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Evaluation of Domain Observation in $Pb(Zn_{1/3}Nb_{2/3})O_3$-20%$PbTiO_3$ by Kelvin Force Microscopy

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Ferroelectric and ferroelastic domain wall structures on the etched surfaces in the solid solutions of $Pb(Zn_{1/3}Nb_{2/3})O_3$-$x$$PbTiO_3$ (PZN-xPT; $x \leq 20\%$) were investigated by the scanning probe microscopy (SPM). We showed that both the 90° and 180° domain-wall structures in the PZN-xPT (x = 10-20%) can be observed on the etched surface using the SPM. We found that complex 180° domain-wall structures with typical size of 1-2 μm order exist in the c-domain on the (001)-crystal surface of the PZN-20%PT. We also showed that it is possible to distinguish between tail and head of the polarization on the surface of the PZN-20%PT, measuring the surface potential due to the pyroelectric charge by the Kelvin force microscopy (KFM). In order to estimate the electrostatic potential value due to the pyroelectric charge on the surface observed, the dielectric constant and temperature dependence of the remnant polarization were measured in the bulk crystal of the PZN-20%PT. The value of the electrostatic potential observed by the KFM was evaluated.

Key words: relaxor, PZN, AFM, KFM, ferroelectrics, domain wall

1. INTRODUCTION

It is known that ferroelctrics belonging to the solid solution system between the perovskite-type relaxor and $PbTiO_3$ such as $Pb(Zn_{1/3}Nb_{2/3})O_3$-$x$$PbTiO_3$ (PZN-xPT) show excellent properties for applications such as electrostrictive actuators and sensors, because of the large dielectric constant and high electro-mechanical 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]. We have theoretically pointed out that the large electro-mechanical 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.[8,9] 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]

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.[10-13] The polarization charge on the ferroelectric surface was observed by Kelvin force microscopy (KFM).[14]

In the previous papers with respect to the PZN-xPT solid solution system[15-17], we reported the observation of the domain-wall structure near the MPB region by the scanning prove microscopy (SPM). In the present paper, we report observation of the domain wall structure in PZN-20%PT by KFM and its evaluation.

2. EXPERIMENTAL

2.1 Crystal growth

Single crystals of the PZN-20%PT were grown by 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 Scanning probe microscopy (SPM)

SPM images were obtained by using a commercial scanning probe microscope (Shimazu SPM-9500). The sample temperature was maintained by a thermocontroller. Two kinds of scanning modes were used to obtain domain images of the etched surface. One is contact mode atomic force microscopy (AFM), and the other is noncontact KFM which measures the electrostatic potential on the surface.[18,19] A topographic image was observed in contact mode AFM with a Si cantilever (Olympus OMCL-TR800PSA-1), where the typical scanning speed is approximately 1 Hz. In KFM, Pt and Ir coated Si cantilever (Nanosensors EFM-16) was used in the dynamic mode, where the typical scanning speed is approximately 0.2 Hz.

2.3 Electrical measurement in bulk crystal

For the electrical measurement in PZN-20%PT, sample plate perpendicular to the <001> direction with an area of about 25 mm^2 and thickness of about 0.3 mm was cut out and polished with a polishing sheet (0.3 μm size). Measurement of the dielectric constant at 100Hz was carried out by using an impedance analyzer (Schlumberger SI 1260), and *P-E* hysteresis loop at 100Hz was observed using hand made Sawyer-Tower circuit.

3. RESULTS

PZN-20%PT belongs to the tetragonal system at room temperature. We observed the domain wall structure on the etched surface of the PZN-20%PT crystal. Figure 1 shows a topographic image on the etched surface of the PZN-20%PT observed by the contact AFM, where the size of the image is 40 μm×40 μm. The sample plate is perpendicular to the <001>-direction of the cubic coordinate. Two kinds of domain patterns are found in Fig. 1. One shows a homogeneous pattern (left-hand side in Fig. 1), and the other shows the complex island like pattern (right-hand side in Fig. 1). It was confirmed that the former (with the homogeneous pattern) and the latter (with the island-like pattern) correspond to the *a*- and *c*-domains, respectively.[15-17]

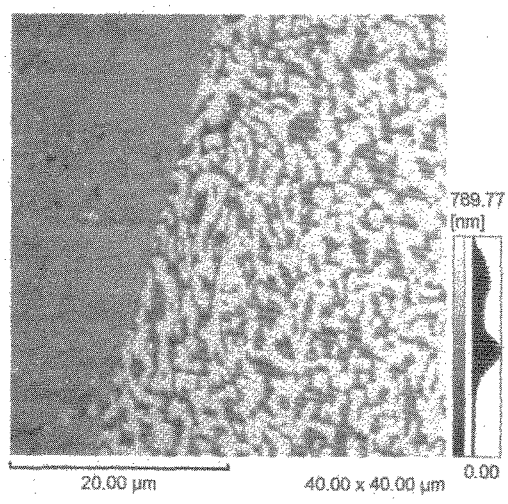

Fig. 1 Topographic image of the (001)-plate sample surface of the PZN-20%PT by the contact AFM.

