Domain structure and evolution in $(PbMg_{1/3}Nb_{2/3}O_3)_{0.75}(PbTiO_3)_{0.25}$ single crystal studied by temperature-dependent piezoresponse force microscopy

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Ferroelectric domain structure and evolution in (110)-cut relaxor ferroelectric $(PbMg_{1/3}Nb_{2/3}O_3)_{0.75}(PbTiO_3)_{0.25}$ (PMN-25PT) single crystal have been studied by means of temperature-dependent piezoresponse force microscopy. It revealed that, during heating, the as-grown PMN-25PT single crystal exhibits a transition from a ferroelectric microdomain structure to a paraelectric phase; while after being cooled back to room temperature the microdomain structure is rebuilt. Domains with size of tens of nanometers were also observed embedded in the microdomains. By contrast, the poled sample exhibits transitions from macro- to microdomain structures at 90 °C and from microdomain structure to paraelectric phase at 115 °C. These direct observations are consistent with temperature-dependent relative permittivity measurements. *In situ* polarization switching of the domains was also demonstrated. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1890454]

I. INTRODUCTION

As well-known and interesting relaxor ferroelectrics, single crystals of $(PbMg_{1/3}Nb_{2/3}O_3)_{1-x}(PbTiO_3)_x$(PMN-$x$PT) are attracting more and more interest in recent years. Due to their extremely high piezoelectric coefficient (>2500 pm/V) and electromechanical coupling factors (0.94%), many applications of PMN-xPT have been realized such as transducers, sensors, and actuators.[1–6] PMN-xPT also has potentials in the electro-optical application because of its high electro-optical coefficient.[7] $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) is relaxor ferroelectrics and if doped with $PbTiO_3$ (PT), a complete crystalline solution of $(PbMg_{1/3}Nb_{2/3}O_3)_{1-x}(PbTiO_3)_x$ can be formed. Relaxor ferroelectricity can be interpreted by composition nonuniformity-induced microdomains with different Curie temperatures T_C and their conversion to paraelectrics. The PMN-xPT single crystals naturally have a morphotropic phase boundary (MPB) in the range of 28%–36% of PT,[8] and for $x<28\%$, only rhombohedral microdomains exist in the single crystals; and these microdomains can be transformed to macrodomains if poled by an external electric field. Therefore, the relaxor characteristic of poled PMN-xPT can be revealed by two temperatures T_d and T_m, where T_d is the transition temperature from macrodomain to microdomain and T_m represents the transition temperature from ferroelectric to paraelectric phase.[2,9,10] There have been many reports on this phenomenon in PMN-xPT single crystals with different compositions by studying the temperature dependence of relative permittivity, etc.,[2,9–12] but few reports on the direct observation of microdomain structures and their evolutions have been reported. Very recently, Shvartsman and Kholkin reported the results on as-grown PMN-20PT microdomains observation by piezoresponse force microscopy (PFM) under increasing temperature.[13] However, the evolution from macrodomain to microdomain in poled PMN-xPT has not been reported yet. In this paper, we report the study of temperature-dependent domain structures and their evolution in as-grown and poled PMN-25PT relaxor ferroelectric single crystal by temperature-dependent PFM.

II. EXPERIMENTAL PROCEDURE

The PMN-25PT single crystal was synthesized by the modified Bridgman technique and the major faces were cleaved normal to the ⟨110⟩ direction.[14] Here, the direction "⟨110⟩" refers to the pseudocubic axes, and hereafter the single-crystal cut perpendicular to this direction is called "(110)-cut" single crystal. Au was coated on both surfaces as electrodes, and one sample was poled along the ⟨110⟩ direction by an electric field of 4.5 kV/cm at 70 °C for 15 min, and 2.25 kV/cm in the process of cooling down to room temperature. Using an impedance analyzer (HP4194A) equipped with a temperature chamber (Delta 9023), the temperature dependence of the relative permittivity for the as-grown and poled single crystals were measured at temperatures of 20–240 °C at frequencies of 100 Hz 1 kHz and 10 kHz. For the PFM domain structure characterization, the as-grown and poled samples were mechanically polished to a thickness of about 15 μm and a temperature-dependent PFM

