–10 One of the most accepted models is called “random field model”.6 The model is based on a heterogeneous crystal field model. The model contains two sub-structures that are ordered/disordered structures of B-site ions Mg$^{2+}$ and Nb$^{5+}$: “Polar Nano Region (PNR)”, a disordered region with rotatable polarization, and “Chemically-Ordered Region (COR)”, an ordered and polarized region.11–15 The fluctuation of PNR is considered as origin of the relaxor phenomena. In particular, PNR is considered as a more effective structure for the relaxor phenomena than COR,16 so relaxor ferroelectrics containing large PNRs are desirable to be used at room temperature. However, there has been no report of the direct observation of PNRs because it is difficult to obtain any signals from disordered phase. On the other hand, the growth of PNR is suppressed by CORs that already exist at the crystalization temperature because PNRs start to grow during cooling process; the temperature is called “Burns temperature $T_b$”. These factors indicate that suppressing the growth of CORs is necessary to control the microscopic behavior.

In early studies, the growth behavior of CORs was discussed for PMN bulk crystals. Those bulk crystals were prepared at high crystallization temperatures, ranging 1000–1300°C.17–22 In other words, the bulk crystals were prepared under conditions close to equilibrium. Thus, CORs already finished growing in the bulk crystals. We considered that crystallization at a low temperature is one of the most effective ways to suppress the growth of CORs.23–25 Thin film formation is a common way to prepare crystals at low temperatures. In our early researches, we prepared PMN thin films at 650°C that is about a half of the temperature of the bulk crystallization. We used chemical solution deposition (CSD) processes using metallo-organic decomposition (MOD) solution.26–28

In this study, we have investigated the morphology of CORs and the effect of annealing temperatures on the growth of CORs in epitaxial PMN thin films using an aberration-corrected scanning transmission electron microscopy (STEM).

2. Experimental procedure

PMN thin films were prepared on SrTiO$_3$ (001) substrates by the CSD process. We used MOD solutions 10% Pb-rich composition, Pb$_{1.0}$(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (Toshima Manufacturing Co. Ltd., Japan), as the starting chemical. This is because the reduction of Pb in the film due to PbO evaporation is anticipated during the heating process. PMN 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 technique. First, the solution was spin-coated at 500 rpm for 5 s followed by spinning at 4000 rpm for 35 s using a spin coater (MS-A100, Mikasa Co. Ltd., Japan). Second, the spin-coated thin films were dried at 120°C for 5 min for pyrolysis, and annealed at 350°C for 10 min in air for decomposition of the solution. Third, the films were crystallized at 650°C for 10 min in the flow of O$_2$ gas, by using a rapid thermal annealing (RTA) technique in an infrared lamp image furnace (MILA-3000; ULVAC-RIKO. Inc.). Here, the nominal heating rate was 30°C/sec and the O$_2$ gas flow rate during crystallization was 300 ml/min. The crystallization was completed growing in the bulk

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performed under facing annealing condition. We repeated 5 cycles of these processes to achieve a thickness of about 100 nm for subsequent analyses. After the crystallization cycles, post-annealing was executed at 700 or 800°C to investigate the growth behavior of CORs.

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 Kα; λ = 0.15406 nm). The diffraction system is equipped with a parallel plate collimator (0.27°) to keep high resolution and intensity of the diffracted beam.

Cross-sectional specimens were prepared by a low energy Ar ion milling at 5.0–0.2 kV (PIPS model 691; Gatan Inc., U.S.A.). Selected-area electron diffraction (SAED) patterns were obtained using TEM (EM-002B; JEOL Ltd. (Topcon Corp.), Japan) operating at 200 kV. Atomic-resolution imaging used high-angle annular dark field-STEM (HAADF-STEM) images that were obtained by using aberration-corrected STEM (JEM-ARM200F; JEOL Ltd., Japan) operating at 200 kV. In our experiments, the convergent semi-angle (α) was 30 mrad in order to set the focal depth around 5 nm. The acceptance semi-angle, θ_in–θ_out, was 90–175 mrad. Images were analyzed with DigitalMicrograph™ (Gatan Inc., U.S.A.). Particularly, HAADF-STEM images were processed with deconvolution software to improve the image contrast and resolution.

3. Results

Figure 1(a) shows 2θ/ω profiles of the PMN thin films annealed at (i) 650°C, (ii) 700°C and (iii) 800°C. These results show that these annealed PMN thin films are composed of single phase. SAED patterns of Fig. 2 show that all films have cube-on-cube epitaxial relationship with STO substrates (001)PMN//(001)STO and [110]PMN//[110]STO. Figures 1(b) and 1(c) show rocking curves of PMN 002 peak and the full width at half maximum (FWHM) of these rocking curves to examine an influence of post-annealing temperature on the mosaicity of thin films. FWHM of all films are around 0.1°; thus the orientation in thin films is high enough for the atomic-resolution analysis. These values are close to angular resolution of the XRD optics, ~0.08°. The slight deviation of the FWHM is less than the experimental error in this study. Then, the FWHM of our films are almost independent to the post-annealing temperature.

Figure 2 presents cross-sectional TEM images, SAED patterns and intensity profiles along (111) direction on the SAED patterns of the thin films annealed at (a) 650°C, (b) 700°C and (c) 800°C. These TEM images show that PMN thin films of each post-annealing condition are obtained mainly single perovskite phase. All SAED patterns and the intensity profiles indicate the existence of weak super spots at h + 1/2, k + 1/2, l + 1/2. The existence of the super spots shows that there is an ordered structure along [111] direction with 1:1 order, i.e. CORs, in all PMN thin films. The intensity of the superlattice spots becomes unambiguous with increasing of post-annealing temperature.

