Domain Wall Creep in Epitaxial Ferroelectric Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ Thin Films

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Ferroelectric switching and nanoscale domain dynamics were investigated using atomic force microscopy on monocrystalline Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ thin films. Measurements of domain size versus writing time reveal a two-step domain growth mechanism, in which initial nucleation is followed by radial domain wall motion perpendicular to the polarization direction. The electric field dependence of the domain wall velocity demonstrates that domain wall motion in ferroelectric thin films is a creep process, with the critical exponent μ close to 1. The dimensionality of the films suggests that disorder is at the origin of the observed creep behavior.

Understanding the propagation of elastic objects driven by an external force in the presence of a pinning potential is a key to the physics of a wide range of systems, either periodic, such as the vortex lattice in type II superconductors [1], charge density waves [2] and Wigner crystals [3], or involving propagating interfaces, such as growth phenomena [4], fluid invasion [5], or magnetic domain walls [6]. In particular, the response to a small external force is of special theoretical and practical interest. It was initially believed that thermal activation above the pinning barriers should lead to a linear response at finite temperature [7]. However, it was subsequently realized that a pinning potential, either periodic [1] or disordered, [1,8–10], can lead to diverging barriers and thus to a nonlinear "creep" response where the velocity is of the form $v \propto \exp[-\beta R(f_c/f)^\mu]$. β is the inverse temperature, R a characteristic energy, and f_c a critical force. The dynamical exponent μ reflects the nature of the system and of the pinning potential. Despite extensive studies of the creep process in periodic vortex systems [1], precise determination of the exponents has proven difficult, given the many scales present in this problem [11]. For interfaces, the creep law has been recently verified in ultrathin magnetic films [6], where the measured exponent $\mu = 0.25$ is in very good agreement with the expected theoretical value for this system. Quantitative studies of creep in other microscopic systems with other pinning potentials are clearly needed.

In this respect, ferroelectric materials are of special interest. These systems possess two symmetrically equivalent ground states separated by an energy barrier U_0, as illustrated in Fig. 1. Each state is characterized by a stable remanent polarization, reversible under an electric field. Regions of different polarization are separated by elastic domain walls. The application of an electric field favors one polarization state over the other, by reducing the energy necessary to create a nucleus with a polarization parallel to the field, and thus promotes domain wall motion. In addition to theoretical interest, understanding the basic mechanism of domain wall motion in ferroelectrics has practical implications for technological applications, such as high-density memories. In bulk ferroelectrics, switching and domain growth were inferred to occur by stochastic nucleation of new domains at the domain boundary, a behavior observed in BaTiO$_3$ and triglycine sulphate, using combined optical and etching techniques [12,13]. Domain wall propagation via such nucleation was also invoked in early analyses of bulk systems to explain the reported field dependence of domain wall speed, $v \sim \exp[-1/E]$ [14].

In this Letter, we report on studies of ferroelectric domain wall motion in single crystal Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$ films by atomic force microscopy (AFM), allowing noninvasive investigation of domain dynamics with nanometer resolution. In this model system, we identify domain wall motion to be a disorder-controlled creep process. The dynamical exponent μ is found to be close to 1. The activation energy increases significantly from 0.5 to 1.3 MV/cm as the film thickness is reduced from 810 to 290 Å.
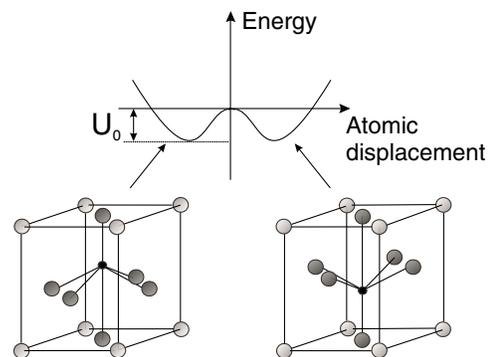

FIG. 1. Schematic of a tetragonal perovskite ferroelectric, characterized by two oppositely polarized ground states, separated by an energy barrier U_0. For Pb(Zr$_{0.2}$Ti$_{0.8}$)O$_3$, the corner Pb ions and the center Ti/Zr ions are positively charged, and the face O ions are negatively charged.

