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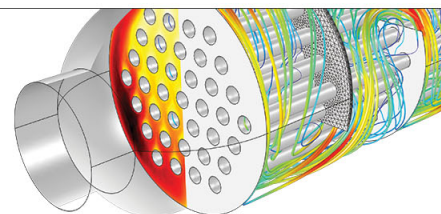
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# Polarization switching in (001)-oriented $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\%\text{PbTiO}_3$ crystals: Direct observation of heterogeneous nucleation by piezoreponse force microscopy

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Polarization switching in (001)-oriented  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\%\text{PbTiO}_3$ , PMN- $x\%$  PT, crystals for  $x=20$  and 35 has been investigated *in situ* by scanning force microscopy in a piezoresponse mode, under a step-increased dc electrical voltage ( $V_{dc}$ ). The results demonstrate that switching initiates by the nucleation of nanosized polar regions with a reversed polarization. For  $x=20$ , nucleation occurs heterogeneously throughout the volume of the crystal. However, with increasing PT content, nucleation tends to preferentially initiate near preexisting twin boundaries; with increasing  $V_{dc}$ , the domains becoming increasingly “diffuse” due to heterogeneous nucleation and growth throughout the crystal. © 2004 American Institute of Physics. [DOI: 10.1063/1.1819993]

Oriented poled single crystals of  $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$  (PZN- $x\%$  PT) and  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$  (PMN- $x\%$  PT) have attracted attention because of enormous piezoelectric ( $d_{33}\sim 1800$  pC/N) and electromechanical coupling ( $k_{33}\sim 0.94$ ) coefficients.<sup>1,2</sup> Maximum property coefficients are found in the vicinity of a morphotropic phase boundary (MPB) between rhombohedral ( $\text{FE}_r$ ) and tetragonal ( $\text{FE}_t$ ) ferroelectric phases. The enormous responses have been attributed to the presence of intermediate monoclinic ( $\text{FE}_M$ ) ferroelectric phases.<sup>3,4</sup> Polarization rotation instabilities under field within  $\text{FE}_M$  phases are known, where rotation occurs against a very small anisotropy.<sup>5</sup> Investigations of the induced polarization ( $P$ ) have shown significant differences depending upon whether the crystals are driven under unipolar or bipolar electric field ( $E$ ):<sup>6–8</sup> unipolar results in anhysteretic  $P$ – $E$  responses, whereas bipolar results in significant hysteresis. Clearly, domains play an important role in polarization switching under bipolar drive.

Polarization switching has been extensively investigated in normal ferroelectric materials by measuring current transients in response to square wave electrical pulses of reverse electric field ( $E$ ).<sup>9–13</sup> Early investigations by Mertz<sup>9</sup> revealed a model for polarization reversal where 2D nucleation of reversed clusters is restricted to  $180^\circ$  domain walls, and where 1D growth of reversed step-like domains is restricted to be coherent in a direction perpendicular to that of  $E$ . It is known in finite-size systems that the Mertz model is inapplicable,<sup>14</sup> which has been modified by Scott *et al.*<sup>15</sup> However, it was not until recently<sup>16–18</sup> that defects were considered to play a vital role in polarization switching. For example, polarization switching in PMN- $x\%$  PT under  $E$  has been understood by heterogeneous nucleation in the vicinity of quenched random fields that act conjugate to  $E$ .<sup>18</sup>

However, direct (*in situ*) evidence of polarization switching by heterogeneous nucleation in the vicinity of random fields has not previously been reported. This may in part be due to (i) the lack of resolution in optical microscopy to reveal small scale features; and (ii) difficulties in performing *in situ* electron microscopy (TEM) with an electric field

stage. In recent years, scanning force microscopy (SFM) in the piezoresponse mode has been used to study ferroelectric domains. Small irregular domain features have been reported in unpoled and poled PMN- $x\%$  PT and PZN- $x\%$  PT,<sup>19,20</sup> demonstrating that small scale ferroelectric domain features can be identified by this method. However, investigations of polarization switching under superimposed dc electrical voltage ( $V_{dc}$ ) have not yet been performed.

The purpose of this investigation was to study the domain evolution of (001)-oriented PMN-20% PT and PMN-35% PT crystals with changing dc electric bias by SFM in the piezoresponse mode. The results provide direct evidence of heterogeneous domain nucleation and growth, where nucleation is not restricted to occur at domain boundaries.

