Depolarizing-field-mediated 180° switching in ferroelectric thin films with 90° domains

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Switching of the out-of-plane and in-plane polarizations in polydomain epitaxial $PbZr_{0.2}Ti_{0.8}O_3$ thin films is studied using three-dimensional piezoresponse force microscopy (PFM). It is found that, under an electric field induced between the PFM tip and the bottom electrode, the 180° switching occurs in both c and a domains. After the removal of this field, the spontaneous reversal of the out-of-plane and in-plane polarizations back to the initial orientations takes place, evolving via heterogeneous development of antiparallel 180° domains. The switching of in-plane polarization inside a domains and the preferential formation of reversed 180° domains at 90° domain walls are explained by the effects of the depolarizing fields caused by transient polarization charges appearing on these domain walls. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1448653]

Recent advances in the application of the scanning force microscopy to the studies of ferroelectric films made possible the nanoscale imaging of polarization reversal.[1] A powerful tool to investigate and manipulate the domain structure is a modification of the scanning probe microscope[2] (SPM) termed piezoresponse force microscope (PFM).[3] Up until now, PFM was applied mainly for the detection of the polarization components normal to the film surface.[4–6] Recently, it was shown that this technique enables the observation of in-plane polarization as well.[7]

In this letter, we report PFM investigations of the polarization switching in epitaxial $PbZr_{0.2}Ti_{0.8}O_3$ (PZT) thin films containing multiple 90° domains (twins). Changes of both out-of-plane and in-plane polarizations in the film are monitored. A phenomenological theory is used to explain the experimental observations.

The ferroelectric heterostructure used in this study consisted of a 400 nm-thick PZT film epitaxially grown on a [001] single crystalline $SrTiO_3$ (STO) substrate with an intermediate 50 nm-thick $La_{0.5}Sr_{0.5}CoO_3$ (LSCO) oxide layer employed as the bottom electrode. PZT films were fabricated by pulsed laser deposition at $T_g = 650\,°C$ and a partial oxygen pressure of 100 mTorr (see Ref. 8 for details). At room temperature, as-grown PZT films displayed the presence of a two-dimensional grid of 90° domains embedded into the ferroelectric matrix with the tetragonal c axis being oriented orthogonal to the substrate.[5]

Nanoscale visualization of the film domain structure was carried out with the aid of a commercial Digitial Instruments Nanoscope IIIA Multimode SPM. Details of the PFM technique can be found elsewhere.[3] This technique enables us to differentiate between the c and a domains and to determine their polarization directions. Investigation of the as-grown film showed that the out-of-plane polarization in c domains points preferentially towards the bottom electrode [see Fig. 1(a)]. In the further discussion, such domains exhibiting a downward polarization will be termed c^- domains. From the asymmetry of the piezoresponse signal across a particular a domain, it can be deduced at which angle (45° or 135°) the boundaries of this a domain are inclined to the substrate.[5] The inspection of the piezoresponse images shows that the observed configuration is always of the "head-to-tail" type (see Ref. 9 for detailed analysis).

The native c^- domains were switched to 180° into c^+ domains by applying a negative voltage of −8 V to the conductive cantilever and ground to the bottom electrode while scanning a square pattern of approximately $4 \times 4\ \mu m^2$. This area then was rescanned with a zero dc field between the tip and electrode. From the piezoresponse image shown in Fig. 1(c), we see that the poled c^- domains transformed almost completely into the c^+ ones. Moreover, the in-plane polarization in most parts of the a domains was observed to switch by 180° as well [see Fig. 1(d)], though the electric field is applied mainly in the film-thickness direction.[5]

Figure 2 demonstrates the evolution of the piezoresponse images during the time period after poling. It can be seen that the polarization configuration gradually relaxes back to the initial state. Several needle-like c^- domains appear near 90° walls and then grow laterally in the film plane, as shown

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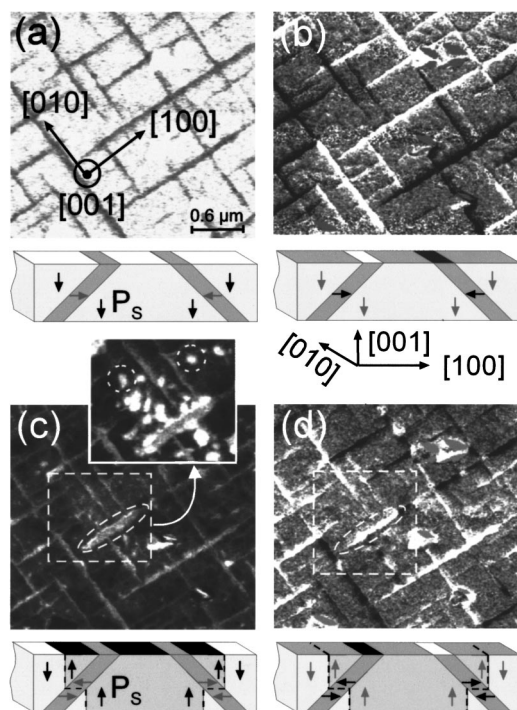
FIG. 1. Piezoresponse images of the polydomain (twinnerd) PZT film in the as-grown states [(a) and (b)] and after poling [(c) and (d)]. The "out-of-plane" PFM signal is shown in (a) and (c), whereas the "in-plane" signal in (b) and (d). Regions with bright, dark, and intermediate contrast correspond to different orientations of the out-of-plane and in-plane polarizations in ferroelectric domains, as shown schematically in the sketches below the PFM images. The ellipse in (c) and (d) demonstrates a specific region, where the polarization orientation remains unchanged after poling. The inset in (c) shows that from this region the polarization backswitching starts.