The ferroelectric materials investigated were epitaxial c axis oriented $Pb(Zr_{0.2}Ti_{0.8})O_3$ thin films, rf magnetron sputtered onto conducting (100) Nb-doped $SrTiO_3$ substrates [15,16]. This system allows precise control of film thickness and crystalline quality, exhibiting atomically flat surfaces with a polarization vector parallel or antiparallel to the c axis [15,16]. To study switching dynamics in these films, we used a conductive AFM tip to artificially modify domain structure [15,17,18]. Domains were polarized by applying a voltage pulse across the ferroelectric film, between the tip and the substrate. Their sizes were subsequently measured by piezoelectric microscopy [17], as a function of pulse width and amplitude. For every pulse width, we used 12 V pulses to polarize an array of 16 domains, and calculated an average domain size based on their vertical and horizontal radii. The rms error was ~10%. All domains studied were written in a uniformly polarized area.

Figure 2(a) shows domain radius as a function of pulse width, and three piezoelectric images of ferroelectric domain arrays written with 50 μs, 1 ms, and 100 ms voltage pulses. As can be seen, varying the writing time (pulse width) markedly changes the size of the AFM-written domains. We observe that domain radius increases logarithmically with increasing writing time for times longer than ~20 μs. Below 20 μs, and down to 100 ns, the shortest times investigated, domain radius is found to be constant and approximately equal to 20 nm, as shown by the shaded area in Fig. 2(a) [19]. All of our data suggest that this minimum domain size is related to the typical tip size used for the experiments, whose nominal radius of curvature is ~20–50 nm. In previous studies, we have observed that domain size also depends linearly on writing voltage, above a threshold related to the coercive field [19]. A detailed analysis of the data reveals only well-defined homogeneous domains with regular spacing, as can be seen in the piezoelectric image of a regular 90-domain array, written with 1 ms pulses in Fig. 2(b). We note that the topographic image of the same area is featureless, with a rms roughness of ~0.2 nm. Within our ~5 nm resolution we do not detect any randomly nucleated domains. The data thus suggest a two-step domain switching process in which nucleation, originating directly under the AFM tip, is followed by radial motion of the domain wall outwards, perpendicular to the direction of polarization.

To analyze this lateral domain wall motion, we note that the force exerted on the wall is given by the electric field E. To obtain the electric field distribution, we model the tip as a sphere, with radius a. The potential at the ferroelectric surface, a distance r from the tip is then $\Phi \sim \frac{Va}{r}$, and the local field across the ferroelectric $E = \frac{Va}{rd}$, V being the applied tip bias and d the film thickness. This equation will allow us to relate the change in domain size to the local electric field near the domain boundary. Note that the electric field produced by the tip, although inhomogeneous at large length scales, can be taken as constant over the thin
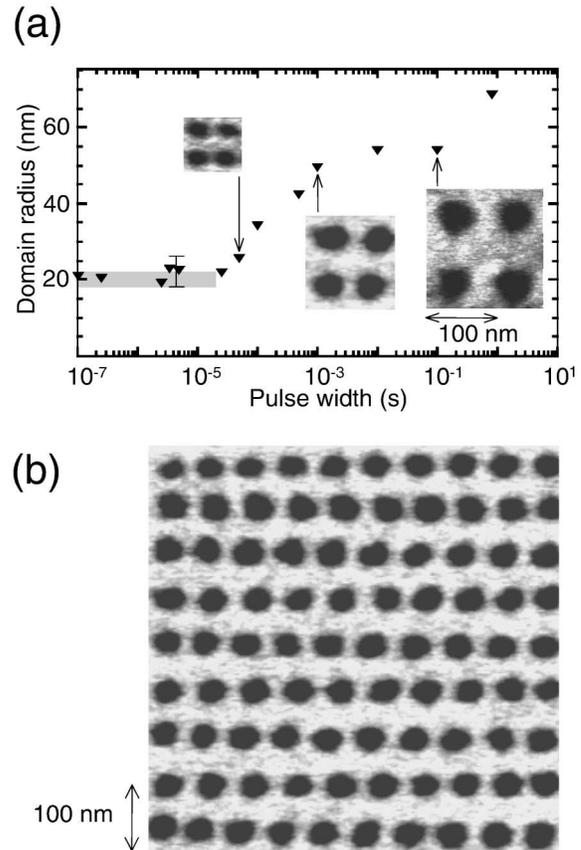

(a)

(b)

FIG. 2. (a) Domain size increases logarithmically with pulse widths longer than ~20 μs, and saturates for shorter times as indicated by the shaded area. In all cases, the domains are homogeneous and no random nucleation is detected, as shown by three piezoelectric images of domain arrays on a 370 Å thick film written with 50 μs, 1 ms, and 100 ms voltage pulses. The scale is the same in all images. In (b), a large array shows that domains are centered only where the AFM tip was positioned during writing.