Single crystals of PMN- $x\%$  PT ( $x=20$  and 35) oriented about (001), which were obtained from HC Materials (Urbana, IL), were cut into plates with typical dimensions of  $4\times 4\times 0.3$  mm<sup>3</sup>. The top faces of the crystals were polished to 0.25  $\mu\text{m}$  finish. PFM images were obtained using a commercial unit (Vecoo DI 3100a). All scans were performed at room temperature, using a conductive silicon-tip coated with cobalt (tip radius of  $\sim 20$  nm). Before measurements were begun, all crystals were annealed at 550 K for 30 min to remove surface stresses. Gold electrodes were deposited on the bottom face of each sample by sputtering. The electroded faces were then glued to the SFM sample stage. During image scanning, an ac voltage with a frequency of 20 kHz and amplitude between 1 and 10 V was applied between the conductive tip and the bottom gold electrode. During polarization and/or switching, the ac bias was reduced to zero; and a step-changed dc bias was superimposed on the bottom electrode to switch the polarization within a small central portion of the initial image, which was achieved by moving the grounded SFM tip only over this small area.

Figure 1 shows the piezoresponse force images of PMN-20% PT for various electrical histories. Data are shown in this figure beginning from the initial annealed state, followed by increasing positive  $V_{dc}$  on the central  $2\times 2$   $\mu\text{m}^2$  area (left-hand column), subsequently followed by increasing magnitude of negative  $V_{dc}$  on the central  $1\times 1$   $\mu\text{m}^2$  area (right-hand column). The sequence of bias changes can be

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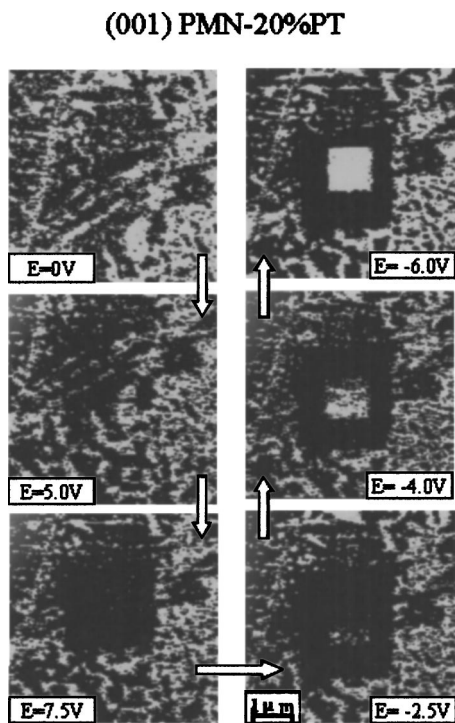


FIG. 1. Piezoresponse force images for a (001)-oriented PMN-20% PT crystal under various dc electrical voltages, left top: the initial annealed condition; left-hand column: under positive bias on the bottom electrode; right-hand column: under negative bias on the bottom electrode.

followed by the arrows in the figure. In the initial annealed condition (left top), polar nanodomains (PND) were observed, somewhat similar to those previously reported by electron microscopy.<sup>21</sup> The distribution of PNDs was almost random, although there was evidence of organization of PND into regular colonies with some spatial correlation. On application of positive  $V_{dc}$  (left-hand column), the self-organization of the colonies was broken down, leaving only randomly distributed polar regions of nanometer size. With increasing  $V_{dc}$ , the density of the PND was decreased, eventually becoming a single domain state at  $V_{dc}=10$  V (solid dark area). On subsequent application of negative  $V_{dc}$  (right-hand column), nanosized polar nuclei were formed, which were randomly distributed within the matrix. With increasing  $V_{dc}$ , the density of these nuclei was increased, until a reversed single domain state (solid bright area) was formed. These results directly show that polarization switching in (001)-oriented PMN-20% PT crystals occurs by heterogeneous nucleation, where nuclei creation is not confined in the vicinity of domain boundaries, but can occur throughout the crystal volume.

Figure 2 shows the PFM images of PMN-35% PT for various electrical histories, presented in a similar manner as that of Fig. 1. In the annealed condition (left top), long and thin domain striations oriented along  $\langle 110 \rangle$  were apparent, which had a somewhat regular spacing. The domain lengths were on the order of tens of microns, whereas the widths were dramatically less,  $\sim 0.35 \mu\text{m}$ . On application of positive  $V_{dc}$  to the central  $4 \times 4 \mu\text{m}^2$  area (left-hand column), the striations became thinner and less regular. With increasing  $V_{dc}$ , the striations broke down into isolated PND, eventually becoming a single domain of the same polarization at  $V_{dc}=12$  V (solid dark area). On subsequent application of negative  $V_{dc}$  to the central  $2 \times 2 \mu\text{m}^2$  area (right-hand column),

