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Domain Imaging in $0.68Pb(Mg_{1/3}Nb_{2/3})O_3 - 0.32PbTiO_3$ Single Crystals using Contact Resonance Piezoresponse Force Microscope

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The domain structure images of (001) plates of $0.68Pb(Mg_{1/3}\ Nb_{2/3})O_3$–$0.32PbTiO_3$ (PMN-32%PT) single crystals were successfully obtained using contact resonance mode piezoresponse force microscope (PFM) at sample temperatures more than 200 °C. In contact resonance mode PFM, we could operate PFM imaging with reduced amplitude of the modulation signal (typically $4.0\,V_{p-p} \rightarrow 0.1\,V_{p-p}$). It was found that micron-size complex domain structure faded out and dot like domains submicron size in diameter emerged gradually as the temperature increased from 206 °C to 226 °C.

Key words: piezoresponse force microscopy; domain imaging; contact resonance; relaxor ferroelectrics; PMN-PT;

1 INTRODUCTION

There is remarkable interest in $PbTiO_3$(PT) doped relaxor ferroelectric single crystals such as $(1-x)Pb(Zn_{1/3}\ Nb_{2/3})O_3$–$xPbTiO_3$ (PZN-PT) and $(1-x)Pb(Mg_{1/3}\ Nb_{2/3})O_3$–$xPbTiO_3$ (PMN-PT). In these single crystals, an electromechanical coupling factor of greater than 0.9 has been reported for compositions close to the morphotropic phase boundary between rhombohedral ferroelectric and tetragonal ferroelectric phases. Therefore, these single crystals have been attracting considerable attention for medical imaging and actuator applications.[1,2)]

Nevertheless, the origin of their excellent properties has not been clarified. Expensive experimental and theoretical studies have been focused on the relaxors for more than 40 years. Recently, peculiar properties of representative pure (PT undoped) relaxors were discussed and mostly understood in terms of microdomains (polarized micro clusters) tens or hundreds of angstroms in diameter. Besides, PT doping made the size of these microdomains increased to be submicron and properties were determined as a function of the composition rate x of PT.

Hence, to clarify the PT doping effect for the relaxors, it is useful to study kinetics and morphology of domains under a wide variety of conditions.

Piezoresponse force microscopy (PFM)[3,4)] is most effective technique for domain observations. This is because PFM has enough sensitivity to reveal the polarization on a ferroelectric sample and can be easily employed for visualizing domain structures on various ferroelectric samples (single crystals, ceramics and thin films).

In our previous work,[5)] we performed domain imaging in (001) plates of PZN-9%PT and PMN-32%PT at various sample temperatures ranging from 25 °C to 200 °C and reported that it was difficult to visualize domain structures at higher sample temperatures. As sample temperature increases up to its Curie temperature, the coercive field decrease to 0. Consequently, at sufficiently higher temperature, the modulation voltages applied between the tip and the counter electrode during PFM observations induced polarization reversals and destroyed local domain structures under the tip. For (001) plates of PMN-32%PT, these polarization reversals were observed at more than 200 °C.

In this article, we report the domain structure images of PMN-32%PT single crystals obtained by contact resonance[6)] (see Fig. 1) mode PFM at more than 200 °C. In contact resonance mode, the frequency of the modulation signal was maintained at the resonance frequency of the cantilever deflection when in contact with the sample surface. Utilizing contact resonance, we could op-

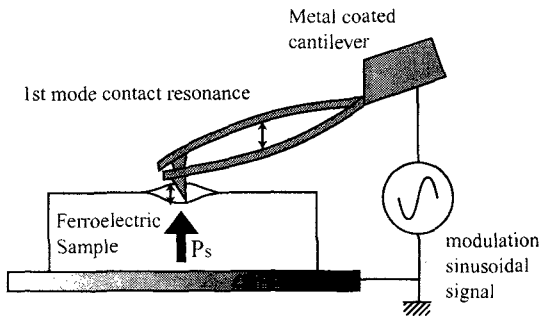

Fig. 1 1st mode contact resonance vibration of a cantilever.

