We report on the polarization relaxation of epitaxial PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films grown by pulsed laser deposition. Figure 1 (a) shows the piezoresponse domain image of 0.5 by 0.5 µm region of the film. The a/c/c domain grid structure is clearly observed. To investigate the kinetics of relaxation at very small scales, the region inside the square cell was scanned under a DC bias of ~8 Volts. Figure 1(b) is the scan of the region after 2800 seconds. As seen in the figure the region is switched into opposite polarization, and hence is black in contrast. Secondly at the 90° domain interfaces reverse nuclei have formed, which revert the polarity back to the original white contrast. They are marked as primary nuclei or “P”.

After 5700 seconds and longer times, incipient nuclei reverse the domains inside the square region, and are marked as secondary sites or “S”. This is shown in figures 1(c) and (d). The relaxation was modeled to a stretch exponential relation of the form

$$y = 1 - e^{-k(t-t_0)^n}.$$
Figures 2(a)-(f) show how the radius of curvature changes systematically with time. In the beginning the curvature is very small, indicating a high surface energy. To reduce the energy the wall moves rapidly and increases in curvature, analogous to the famous Gibbs-Thomson effect. Eventually the relaxation comes to a halt where neat facets have been formed, with infinite radii of curvature, thus symbolizing a metastable state. The relaxation proceeds again with further perturbation till the next stage where again a faceted, but a smaller region is observed. This is shown in figure 3. Figure 3(f) shows how for this particular cell, the relaxation proceeds in the form of steps, each step indicating the forming and dissolution of a continuously shrinking faceted black region.

Fig. 4 (a)-(f) Effect of radius of curvature on the rate of relaxation.

Figure 4 shows the pinning of domain walls during the relaxation. In figure 4(e), we observe that even after 7 days parts of the propagating wall is pinned, thus stabilizing the inverted domain structure. After annealing it is seen that the reversal is complete. This is possible because now the the propagating walls have sufficient thermal energy to overcome the pinning sites. Our observations lead us to believe that modified classical kinetic relaxation scenarios can be used to explain the rich physics behind polarization reversal in nanoscale ferroelectric structures.