by circles in Figs. 2(a) and 2(c). Similar results were recently reported for ferroelectric $BaTiO_3$ ceramics under compressive stress.[10] The backswitching of the polarization may also develop via the expansion of the residual c^- domains adjacent to nonswitched a domains [see Fig. 1(c) and inset]. Taking a closer look at Fig. 2(c) in the area denoted by black arrows, we also find that the a domain represents an obstacle for the in-plane growth of the c^- domains. Remarkably, when the switched area eventually penetrates through the obstacle [white arrow in Fig. 2(c)], the adjacent part of the a domain appears to be switched back to its initial state [compare the regions shown by black arrows in Figs. 2(b) and 2(d)].

Now, let us analyze the experimental data with the aid of a phenomenological theory. The spontaneous polarization $\mathbf{P}_s$ and equilibrium domain structure of epitaxial ferroelectric films should strongly depend on the misfit strain S_m between the film and substrate.[11–13] The misfit strain at $T = 35\,°C$ can be evaluated as $S_m \approx (\alpha_b - \alpha_0)(T - T_g)$, where α_b and α_0 are the thermal expansion coefficients (TECs) of the substrate and the film prototypic cubic phase, respectively.[14] Taking for TECs of STO and PZT 20/80 the average values of $\alpha_b \cong 11 \times 10^{-6}\,K^{-1}$ and $\alpha_0 \cong 6 \times 10^{-6}\,K^{-1}$,[15] we obtained $S_m \cong -3 \times 10^{-3}$. At this misfit strain, as follows from the nonlinear thermodynamic theory,[11] a well-defined polydomain $c/a/c/a$ state should form in PZT 20/80 films. Moreover, the formation of this domain pattern in the PZT/LSCO/STO epitaxial system during the cooling is predicted to proceed via the following two-stage process: paraelectric
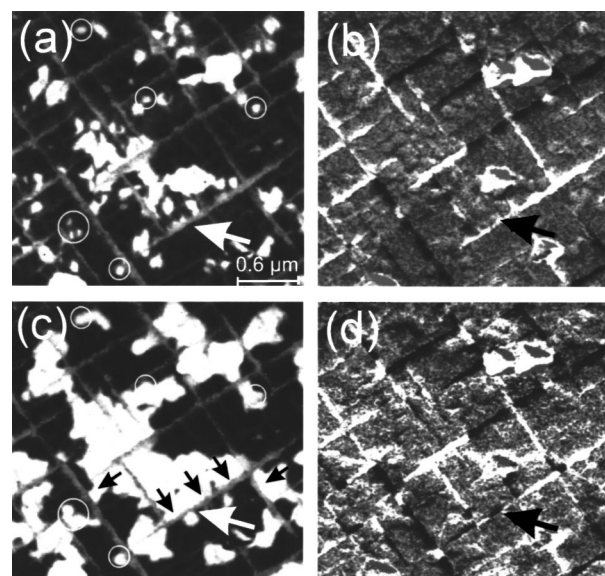

FIG. 2. Evolution of the polarization relaxation after poling. Images representing the out-of-plane [(a) and (c)] and in-plane [(b) and (d)] PFM signals were taken after $10^4\,s$ [(a) and (b)] and after $2.6 \times 10^4\,s$ [(c) and (d)]. The circles show reversed needle-like c^- domains near 90° domain walls. The black arrows in (c) indicate that the a domain is an obstacle for the growing c^- domain, within which the polarization backswitching takes place. The penetration of the switched area through the obstacle [white arrow in (c)] also includes 180° switching of the a domain back to its initial polarization state [black arrow in (d)].

phase→single-domain ferroelectric c phase→polydomain $c/a/c/a$ state. Therefore, the a domains nucleate within an already polarized matrix. (Self-polarization of ferroelectric films has been reported several times in literature and attributed to the presence of an internal field in the ferroelectric or at the interface.)[16] Since the out-of-plane polarization P_3 has a preferential orientation in our films, it is energetically most favorable to form uniformly polarized a domains with the head-to-tail orientation of the in-plane polarization P_1 (or P_2) with respect to the matrix polarization P_3, as illustrated in Fig. 3(a). This conclusion is supported by the analysis of stability of the plate-like a domains, which have "head-to-
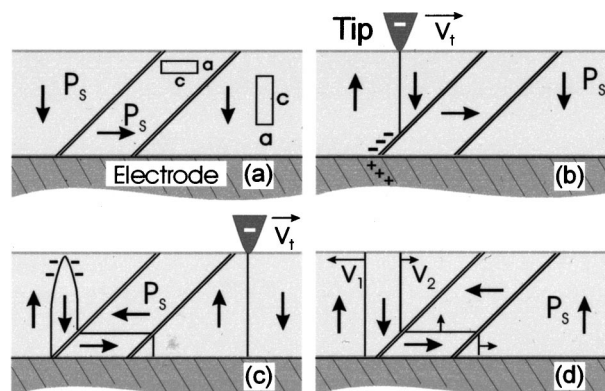