(a few lattice constants) ferroelectric domain wall. By writing arrays with different pulse widths, and subsequently calculating the average domain size for a given time, we can extract the speed of the domain wall as $v = \frac{r(t_2)-r(t_1)}{t_2-t_1}$ and the corresponding electric field $E(r)$ where $r = [r(t_1) + r(t_2)]/2$.

Figure 3 shows the wall speed as a function of the inverse field for three different film thicknesses. The data fits well to a creep formula

$$v \sim \exp-\frac{R}{k_BT}\left(\frac{E_0}{E}\right)^{\mu}, \qquad (1)$$

with $\mu = 1$. The exact dynamical exponent μ is found to be 1.12, 1.01, and 1.21 for the 290, 370, and 810 Å thick films, respectively, with an estimated 10% rms error on the field [20]. We find the effective "activation energy" $[R/(k_BT)]^{1/\mu}E_0$ to be 1.32, 1.30, and 0.50 MV/cm for 290, 370, and 810 Å thick films, typically 1 order of
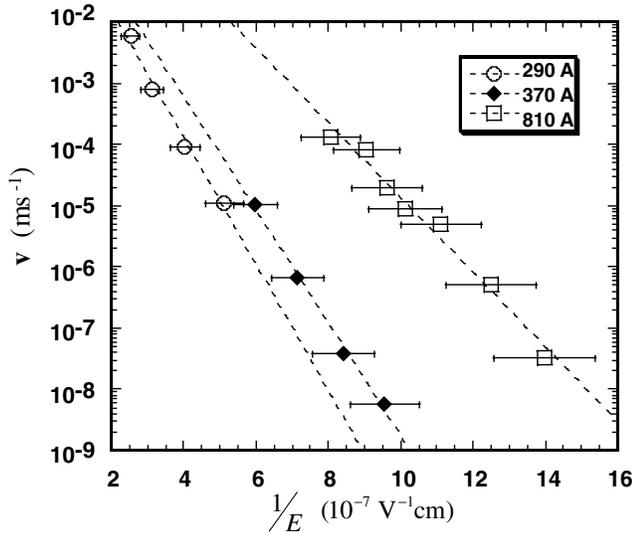
FIG. 3.   Domain wall speed as a function of the inverse applied electric field for 290, 370, and 810 Å thick samples. The data fit well to $v \sim \exp[-\frac{R}{k_B T}(\frac{E_0}{E})^\mu]$ with $\mu = 1$, characteristic of a creep process.

magnitude larger than the applied fields during the polarization process [21]. Integrating $dt/dr = 1/v$ using the creep expression leads to $r \sim V$ with a slowly varying logarithmic correction factor of the form $\ln[(t-c)/V]$, where c is an integration constant. This is in agreement with the experimentally observed linear dependence of domain size on writing voltage [19], and further supporting creep as the mechanism of lateral domain wall motion.

Let us now consider the possible microscopic origins of the observed creep behavior. Creep phenomena are a consequence of competition between the elastic energy of a propagating interface, tending to keep it flat, and a pinning potential, preventing it from simply sliding when submitted to an external force. The dynamical exponent in the creep scenario depends on both the dimensionality of the system, and the nature of the pinning potential. Although creep processes are generally associated with the glassy behavior of disordered systems, they can also be observed in a periodic potential if the dimensionality of the object is larger than or equal to 2. For thick films, as for bulk ferroelectrics, the domain wall is a two-dimensional object. In this case, from free-energy considerations, and neglecting the anisotropic dipole field present in a ferroelectric, one would expect the exponent to be $\mu = 1$ [1]. In PbTiO$_3$, it has been shown theoretically that domain wall energy depends upon whether the wall is centered on a Pb or Ti plane [23,24], giving rise to an intrinsic periodic pinning potential. One possible explanation could thus be that the observed creep is due to the motion of the two-dimensional wall in this periodic potential. Note that this scenario is a generalization of the nucleation model developed for bulk ferroelectrics [14]. In order to test this hypothesis we calculated the size of the critical nucleus, using the formula

derived by Miller and Weinreich [14]. To estimate l^*, the critical length along the c axis, we used the standard remanent polarization, lattice parameters, and dielectric constant values for PZT, the 169 mJ/m^2 domain wall energy derived for PbTiO$_3$ [24], and the corrected values for the electric field across the ferroelectric film. We find l^* to vary, depending on the field range, between 200 and 500 Å, 600 and 1100 Å, and 900 and 1700 Å for the 290, 370, and 810 Å films. The critical nucleus would thus need to be larger than the thickness of the system. Furthermore, the effective "activation energy" calculated for the nucleation model is 2 orders of magnitude greater than the 0.5–1.3 MV/cm determined experimentally. Calculations directly starting from the periodic potentials given in [24] lead to similar conclusions. These results strongly suggest that the films are in a two-dimensional limit, and that the nucleation model, or equivalently, motion through a periodic potential, does not adequately explain the experimental data [25].

