Polarization Relaxation Phenomena in Ferroelectric thin films

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The time-dependent relaxation of remanant polarization in epitaxial lead zirconate titanate [$PbZr_{0.2}Ti_{0.8}O_3$] ferroelectric thin films, containing a uniform two-dimensional grid of 90° domains (c axis in the plane of the film), is examined using voltage-modulated scanning force microscopy. As shown in figure 1 the 90° domain walls preferentially nucleate 180° reverse domains during relaxation, which grow and coalesce as a function of relaxation time. Relaxation is seen to saturate at different levels depending on the write voltage. Late (saturation) stages of relaxation are accompanied by pinning and faceting of the domain walls (drastically reducing the wall mobility), which is direct evidence of the role of defect sites and crystallographic features on polarization relaxation. The kinetics of relaxation is modeled through the nucleation and growth Johnson-Mehl-Avrami-Kolmogorov theory with a decreasing driving force. It is assumed that the relaxation proceeds via the cylindrical growth of 2-D domains as shown in figure 2(a) and that the domain wall is required to jump over pinning sites as shown in figure 2(b). The rate of domain growth can be described as:

$$\frac{dR}{dt} = -\frac{L}{2pRh_f}\frac{d\Delta F}{dR} \qquad (1)$$

In the above equation *DF* is the change in free energy given as:

$$\Delta F = -pR^2 h_f P_s E(1-f-a) + 2pR\Gamma h_f \quad (2)$$

and L is the kinetic coefficient given as

$$L = \frac{l_0 n u_a}{k_B T} e^{\frac{-U_a}{k_B T}} \qquad (3)$$

The above equation leads to the final equation given as:

$$f = 1-\exp(-N_0 V(t))$$

$$= 1-\exp\left\{-N_0 p P_s^2 E^2 L^2 \left(\int_0^t (1-f-a)dt\right)^2\right\}$$

(4)

Figure 2(c) shows the relaxation fitted to the above expression.

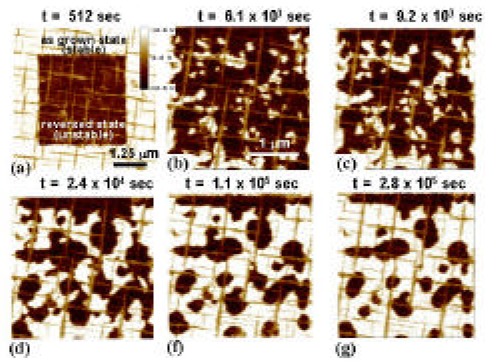

Fig. 1 (a) Piezoresponse image from 5 by 5 mm^2 region of PZT film showing the as grown region(light contrast) and central 3 by 3 mm^2 switched region(black contrast). Piezoresponse images from the center region from (a) which was switched into the opposite polarization (with respect to the as-grown state) state by scanning the surface with the tip biased at -10 V. Images taken after wait times of (b) 6.1 x 10^3 , (c) 9.2 x 10^3 , (d) 2.4 x 10^4 , (e) 1.1 x 10^5 , and (f) 2.8 x 10^5 s.

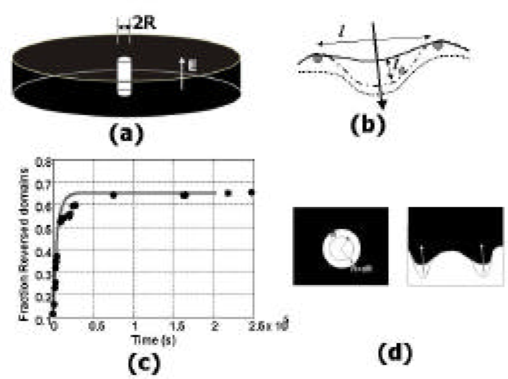

Fig. 2 (a) schematic of the 2-D reverse nuclei. (b) Schematic of 180^o domain wall and pinning sites(c) Fraction reverse domain fitted to eqn (4).(d) Effect of radius of curvature on the relaxation process.