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DOMAIN-WALL OBSERVATION IN $Pb(Zn_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ SOLID SOLUTIONS BY AFM

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Morphologies on the surfaces of as grown and etched samples in the solid solutions of $Pb(Zn_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ (PZN-xPT) were investigated by atomic force microscopy (AFM). We showed that both the 90° and 180° domain-wall structures in the PZN-xPT can be observed on the etched surface by means of the AFM. We found that complex 180° domain-wall structures with typical size of 1 μm order exist in the c-domain on the (001)-crystal surface of the PZN-20%PT. Finger print pattern was also found in PZN-8%PT.

Key words: relaxor, MPB, AFM, ferroelectrics, finger print pattern

1. INTRODUCTION

Ferroelctric materials belonging to the solid solution system between the perovskite-type relaxor and $PbTiO_3$ such as $Pb(Zn_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ (PZN-xPT) are known to manifest some excellent properties as electrostrictive actuators and sensors, because of the large dielectric constant and high electro-machanical coupling constant.[1,2] These available properties are considered to be due to the existence of the morphotropic phase boundary (MPB) near $x = 9\%$ [3,4]. It was theoretically clarified that the large electro-machanical coupling constant near the MPB originates from the instability perpendicular to the spontaneous polarization, which is called transversal instability[5-7]. Furthermore, it was reported that the domain-wall structure in the range of the concentration, x, located near the MPB and relaxor shows the complicated pattern with the dimension of the micron order.[8] It is guessed that the complex domain-wall structures in these materials also originate from the transverse instability, and they may contribute to the electric and electromechanical properties in these materials.[9]

In the previous papers with respect to the PZN-xPT solid solution system, we reported the experimental results of the Raman scattering and electron diffraction,[10,11] and the observation of the domain-wall structure near the MBP region by the scanning prove microscopy (SPM) and the optical microscope.[9,12]

To clarify the macroscopic properties for device applications such as dielectric constant, piezoelectricity and switching behavior, in general, study of the ferroelectric domain-wall structure is considered to be important. Recently, it was reported that the scanning probe microscopy (SPM) is a powerful method to observe the domain-wall structure on the surface in ferroelectric materials.[13-16] In the present paper, we report the experimental result with respect to observation of the domain-wall structure on the surfaces of as grown and etched samples in the PZN-xPT crystal plate by the AFM.

2. EXPERIMENTAL

2.1 Crystal growth

Crystals of the PZN-xPT were grown by means of the flux method from the PbO-ZnO-Nb_2O-TiO_2 system. The mixture in a platinum crucible was heated to 1150°C and held at this soak temperature for 10 h, then the melt was cooled to 850°C at the rate of -5°C / h. Synthesized crystals were yellowish in color and of 3 mm typical size. All of the synthesized crystals were confirmed by the X-ray powder diffraction studies as being the single perovskite phase.

2.2 Atomic force microscopy

For domain-wall observation by the AFM, plate-like samples with an area of about 5 mm^2 and thickness of about 200 μm were cut out, where orientation of the crystal axis was determined by the back Laue method. For the sample with etched surfaces, plate-like samples were polished with a polishing sheet (0.3 μm size), and were etched at room temperature by aqueous solutions of a mixture of HF (4.6wt%) and NH_4F (36.4wt%).

AFM images were obtained by a commercial scanning probe microscope (Shimazu SPM-9500). Topographic image was acquired in the contact mode AFM with Si cantilever (Olympus OMCL-TR800PSA-1), where typical scanning speed is about 1 Hz.

3. RESULTS AND DISCUSSIONS

3.1 Surface of as grown crystal

Figure 1(a) shows topographic image on the as grown surface of the PZN-20%PT by the contact AFM, where size of the image is 50 μm×50 μm. The sample-plate is perpendicular to the (001)-direction of the cubic coordinate. Stripe pattern showing the 90° domain-wall structure in tetragonal phase is found.[14] Figure 1 (b) shows the cross-sectional profile along the line A-B drown in Fig. 1(a). The surface bending angles, θ, in Fig 1 (b) are obtained as 1.4°, 1.8° and 1.5°. This angle can be calculated from the lattice constants a and c, i.e.,

$$\theta = \left(90 - 2\tan^{-1} c/a\right)^{\circ}. \tag{1}$$

For the PZN-20%PT, θ is estimated as $\theta = 1.7°$ with $a / c = 0.97$.[17] It is seen that the values of θ from AFM are quite reasonable. Thus, it is confirmed that the 90° domain-wall structure is observed on the as grown surface in tetragonal PZN-20%PT crystal.

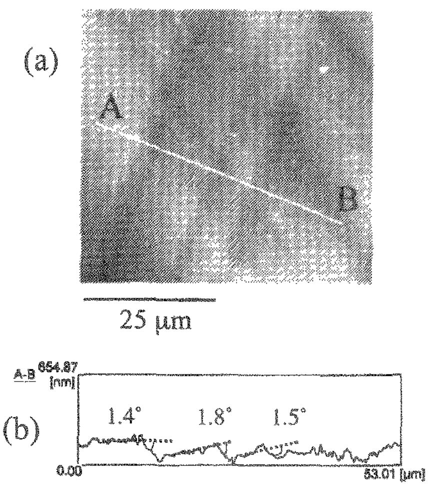

Fig. 1 (a) Topographic image of the (001)-plate sample surface of the PZN-20%PT by the AFM. (b) The cross-sectional profile along the line A-B

3.2 Surface of etched crystal

Figure 2 shows topographic image on the etched surface of the PZN-20%PT by the contact AFM, where size of the image is 125 μm×125 μm. The sample-plate is perpendicular to the (001)-direction of the cubic coordinate. Stripe pattern showing the 90° domain-wall structure is found including two types of domains, where some domains show pale hatched lines, and others show complex island structure.