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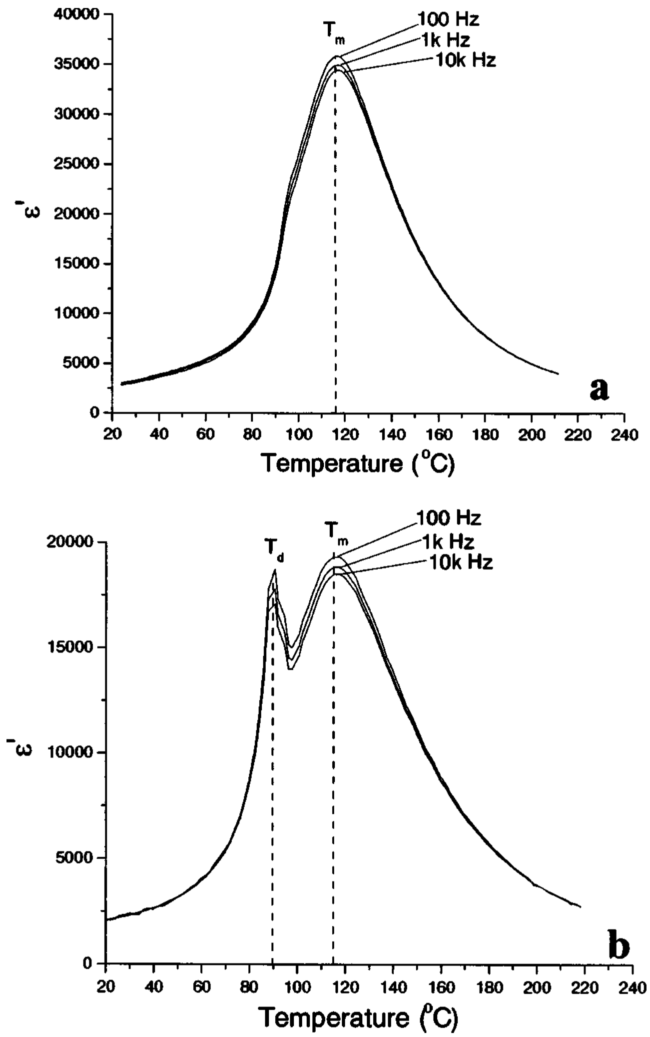

FIG. 1. Temperature dependence of the relative permittivity of as-grown (a) and poled (b) (110)-cut PMN-25PT single crystals upon heating measured at frequencies of 100 Hz, 1 kHz, and 10 kHz.

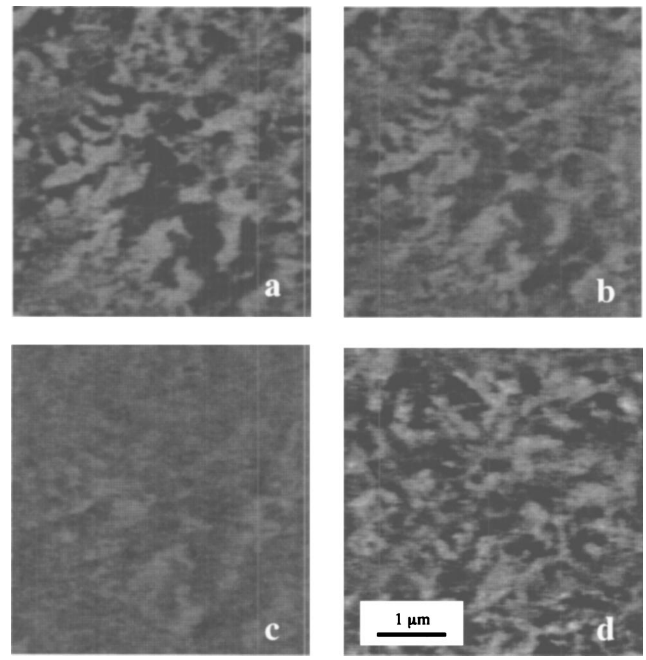

FIG. 2. Temperature-dependent piezoresponse images of the as-grown (110)-cut PMN-25PT single crystal upon heating: (a) 25, (b) 110, (c) 140, and (d) cooled back to 25 °C.