It is seen in the *c*-domain of Fig. 1 that there are two regions with bright and dark contrast, corresponding to upper and lower height levels, respectively. In order to confirm the direction of the spontaneous polarization in the *c*-domain, we observed the surface potential due to the charge of the pyroelectric polarization on the (001)-plate of the PZN-20%PT using KFM. First, the sample was maintained at 35°C for a day to cancel the polarization charge on the surface, and using KFM the polarization charge was confirmed to be screened by mobile charge carriers. After that, the sample temperature was rapidly changed to 45°C, and the surface potential due to the pyroelectric charge in the *c*-domain was imaged by the KMF. The topographic and potential images in the same region are shown in Figs. 2(a) and 2(b), respectively, where the size of the image is 6.7 μm×6.7 μm. The bright and dark regions in the potential image (Fig. 2(b)) indicate the high and low electrostatic potentials, respectively. Since the pyroelectric effect reduces the value of the spontaneous polarization on heating process, a charge with the opposite sign of the polarization appears on the surface. Then, it is concluded that the bright (dark) region in Fig. 2(a) corresponds to the tail (head) of the polarization. It is seen that the value of the potential between two domains with up and down polarizations is about 5V. On the other hand, it was reported that the positive end (head) of the polarization etches rapidly in HCl (for $BaTiO_3$)[20] and a mixture of HCl and HF (for $PbTiO_3$)[12] while the negative end (tail) of the polarization etches very slowly. Our result is consistent with the results reported with respect to the etching method.[12,20] We were able to distinguish between the tail and head of the polarization on the surface of the PZN-20%PT.

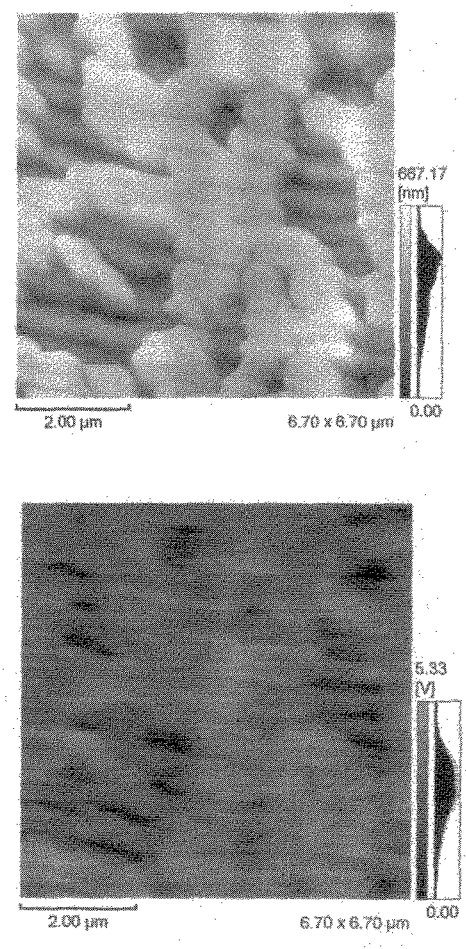

Fig. 2 Topographic (a) and potential (b) images of the etched sample surface of PZN-20%PT obtained by noncontact AFM and the KFM, respectively.

In order to evaluate the potential value measured by KFM, we measured temperature dependence of the remnant polarization and the dielectric constant in the PZN-20%PT crystal, where the crystal measured is obtained from the same crucible as the crystal used for KFM observation. Figure 3 shows temperature dependence of the remnant polarization, p_r, in PZN-20%PT. It is found that the change of the polarization due to the pyroelectric effect from 35°C to 45°C is estimated to be about 2 μC / cm^2. On the other hand, from the measurement of the dielectric constant in PZN-20%PT with multidomain state, the value of the dielectric constant, ε_r, is obtained to be about 500 at room temperature.