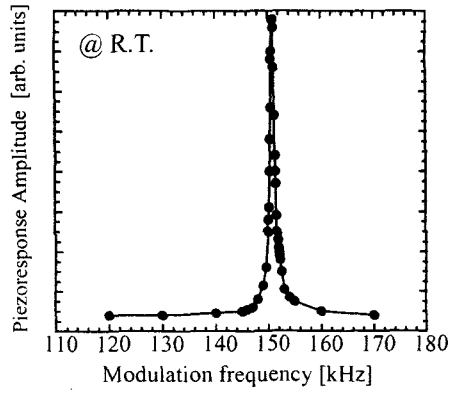

Fig. 2 The frequency spectrum of a cantilever (Seiko instruments, SI-DF3-R) when in contact with (001) plate of PMN-32%PT single crystal surface. The 1st mode contact resonance frequency and its quality factor Q were 150.9 kHz and 190, respectively.

erate PFM imaging with lower amplitude of the modulation signal and address the issue of the polarization reversals at higher temperature.

2 EXPERIMENTAL

During PFM observations, domains were visualized by detecting the inverse piezoelectric oscillations caused by the modulation sinusoidal voltage $U(t) = U_0 \sin(\omega t)$ applied between the conducting tip and an electrode on the backside of the sample.[4] These vibrations resulted in the cantilever deflection owing to the tip in contact with the ferroelectric sample surface. This modulated cantilever deflection was acquired and amplified using a lock-in amplifier. Accordingly, it was possible to determine the projection of the polarization vector onto vertical direction (P_z). The details of PFM imaging principle were described elsewhere.[5,7]

The experimental setup of PFM consisted of a commercial atomic force microscope (AFM) (Seiko Instruments, SPA300 and SPI3700) connected to a lock-in amplifier (NF Electronic Instruments, LI-575). The sample stage was temperature-controlled by ceramic heater, while the piezoelectric tube scanner was maintained to be low temperature ($< 80\,^\circ$C) using water cooler. A conductive rhodium coated Si cantilever (Seiko Instruments, SI-DF3) was used for domain visualization. The force constant and the natural resonance frequency of the cantilevers were 1.8 N/m and 28 kHz, respectively. The sample temperature was monitored using a $\phi 80\,\mu$m chromel-almel thermocouple located on the sample surface. All PFM imaging operations were operated in the air.

The setup of contact resonance PFM was similar to that of normal PFM. The only difference was the frequency of the modulation signal. The selection of modulation conditions will be discussed in Section 3.

PMN-32%PT single crystals were grown by the Bridgman method. Obtained PMN-PT ingot was sliced into 0.5 mm thick (001) plates. Pt/Ta electrodes were deposited on backside of the samples by rf-sputtering.

3 RESULTS AND DISCUSSION

Figure 2 shows the frequency spectrum of the cantilever SI-DF3-R when in contact with (001) plate of PMN-32%PT single crystal surface. Here, the cantilever was exicted by the local inverse piezoelectric oscillations caused by the modulation signal. The 1st mode contact resonance frequency and its quality factor Q were 150.9 kHz and 190, respectively. Thus, ideally, if the modulation frequency is selected to be this contact resonance frequency, the same level of piezoresponse amplitude can be obtained with 1/190 of the modulation signal amplitude applied during normal (off-resonance) PFM operation. Practically, just a little lower frequency (e.g. 150.2 kHz) than this contact resonance frequency was selected. This is because the contact resonance frequency changes easily depending upon the tip-surface interaction conditions. Besides, the phase shift offset adjustment of the lock-in amplifier was also optimized manually to obtain the best contrast PFM images.

Operating this contact resonance (150.2 kHz) mode PFM, the amplitude of the modulation signal was typically 0.1 V_{p-p}. We needed 4.0 V_{p-p} for off-resonance (5 kHz) mode operation.[5,7]

Figure 3(a) shows 8.2μm×8.2μm topographic image on (001) plate of PMN-32%PT single crystal. The surface of the PMN-32%PT plate was polished and root mean square of surface roughness was 3.1 nm.