In order to distinguish between a- and c- domains, this sample was polished to 50 μm in thickness, and then, it was confirmed with an optical polarizing microscope that the former (with pale hatched lines) and the latter (with complex island structure) are a- and c-domains, respectively. Cause of the pale hatched lines in a-domains is not known.

Figure 3 shows topographic image of the c-domain on large scale, where size of the image is 25 μm×25 μm. It is seen that there are two regions with upper and lower height levels in the c-domain. It was reported that the positive end (head) of the polarization etches quite rapidly in HCl (for $BaTiO_3$) [18] and mixture of HCl and HF (for $PbTiO_3$) [15] while the negative end (tail) of the polarization etches very slowly. It was confirmed on the basis of the result by electrostatic force microscopy (EFM) that the 180° domain-wall structure can be observed in the c-domain on the (001) etched surface and upper and lower regions of the topographic image in the c-domain correspond to the domains with the tail and head of the polarizations, respectively.[12] The schematic view of the etched surface of the c-domain is illustrated in Fig. 4.

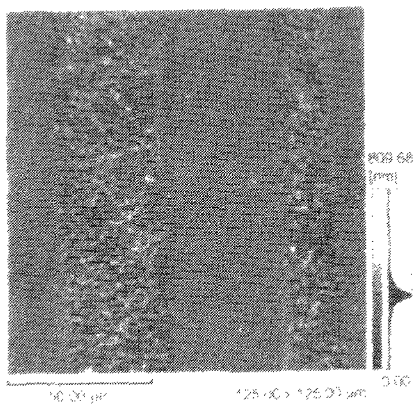

Fig. 2 Topographic image of the (001)-plate sample surface of the PZN-20%PT by the AFM.

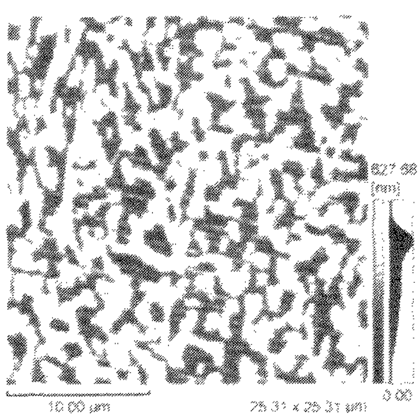

Fig. 3 Topographic image of the c-domain on large scale.

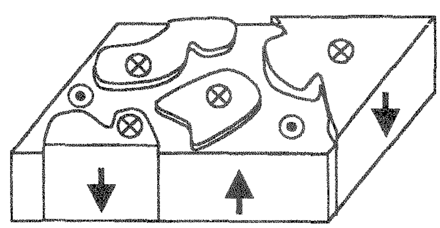

Fig. 4 The schematic view of the etched surface of the c-domain

We showed that both the 90° and 180° domain-wall structures in the PZN-20%PT can be observed on the etched surface by means of the AFM. We found that complex 180° domain-wall structures with typical size of 1 μm order exist in the *c*-domain on the (001)-crystal surface.

Next, let us show the topographic image on the etched surface of the PZN-8%PT crystal in Fig. 5, where size of the image is 30 μm×30 μm. The sample-plate is perpendicular to the (111)-direction of the cubic coordinate. In room temperature, PZN-8%PT is considered to be rhombohedral. Finger print pattern is found on the surface of the PZN-8%PT crystal. The characteristic size of the finger print pattern is roughly estimated to be about 1 μm. Recently, it was reported on the basis of observation by the piezoelectric force microscopy (PFM) that in the PZN-8%PT, finger print pattern is observed with the typical size of 1 μm as a ferroelectric domain-wall structure.[19,20] In the present section, we have shown that morphology on the etched surface reflects the polarization direction. The typical size of the finger print pattern observed above is coincides with the reported one. Then, we guessed that finger print pattern as a ferroelectric domain-wall structure in the PZN-8%PT can be observed on the etched surface by AFM.

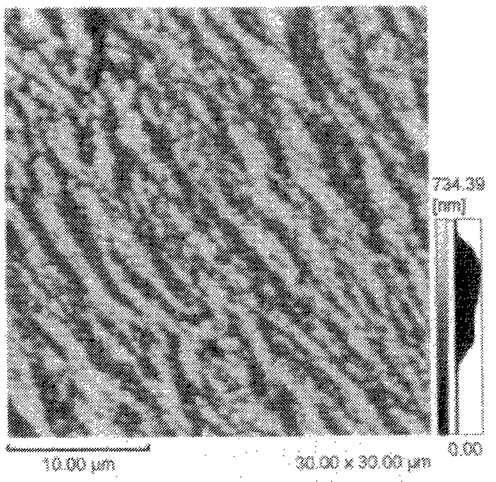

Fig. 5 Topographic image of the (111)-plate sample surface of the PZN-8%PT by the AFM.

It was reported that in $BaTiO_3$, the 180° domain-wall structures with 5 μm order in typical size are observed by the PFM.[14] The typical size of the 180° domain-wall structure in $PbTiO_3$ (PT) was reported to be about 50 μm.[15] This size in the PT seems to be quite large in comparison with one in the PZN-20%PT. Furthermore, finger print pattern with the typical size of 1μm is observed in PZN-8%PT. On the other hand, in the relaxor PZN, existence of the polar nano region is predicted.[21] It is conjectured that typical size of the domain structures and patterns in these solid solutions depend on the concentration. Investigation of the concentration dependence of typical size of the domain-wall structure in the PZN-*x*PT solid solution system is in progress.

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