(Nanoscope IV, Digital Instruments) utilizing a conductive tip coated with Pt was carried out. In the experiments of domain imaging, the tip was electrically grounded while a modulating voltage of 6 V ($V_{p\text{-}p}$) with a frequency of 11 kHz was applied through the bottom electrode. In the process of polarization switching, the dc voltage was also applied through the bottom electrode.

III. RESULTS AND DISCUSSION

The temperature-dependent relative permittivities of the as-grown and poled PMN-25PT single crystals are shown in Fig. 1. Relaxor ferroelectricity is apparent as illustrated in Figs. 1(a) and 1(b), where the T_m is determined to be 115 °C. Corresponding to the experience equation $T_m = 5x - 10$,[15] where x represents the composition of PT, the composition of the single crystal can be confirmed to be 25% PT. Figure 1(b) also reveals a transition temperature at $T_d = 90$ °C, where the dispersion feature for different frequencies at $T > T_d$ suggests a macrodomain to microdomain transition.[2,9,10] By contrast, there is only a small shoulder at 90 °C for the as-grown sample, indicating that the microdomain structure is dominant.

Figure 2 shows the piezoresponse images of the as-grown sample at different temperatures. It can be seen from Fig. 2(a) that the speckle-shaped domains with sizes varying from a few micrometers to less than 100 nm are the dominant domains in the sample at room temperature. Similar domain structure has also been reported recently and the nanometer-sized domains were referred nanodomains and their coalition result in microsized domains that are referred microdomains.[13] It should be noted that because of the fine polishing, there was no significant features observed from the topography image. During heating, the contrast between the opposite domains decreases and the boundaries of the domains become rougher [Fig. 2(b)], and eventually the microdomain structure disappears when temperature is well above the transition temperature of 115 °C [Fig. 2(c)]. When the sample is cooled back to room temperature, the microdomain structure appears in the same area again, as shown in Fig. 2(d). This domain structure evolution is consistent with the temperature-dependent relative permittivity measurement, as shown in Fig. 1(a). It should be noted, however, that when the sample is cooled back to room temperature, the same area presents a different domain pattern compared to that of the as-grown sample. The different domain structure after heating and cooling is believed to be related to the random fields due to the built-in charges in the cooling process.

Figure 3(a) is a piezoresponse domain image of the poled (110)-cut PMN-25PT single crystal at room temperature. Based on the experiment condition, the "black" background contrast corresponds to the macrodomain formed by poling process, and the "white" contrast (stripes and speckles) is believed to be the domains that have not been successfully poled or the domains that have been depolarized. The lamellar shape of the domains is consistent with the reported