The creep behavior thus has to be due to the glassy characteristics of randomly pinned domain walls in a disordered system, with the dynamical exponent dependent on the nature of the disorder. Defects locally modifying the ferroelectric double-well depth U_0 and giving rise to a spatially varying pinning potential would lead to a "random bond" scenario similar to the one for the ferromagnetic domain walls [6]. The exponent μ would be $\mu = \frac{d-2+2\zeta}{2-\zeta}$ where ζ is a characteristic wandering exponent and d the dimensionality of the wall. For one-dimensional domain walls $\mu = 1/4$, whereas for two-dimensional ones $\mu \sim 0.5$–0.6. These estimates are based on only short range elastic forces. Including long range interactions could lead to a higher value of μ. Another possibility is that the defects induce a local field, asymmetrizing the double well, or that there are spatial inhomogeneities in the electric field. In this "random field" scenario $\zeta = \frac{4-d}{3}$ [26] leading to $\mu = 1$ for $1 < d < 4$, compatible with the observed data. Directional internal fields due to disorder, possibly related to oxygen vacancies, have in fact been reported in ferroelectric systems, such as LiTaO$_3$ [27,28], and could give rise to random field behavior. We also note that recent studies [29,30] have shown that oxygen vacancies or structural disorder can pin domain walls and hence affect their dynamics. However, further study, for instance determining the wandering exponent, is needed to ascertain the exact nature of the disorder.

Finally, we note the applications of these results to technological developments. The fact that the domain walls exhibit creep motion with a relatively large exponent $\mu=1$ implies a strong stability of ferroelectric domains in thin films, since the induced speed of the domain wall becomes exponentially small as the driving force goes to zero. All domains studied in this work were stable under ambient conditions for the entire 7 day duration of the experiment, while sub-μm wide line-shaped domains
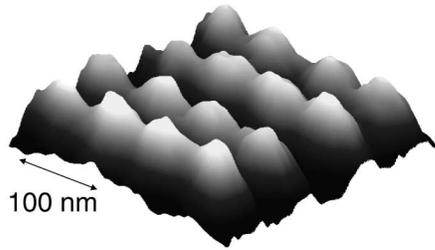
FIG. 4.   Piezoelectrically imaged high-density ferroelectric domain array at 28 Gbit/cm^2, written with 500 ns pulses.

were stable up to one month [31]. Previously, large, regular arrays of ferroelectric domains with densities of $\sim$6 Gbit/cm^2 have been reversibly written [19], and densities up to 150 Gbit/cm^2 have been extrapolated from sizes of individual domains [32]. This work identifies the key parameters controlling domain size: the strength, duration, and confinement of the applied electric field. These can be exploited to increase the information storage density in ferroelectric arrays. By using short voltage pulses, for which the resulting domain size is independent of the writing time, and domain-domain separation as small as 10 nm, regular arrays with densities of the order $\sim$30 Gbit/cm^2 could be written. Figure 4 shows such an array written on a 370 Å thick sample with a density of 28 Gbit/cm^2. Furthermore, it has been suggested that the minimum stable domain size is related to the film thickness or its square root [33,34]. Our data, however, show that the minimum stable domain size, $\sim$40 nm, is independent of the film thickness; rather, it is given by the area over which the electric field is applied during the polarization process. Therefore, by confining the field to a smaller area, domain wall creep will be limited, leading to smaller domains and hence to even higher information densities.

In conclusion, our studies demonstrate that lateral domain wall motion in ferroelectric thin films is a creep process, governed by a characteristic dynamical exponent μ close to 1. The dimensionality of our films suggests that disorder is at the origin of the observed creep behavior, which inherently explains the measured $\exp(-1/E)$ dependence of domain wall speed. The activation energy is found to be around 1 MV/cm, decreasing with increasing film thickness. Finally, these results suggest a high degree of stability for ferroelectric domains in low electric fields and identify the key parameters controlling domain size.

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