FIG. 3. The expected scenario of polarization switching and relaxation in polydomain PZT films: (a) initial $c/a/c$ domain state with the native downward polarization in the c^- domains, (b) imaginary transient domain configuration during the tip-induced local 180ßD switching, which shows polarization charges on the section of 90° domain wall swept by moving 180° wall (related image charges in the electrode are shown as well), (c) forward growth of the residual c^- domain after the removal of the applied field (first stage of the back-switching), (d) lateral motion of the 180° domain boundaries during the second stage of backswitching.

tail'' or ''tail-to-tail'' polarization configurations relative to adjacent *c* ones. Using the nonlinear thermodynamic theory,[11] we found that such *a* domains are completely unstable in PZT 20/80 films at room temperature. This instability is due to the effect of depolarizing field.

The following scenario may be proposed now for the polarization switching caused by the inhomogeneous electric field $\mathbf{E}(\mathbf{r})$ induced between the PFM tip and an extended bottom electrode. Inside c^- domains, the 180° switching easily occurs because the out-of-plane field $E_3(\mathbf{r})$ is rather high [the mean value $\langle E_3(\mathbf{r})\rangle \sim 20$ MV/m], and the depolarizing field of the needle-like c^+ domain formed under the tip promotes its penetration through the whole film thickness. During further polarization reversal, the c^+ domain freely grows in lateral direction, following the displacement of the PFM tip, until its boundary reaches the c/a domain wall. The 90° domain wall represents an obstacle for the moving 180° wall, because once they join, a net polarization charge $\rho = \mathrm{div}\,\mathbf{P}$ appears at the 90° boundary [Fig. 3(b)].

Near the upper film surface, the local driving force $F(\mathbf{r}) = 2P_s E_3(\mathbf{r})$ acting on a 180° wall is very high so that it easily passes through the *a* domain. This proceeds via the *depolarizing-field-induced* 180° switching of the *a* domain. Indeed, after the switching of the c^- domain, the adjacent unswitched *a* domain becomes thermodynamically unstable, which ensures its 180° switching even in the absence of any in-plane applied field.

In the vicinity of the bottom electrode, however, the out-of-plane electric field $E_3(\mathbf{r})$ becomes relatively small[5] so that the force $F(\mathbf{r})$ strongly reduces. Moreover, the in-plane field $E_\alpha(\mathbf{r})$ ($\alpha = 1,2$) disappears at the bottom electrode because it forms an equipotential surface. Therefore, the bottom edge o the 180° wall remains electrostatically pinned at the junction with the c/a wall. Since the upper part of the 180° boundary still follows the moving PFM tip, the wall bends in the film cross section and becomes S-shaped. At some critical curvature, the bent wall loses its stability and splits into a separated pinned domain boundary and the moving 180° wall [Fig. 3(c)]. As a result, three residual 180° domains are left near the junction of the c/a wall with the interface: (i) in-plane antiparallel domain inside the *a* domain, and (ii) two small c^- domains adjacent to the 90° walls and surrounded by the c^+ domains. As soon as the tip moves away, the residual c^- domain transforms into a needle-like one [Fig. 3(c)] in order to reduce the depolarizing field. Under the action of internal electric field, the needle-like c^- domain then grows in the vertical direction until it reaches the upper surface [Fig. 3(d)]. In the next stage of the polarization reversal, the c^- domain grows more slowly in the film plane.

To check whether the proposed evolution of the residual domain is possible, we studied the energetics of the c^- domain. The total energy U of the 180° domain having a volume V and a boundary area S may be evaluated from the relation[17]

$$U = U_{\mathrm{dep}} + \gamma S + 2P_s \int_V E_3(\mathbf{r})dV,$$

where U_{dep} is the energy associated with the depolarizing field, and γ is the domain-wall energy per unit area. Assuming the domain to be half of a prolate spheroid and using Eqs. (3.5) and (4.1) derived in Ref. 17, we studied the dependence of U on the domain height h. (Owing to the electrostatic interaction between the c^- domain and the adjacent *a* one, the transverse size t of the former is fixed at the bottom electrode.) The calculation shows that, for a reasonable values of γ, P_s, and the dielectric constants of PZT, the c^- domain has an optimum height $h^* \gg t$ in the absence of electric field. This result proves that the transformation of the residual c^- domain into a needle-like one may be energetically favorable even at the expense of the surface-energy increase.

The aforementioned scenario explains the most remarkable experimental observations, namely, the 180° switching of the in-plane polarization in *a* domains near the free sample surface, and the preferential nucleation of the reversed c^- domains near 90° walls during polarization relaxation.

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