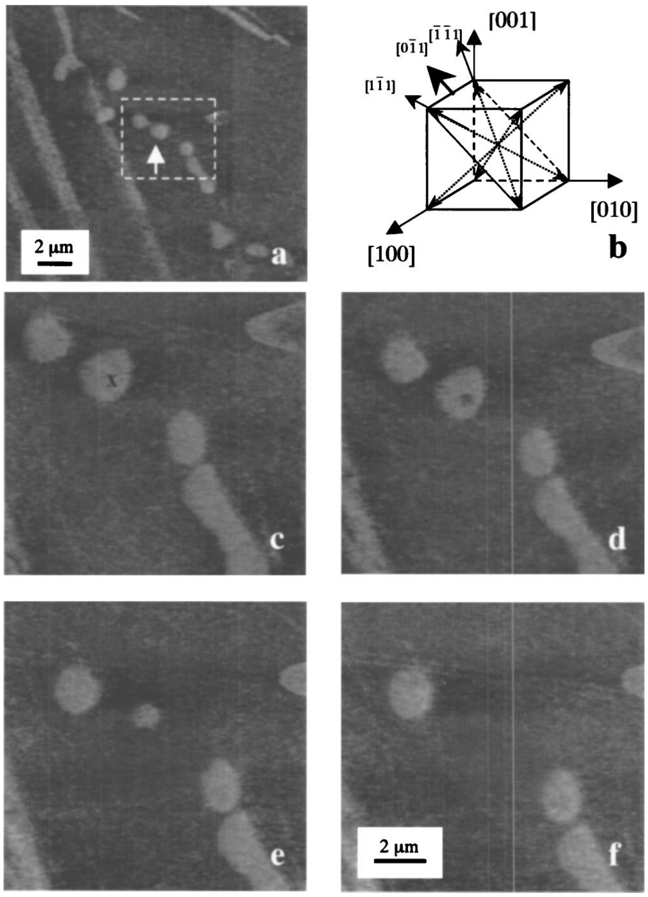

FIG. 3. (a) The piezoresponse image of the poled PMN-25PT single crystal and (b) a schematic diagram showing the relation between the poling (observation) direction and polarization directions. (c)–(f) illustrate polarization reversal of the domain: (c) the original piezoresponse image corresponding to the outlined area in (a), where "*x*" indicates the point where the tip was placed; (d) the piezoresponse image after applying an upward electric field of 6 kV/cm between the tip and bottom electrode; (e) and (f) the piezoresponse image after scanning the arrow indicated domain in (a) in an area of $1.5 \times 1.5\ \mu m^2$ with an upward electric field of 6 kV/cm and 8 kV/cm, respectively.

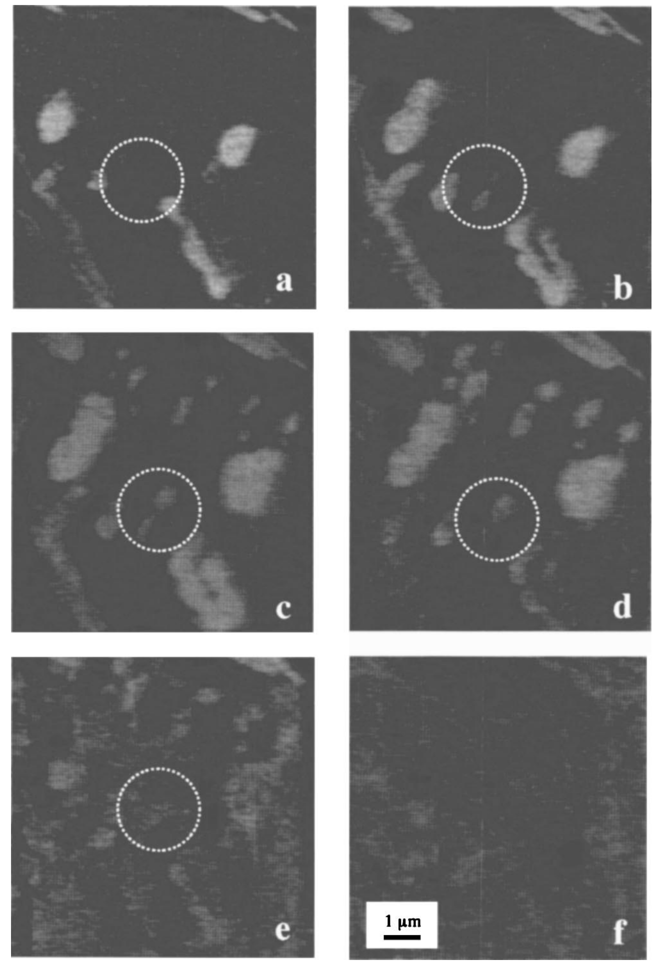

FIG. 4. Temperature-dependent piezoresponse images of the poled (110)-cut PMN-25PT single crystal upon heating: (a) 25, (b) 90, (c) 100, (d) 110, (e) 120, and (f) 140 °C.

optical observations of macrodomains.[4,8,14] The PMN-25PT single crystal has a rhombohedral structure at room temperature, and thus under electric field along ⟨110⟩ poling directions, the polarization should occur along the two ⟨111⟩ orientations close to the ⟨110⟩ directions. Figure 3(b) shows the relation between the poling direction $[0\bar{1}1]$ and the polarization directions of $[\bar{1}\bar{1}1]$ and $[1\bar{1}1]$. Therefore, the observed black domain contrast should be the projections of the lamellar-shaped domains with these polarizations on the observation of $(0\bar{1}1)$ atomic plane.