To analyze the details of the growth behavior of CORs, we examined regions of CORs from intensity profiles of Z-contrast on the HAADF-STEM images along B-site columns. Z-contrast is approximately proportional to Z^2, where Z is an average of atomic number at each atomic column. One of the most reliable models, “charge balanced random-layered model”, shows that CORs include two kinds of B-site columns; (Mg_{2/3}Nb_{1/3})

![Fig. 1. XRD data of (a) 2θ/ω profiles, (b) rocking curves, (c) FWHMs of PMN 002 peaks of PMN thin films. The thin films annealed at (i) 650°C (ii) 700°C (iii) 800°C.](image-url)
columns and Nb columns make 1:1 ordered region. The ratio of Z-contrast of B-site columns in a COR approximately becomes $\Gamma_{\text{Mg}_{2/3}\text{Nb}_{1/3}} : \Gamma_{\text{Nb}} \approx 1:3.6$ (Mg: $Z = 12$, Nb: $Z = 41$). Moreover, The Z-contrast is affected by effective length of the electron channeling, which is dominated by the focal depth. The focal depth in the present experiment was approximately 5 nm under the condition of $\alpha = 30$ mrad. Therefore, we can define regions of CORs by the difference of Z-contrast along B-site columns on the HAADF-STEM image. Figure 3(a) shows a typical HAADF-STEM image of PMN thin film and Figs. 3(b)–
3(d) show intensity profiles along B-site columns (b)-(d) in the image. In this paper, we regard the region like Figs. 3(b) and 3(c) as a COR which shows local B-site ordering. However, the ratio of Z-contrast $I_{\text{Mg}2/3\text{Nb}1/3}:I_{\text{Nb}}$ of Fig. 3(b) is smaller than that of theoretical value 1:3.6 even in the most ordered region in the image. The intensity profile reflects the Z-contrast of CORs overlapping with disordered matrix regions in the projecting direction because the size of each COR is less than the focal depth of 5 nm in this experiment. Based on Fig. 3, Fig. 4 shows atomic-resolution HAADF-STEM images including regions of CORs as rectangles at each annealing temperature (a) 650°C, (b) 700°C and (c) 800°C. According to these images, the number and the total area of CORs are increased with higher post-annealing temperature. The growth of CORs is also appeared in diffractograms of HAADF-STEM images. These diffractograms show superlattice spots of $h+1/2$, $k+1/2$, $l+1/2$. The intensities of superlattice spots are increased with higher post-annealing temperature. It is similar behavior of the growth of superlattice reflection on SAED patterns of Fig. 2. The size of each COR is 1 to 2 nm on each side at crystalized temperature 650°C and changes little after each post-annealing [Figs. 4(b) and 4(c)] even though the total area of CORs is increasing. 

**Figure 5** shows histograms that depict distribution of the size of CORs in the HAADF-STEM images of Fig. 4 by counting the number of Pb atoms in each rectangle. These histograms show that most of CORs include around 10 Pb atoms at each PMN thin film and only a few CORs grow with post-annealing. These results of Figs. 4 and 5 show the unique growth behavior of CORs. The main growth behavior of CORs is nucleation as similar small size clusters with B-site ordered structure. These clusters have habit planes of {100} and {110}. The size of each COR is independent at crystalized temperature 650°C. Then, post-annealing process causes nucleation of new COR clusters. Figures 4(b) and 4(c) indicate that these clusters start to connect or overlap with each other on their habit plane by post-annealing. Consequently, COR clusters join to make a network along (100), (110) and (112) directions.
4. Discussion

In this paper, the effects of post-annealing temperature on the growth of CORs in PMN thin films are described. In this section, we discuss the origin of the growth behavior of CORs based on the present results.

A driving force for nucleation the 1:1 ordered CORs in PMN is caused by the difference of ionic radii between Mg\(^{2+}\), 0.072 nm, and Nb\(^{5+}\), 0.067 nm. However, the 1:1 ordering is unstable, because the charge neutrality of B-site in PMN is Mg\(^{2+}\):Nb\(^{5+}\) = 1:2. These conflicting factors are considered to lead to limit the growth of CORs. The total area of CORs expands with higher post-annealing temperature, 1:1 ordering is expected to be influenced by thermal effects i.e. the atomic diffusion of B-site. In other words, lower crystallization temperature is effective in suppressing the growth of CORs. The regions other than CORs are B-site disordered regions, where PNRs exist. Thus, lower crystallization temperature is expected to enhance indirectly the suppression of growth of CORs.

Finally, we discuss the effect of elastic interaction due to film formation. PMN thin films prepared by CSD process include various stresses from STO substrates, i.e. lattice mismatch, difference of thermal expansion coefficient, and so on. However, the shape of CORs in Fig. 4 shows that CORs do not have anisotropy along the growth direction. For this reason, it is indicated that there is almost no elastic interaction between CORs and thermal stresses.

5. Conclusion

This study presents the morphology and growth behavior of CORs in PMN epitaxial thin film prepared by using MOD process on STO substrate. The results can be summarized as follows.

1. CORs start to nucleate at the crystallized temperature 650°C in a PMN thin film, even though the temperature is low enough in comparison with that of bulk PMN crystal, ranging 1000–1300°C.

2. CORs nucleate as small clusters whose sizes are 1 to 2 nm on each side of habit plane, {100} and {110}.

3. The growth of CORs proceeds by the nucleation of new CORs, not the growth of them.

4. CORs connect each other on their habit plane and make a network along (100), (110) and (112) direction by post-annealing at high temperature.

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