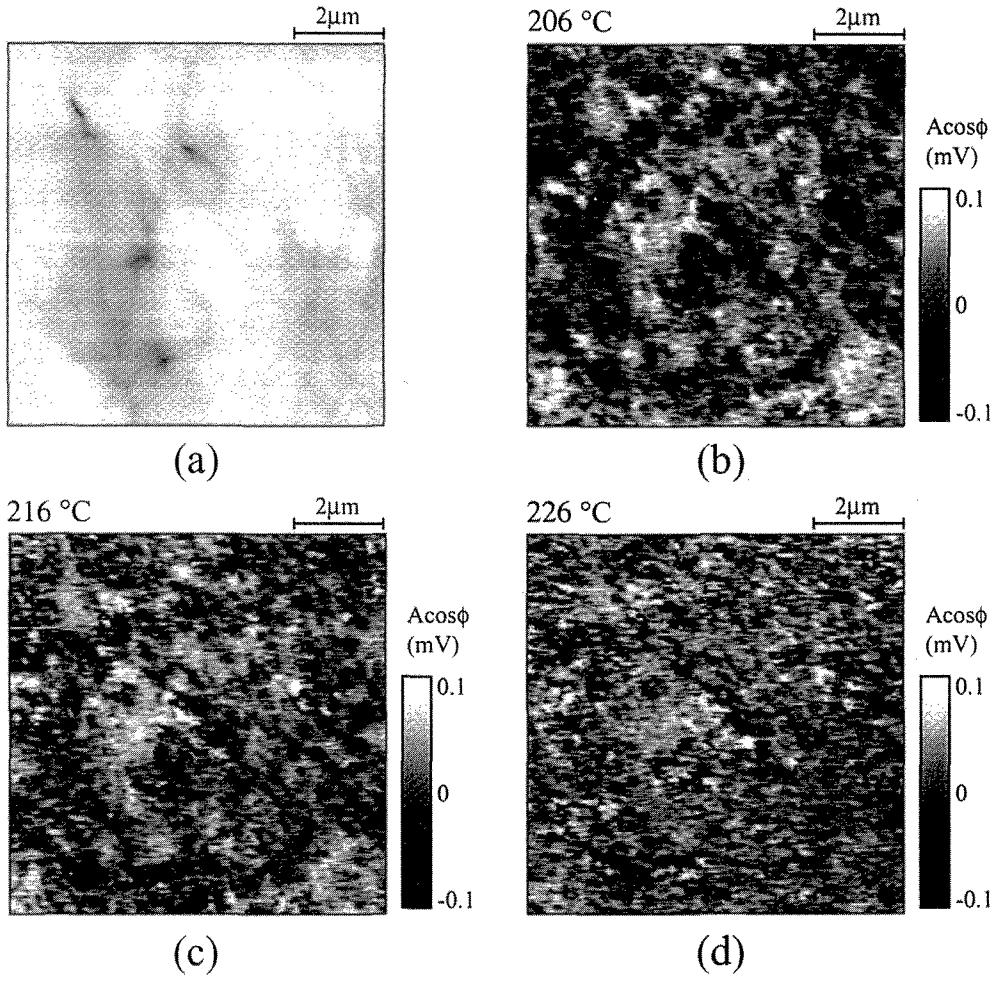

Fig. 3 (a) 8.2μm×8.2μm topographic image and (b)(c)(d) PFM (P_z) images observed at various sample temperatures on (001) plate of PMN-32%PT single crystal.

Figure 3(b) through 3(d) are contact resonance mode PFM images obtained at various sample temperatures ranging from 206 °C to 226 °C. All these images were recorded at the same area with Fig. 3 (a). Here, white and black areas in vertical PFM images represent vertical polarization vectors which exit from and enter into the sample surface, respectively. Because of the tetragonal phase, white and black areas in these images indicated $+c$ and $-c$ domains, respectively.

The domain structures were successfully visualized at temperaturs up to 230 °C. As the temperature increased, micron-size complex domain structure faded out and dot like domains submicron size in diameter emerged gradually.

At 245 °C (not shown), piezoresponse amplitude could not detected without polarization reversals, indicating that the sample temperature overcame the Curie temperature. It must be noted that PMN-32%PT undergoes phase transition from tetragonal-4mm to cubic-m3m near 155 °C.[9] Simultaneously observed optical CCD images suggested that domain boundaries vanished at 150–160 °C. These results implies that bulky phase transition underwent near 155 °C, while the surface temperature of the (001) plate of PMN-32%PT still remained below the Curie temperature due to a convection current of the air. We need to operate PFM imaging in a vacuum to avoid this problem.

4 CONCLUSIONS

The domain structure images of PMN-32%PT single crystals were successfully obtained using contact resonance mode PFM at various sample temperatures ranging from 206 °C to 226 °C. In contact resonance mode PFM, we could operate PFM imaging with reduced amplitude of the modulation signal (typically 4.0 V_{p-p} → 0.1 V_{p-p}).

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