Polarization switching at room temperature was also performed and the white domains can be *in situ* poled by an external dc electric field applied on the PFM tip. The experiment was carried out on the arrowed domain in the outlined region in Fig. 3(a). Figure 3(c) shows the domain pattern in the outlined region before polarization switching was performed, and the "*x*" drawn on the domain indicates the point where the tip was placed. In the polarization switching process, a dc voltage of 6 kV/cm was applied through the bottom electrode while the tip was grounded causing an upward field on the sample. Figure 3(d) shows the domain pattern after poling for 3 min; a black speckle can be clearly observed in the domain indicating that the polarization there has been orientated to the upward direction (substrate to surface) due to the external electric field. The polarization switching was also demonstrated through a scan of this domain area in a size of $1.5 \times 1.5\ \mu m^2$ and after several time scan, the domain size became smaller [Fig. 3(e)]. After further scan using an increased dc voltage of 8 kV/cm, the domain was completely switched as no obvious white contrast can be observed from Fig. 3(f), which shows the domain pattern after further poling.

Figure 4 shows the temperature-dependent domain structure evolution in the poled (110)-cut PMN-25PT, where Figs. 4(a)–4(f) correspond to the domain images at 25, 90, 100, 110, 120, and 140 °C upon heating, respectively. All the images were obtained at the same region. It can be seen that at room temperature the domain walls are smooth and the contrast is sharp [Fig. 4(a)]. In the temperature range from room temperature to 90 °C, there is no significant change of the domain structure both in size and shape. However, when the temperature reaches 90 °C, the sizes of the white speckles and stripes increase and some new speckles appear. At 100 °C, more white speckles with size less than 100 nm appear and one can see that the sizes of the speckles and stripes keep on increasing [Fig. 4(c)]. When the temperature reaches 110 °C, it is also apparent that the stripelike domain contrast becomes weaker and some stripe domains disappear, while the newly appeared speckle domains have their dimensions raised to several hundreds of nanometers [Fig. 4(d)]. The domain structure continues to change with the increasing temperature and when the temperature surpasses T_m, reaching 120 °C, the contrast of the piezoresponse image becomes much weaker and the domain walls became rather blur, as shown in Fig. 4(e). At temperature of 140 °C, which is well above T_m, no obvious domain structure can be identified in the piezoresponse image [Fig. 4(f)], where gray contrast dominates the image, except for a few black and white dots that may correspond to normal ferroelectric domains of PT or defect pined domains.

Figure 4 illustrates the evolution of domain structure in poled relaxor ferroelectric PMN-25PT and there are few points that need to be noticed. First, a domain-wall expansion during heating is apparent for the white domains, as shown in Figs. 4(a)–4(c). This can be understood by the fact that the depolarization field in the poled crystal will back switch the poled area and the new domains tend to nucleate at the domain walls due to the relatively low domain-wall energy. Second, the newly appeared white dots in Fig. 4(b) and their growth are indications of the transition from macrodomain to microdomain structures. The microdomains that possess relatively low T_C will be back switched first and result in the appearance of white dots. Third, when the temperature is higher than T_m, the PMN-25PT changes to paraelectric phase, therefore, no obvious domain contrast can be observed, as shown in Fig. 4(f). It is also worthy to notice that the white dot that has been *in situ* poled by the PFM tip [the circled area in Figs. 4(a)–4(e)], as illustrated in Fig. 3, appears again when the temperature increases and grow until the temperature is higher than T_m. The reason that this domain is difficult to be poled during the sample poling but easy to be switched back after *in situ* poled remains unclear. However, the local random fields due to the built-in charge disorder in PMN-type relaxors may be one of the main reasons.[13]

IV. CONCLUSION

In summary, ferroelectric domain structures and evolution in the as-grown and poled PMN-25PT single crystal have been studied by means of temperature-dependent piezoresponse force microscopy, and the results revealed different domain structures and transitions from macrodomain to microdomain. These direct observations evidence the domain structure and evolution predicted by the temperature-dependent relative permittivity measurement.

ACKNOWLEDGMENTS

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