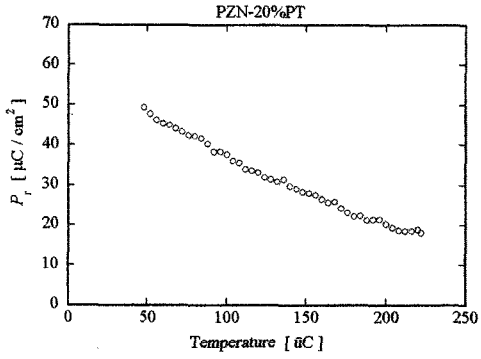

Fig. 3 Temperature dependence of the remnant polarization in PZN-20%PT.

4. DISCISSION

Let us evaluate the electrostatic potential observed on the surface of the crystal with 180° domain wall structure. For simplicity, we consider a model that the domain walls form a periodic structure along x-direction as shown in Fig. 4, where the length of the pair of up and down domains is $2L$. The surface of the crystal is perpendicular to the z-axis, and the surface is located at $z = 0$. The 180° wall exists at $x = L\ (2n - 1) / 2$ (n: integer). At first, the polarization charge on the surface completely chancels under a certain temperature, and a charge density, σ, due to the pyroelectric effect appears just after increasing temperature. We estimate the electrostatic potential due to the charge, σ, using this simple model. We assume that the values of the spontaneous polarization and dielectric constant are the same as the values in the bulk crystal without external field because the electric field due to the pyroelectric charge, σ, in the ferroelectric crystal is not so strong. The charge density on the surface in each domain is assumed to be homogeneous. The potential is expanded as[21]

$$\phi = \begin{cases} \sum_{n=0}^{\infty} A_n \cos(n\pi x / L)\exp(-n\pi z / L), & z \geq 0, \\ \sum_{n=0}^{\infty} B_n \cos(n\pi x / L)\exp(n\pi z / L), & z < 0, \end{cases} \quad (1)$$

where A_n and B_n are constants. After a little algebra, we get the potential above the crystal surface ($z \geq 0$);

$$\phi = \frac{4\sigma L}{\varepsilon_0(1+\varepsilon_r)\pi^2} \times \left[\sum_{n=1}^{\infty} \frac{1}{(4n-3)^2} \cos\left\{\frac{(4n-3)\pi x}{L}\right\} \exp\left\{\frac{-(4n-3)\pi z}{L}\right\} - \sum_{n=1}^{\infty} \frac{1}{(4n-1)^2} \cos\left\{\frac{(4n-1)\pi x}{L}\right\} \exp\left\{\frac{-(4n-1)\pi z}{L}\right\} \right]. \quad (2)$$

Numerical result is shown in Fig. 5, where the values are adopted as $\varepsilon_r = 500$, $\sigma = 2.0$ μC/cm^2, $L = 2$ μm and $z = 50$ nm. It is seen that the value of the electrostatic potential between two neighboring domains with up and down polarizations is roughly estimated to be about 7V. In our experimental result, this value is about 5V. It is concluded that our experimental result of the measurement of the surface potential due to pyroelectric charge is reasonable.

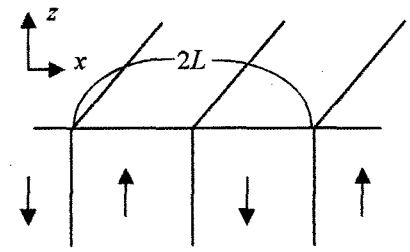

Fig. 4 Model of the domain wall structure.

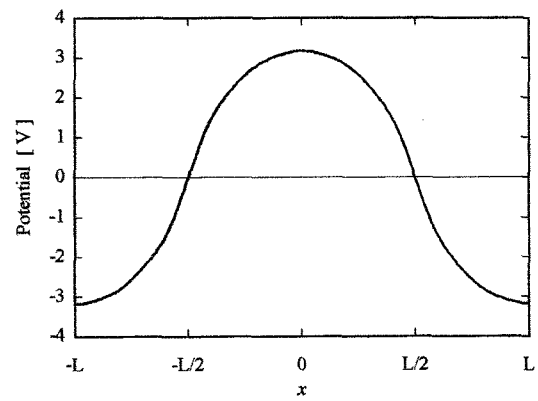

Fig. 5 Numerical result of the potential.

In the present study, we observed that pattern of the 180° domain wall structure shows complex structure with the typical size of about 2 μm. In general, pattern of the ferroelectric domains tends to

be simple in order to decrease the elastic energy if there no pinning of the wall. In fact, 180° domain wall structure in $BaTiO_3$ shows more simple pattern than one in PZN-20%PT.[22] This may imply the existence of a lot of defects in PZN-20%PT crystal.

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