Aberration-corrected STEM analysis of ordered structure in Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ thin films

Cangyu Fan$^1$, Takanori Kiguchi$^2$, Tomoaki Yamada$^3$, and Toyohiko J. Konno$^2$

$^1$Department of Materials Science, Tohoku University, Sendai, 980-8579, Japan
$^2$Institute for Material Research, Tohoku University, Sendai, 980-8577, Japan
$^3$Quantum Science and Energy Engineering, Nagoya University, Nagoya 464-8603, Japan

Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$ (PMN) exhibits excellent electrical characteristics as a relaxor ferroelectric material [1,2]. It is generally said that the origin of the PMN properties is the heterogeneity nano-structure that includes chemically ordered regions (CORs) and polar nano-regions (PNRs). We considered that decreasing CORs makes the relaxor properties better. So far, we discovered lower crystallization or annealing temperature suppress the growth of CORs in PMN thin film with metal-organic decomposition (MOD) method [3]. The crystallization temperature could decrease about half as obtaining bulk PMN. To elucidate more clearly about this estimation, it is one of the powerful measures that observing nano-structure with atomic-resolution electron microscopy. In this study, we use aberration-corrected HAADF-STEM to observe the CORs in PMN thin film and another interested material that Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-PbTiO$_3$ (PMN-PT) solid solution thin film. The ratio of PbTiO$_3$ about 30-35 at% in PMN-PT exists in morphotropic phase boundary (MPB), which has more excellent electrical characteristics. It is also valuable to discuss the ordered structure about PMN.

To deposit PMN thin films, 10at%Pb excess PMN MOD solution was spin coated on SrTiO$_3$ substrate. On the other hand, PMN-PT solution was mixed the PMN solution with 10at%Pb excess PbTiO$_3$ MOD solution. After spin coating, substrate was dried and thermal decomposed. The crystallization process was used rapid thermal annealing (RTA) method with infrared heating furnace. Obtained thin films were post annealed in some cases. The condition of crystallization was 923K-10min and post annealing was 973-1073K-10min. Structural observations were used aberration-corrected HAADF-STEM, ABF-STEM and TEM.

FIG.1 shows a typical HAADF-STEM image of a PMN thin film from [1-10]. Contrast of the image is proportional to $Z^2$ (Z is the atomic number), so there are atomic column with heavy atoms in bright contrast. It is able to distinguish strongly ordered contrasts of Mg/Nb column from the other weakly ordered contrasts. This ordered contrast makes clearly exist of CORs and the square surrounds one of it. FIG.2 is diffractograms of PMN thin films that change their annealing temperature. The conditions are 923K crystallization and 1073K post annealed. On each diffractogram, there are 1/2 1/2 1/2 superlattice reflection which is increased with temperature rising. This superlattice reflection exist with COR growth, so it shows CORs already start grow up about half of bulk crystallization temperature and increase as nucleation with annealing. From selected area diffraction patterns (SADPs) and intensity profiles in FIG.3, 1/2 2/1 1/2 superlattice reflection is able to be observed little in PMN-30PT. This is seems to that the CORs in PMN decrease with B-site replacements. The atomic-resolution images will present on the day of academic meeting.

References
FIG. 1. A typical HAADF-STEM image of a PMN thin film from [110] with the model of PMN. The square surrounds a COR.

(a) 923K crystallization  (b) 1073K post annealed

FIG. 2. The diffractograms of PMN thin films: (a) as-crystallized 923K, and (b) post-annealed at 1073K.

FIG. 3. Cross section TEM images with SADPs and intensity profiles along <111> of 10at%Pb excess PMN-xPT (x=(a)0, (b)30) thin films on SrTiO$_3$ (001) substrate. These sample crystallize at 973K.