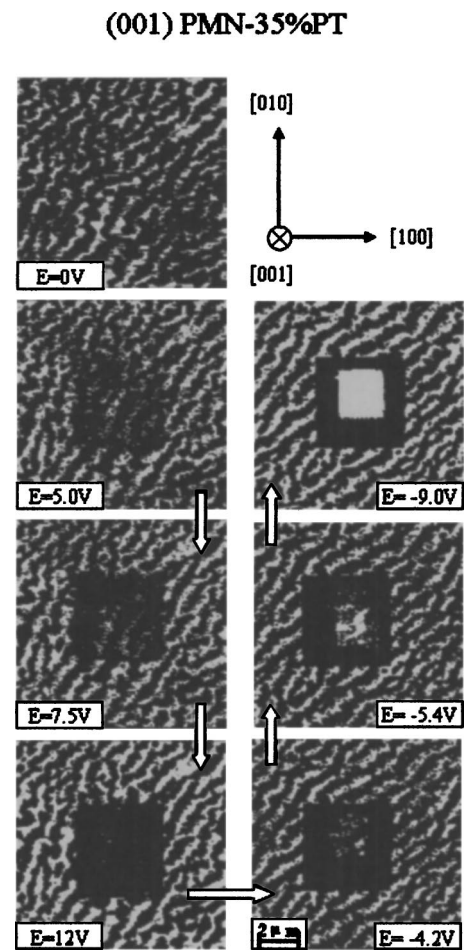


FIG. 2. Piezoresponse force images for a (001)-oriented PMN-35% PT crystal under various dc electrical voltage, left top: the initial annealed condition; left-hand column: under positive bias on the bottom electrode; right-hand column: under negative bias on the bottom electrode.

polar nuclei of nanometer size formed, which were randomly distributed. With increasing  $V_{dc}$ , the nuclei density increased and self-organized into  $\langle 110 \rangle$  striations, indicating a stress-accommodated domain growth process. However, the twin boundaries appeared fuzzy or diffuse, presumably due to the interaction of polarization with charged point defects. These results indicate that polarization switching initiates by preferential nucleation near preexisting twin boundaries; however with increasing  $V_{dc}$ , nucleation occurs heterogeneously throughout the crystal volume. At higher voltages, a reversed single domain state (solid bright area) was found at  $V_{dc}=-9.0$  V.

Our results are consistent with recent pulsed polarization switching investigations of PMN- $x$ % PT and PZN- $x$ % PT by current transient methods.<sup>17,18</sup> In these investigations, polarization switching for PMN-30% PT and PZN-4.5% PT was found to follow stretched exponential behavior. Based on the random-field theory of disordered magnetic systems,<sup>22</sup> the results were explained as heterogeneous nucleation of nanosized domains in the vicinity of quenched random fields that act conjugate to  $E$ . Accordingly, switching occurs by a mechanism where domain walls become diffuse with increasing  $E$ , due to the creation of polar nuclei heterogeneously throughout the crystal volume; rather than by the creation of 2D nuclei of reversed clusters geometrically restricted to the vicinity of preexisting  $180^\circ$  walls. Recent investigations by Jullian *et al.*<sup>18</sup> revealed two long-time tran-

sients that followed stretched exponential behavior: one for  $t > 10^{-2}$  s under moderate  $E$  which was dimensionally confined to domain walls ( $n=2$ ), and a second for  $10^{-4} < t < 10^{-2}$  s under higher  $E$  which was a volume process ( $n=3$ ) that was geometrically unconfined with nucleation preferentially occurring in the vicinity of defects or random fields. For lower PT content crystals which are closer to relaxor systems, our PFM images directly reveal that nucleation is a volume process occurring in the vicinity of quenched random fields; whereas for higher PT content crystals near the MPB, nucleation is initially geometrically confined to domain walls ( $n=2$ ), but with increasing voltage a switchover to a volume process ( $n=3$ ) occurs that is unconfined.

In summary, domain switching of (001)-oriented PMN- $x$ %PT has been investigated by SFM in a piezoresponse force mode under various superimposed dc electrical voltages. The results provide direct evidence of heterogeneous domain nucleation for PMN-20%PT, where nucleation is not restricted to occur at domain boundaries. With increasing PT content to 35%PT, nucleation preferentially initiates near existing twin boundaries; however, the boundaries become diffuse with increasing  $V_{dc}$ , due to heterogeneous nucleation and growth throughout the volume.

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