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Abnormal domain switching in $Pb(Zr,Ti)O_3$ thin film capacitors

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Observation of abnormal (against the applied electric field) domain switching in $Pb(Zr_xTi_{1-x})O_3$ films by piezoresponse force microscopy is reported. In some grains polarization orients opposite to the external field in the presence of the applied field, while the rest of the film volume switches in a normal way. This effect is observed in thin film capacitors which excludes charge injection effect and spontaneous backswitching due the built-in field, which is the possible reason for this behavior. The abnormal switching behavior is attributed to the charge compensation effect at the boundaries of the grains with rhombohedral structure. © *2008 American Institute of Physics*.
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Ferroelectric thin films find applications in a broad range of devices including pyroelectric detectors, piezoelectric microsensors, and micromechanical pumps,[1] which require integration of solution-deposited films into a variety of material structures. One of the most important requirements for ferroelectric thin films in electronic devices is the symmetric switching between two opposite polarization states. To improve the performance of existing devices and develop next-generation devices based on polarization switching, intensive studies of switching characteristics of thin films have been carried out.[2]

Currently, piezoresponse force microscopy (PFM) is widely used for assessment of the local switching properties via visualization of domain structure, after application of an electric potential between the probing tip and the bottom electrode.[3–6] Generally, domain orientation after poling is consistent with the direction of the applied electric field. However, in some cases this trend is disrupted, i.e., after the external field is turned off the resulting domains exhibit polarization opposite to the direction of the applied field.[7–13] Different mechanisms have been proposed to explain this effect which is basically a consequence of asymmetric mechanical and electrical boundary conditions in the PFM experiments. In thin films the formation of domains with polarization opposite to the applied field related to high-order ferroelastoelectric switching induced by compressive stress of the probing tip has been suggested.[7] The mechanical load exerted by the tip may change the sign of the effective piezocoefficient.[8] While specific field configuration beneath the tip and spontaneous domain backswitching was suggested by another group[9] as the reason for abnormal domain formation. Similar effect was reported in lithium tantalate crystals but no explanation was proposed.[10] One of the most plausible models suggested recently by Buhlmann *et al.*[11] implies injection and subsequent charge entrapment in the bulk of the film, which generates an electric field antiparallel to the applied one resulting in domain backswitching during the PFM imaging process. It should be noted that most of these observations concern the PFM experiments performed on free ferroelectric surfaces, i.e., without top electrode, when the resulting domain structure is visualized long after the switching field is turned off. However, formation of domains antiparallel to the applied field was also reported in microscale ferroelectric capacitors[12] and was attributed to spontaneous domain backswitching due to the stress-induced phase transition. In this letter, we report *true* abnormal domain switching, i.e., formation of antiparallel domains in the presence of the applied field, in thin film ferroelectric capacitors. The obtained results suggest that abnormal switching, which we assume results from the charge compensation effect in grain boundaries with rhombohedral structure, is a more common phenomenon than it was assumed before and deserves special attention in view of ferroelectric film applications.

(111)-textured thin $Pb(Zr_xTi_{1-x})O_3$ (PZT) films with different Zr/Ti ratios ($x=0.20$, 0.52, and 0.60, hereafter designated as PZT20/80, PZT52/48, and PZT60/40, respectively), were prepared by sol-gel technique on $Pt/TiO_2/SiO_2/Si$ substrates.[5] The thickness of the films measured in a cross section by scanning electron microscopy was about 370 nm. The PZT capacitors were fabricated by sputtering a gold layer on the surface of the film through a shadow mask.

Two modified commercial atomic force microscopes (Autoprobe M5, Park Scientific Instrument, and Nanoscope IIIA, Veeco) were used for the PFM studies. Pt–Ti coated silicon tips with their resonant frequency at 160 kHz (Micromash, NSC14/Ti–Pt) have been used for application of external poling bias and domain visualization.[14] The PFM images were acquired using an activation ac voltage at 1 V and frequency at 50 kHz. Local piezoelectric hysteresis loops were measured in fixed locations on the film or top electrode surface as a function of a dc bias superimposed on ac modulation voltage. External probes were used to apply external bias to the top electrode of capacitors.

X-ray diffraction (XRD) patterns showed that all PZT films in this study were single-phase materials, containing only a perovskite phase and a strong (111) texture. XRD patterns also evidenced that PZT20/80 film has ferroelectric phase with tetragonal structure, where the peak split in 2θ around 45° clearly shows the tetragonality. No split was detected for PZT52/48 and PZT60/40 films. The (111)-texture

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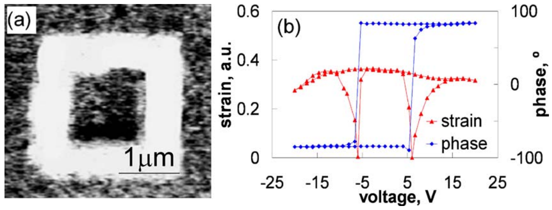

FIG. 1. (Color online) (a) PFM image and (b) piezoresponse hysteresis loop obtained on bare surface of the PZT20/80 film. The bright and dark areas in (a) are poled by dc biases of +10 and −10 V, respectively.

degree α_{111} was calculated from the relative heights of the (111), (100), and (110) diffraction peaks, i.e., $\alpha_{111} = I_{111}/(I_{100}+I_{110}+I_{111})$, and the α_{111} was found to be about 0.93, 0.83, and 0.60 for PZT20/80, PZT52/48, and PZT60/40, respectively.

PFM imaging of the free surface of tetragonal PZT20/80 film after poling showed normal switching with the typical piezoresponse hysteresis behavior (Fig. 1). Positive domains with normal component of polarization pointing toward the film surface appear as bright regions in PFM, while negative domains with polarization oriented toward the bottom electrode appear as dark regions.

In PZT52/48 and PZT60/40 films, the switching behavior exhibited additional features. Figure 2 shows amplitude and phase PFM images of the rhombohedral PZT60/40 films after poling. Both positively and negatively poled regions (appearing as mostly bright and dark regions in the phase image, respectively) exhibit a number of grains with polarization apparently opposite to the applied field, i.e., with dark phase contrast within the bright positively poled regions and vice versa. Meanwhile, these grains are characterized by rather strong amplitude signals suggesting complete switching and ruling out partial depoling as a possible reason for the inverse phase contrast.

Similar behavior was observed in PZT52/48 films with morphotropic composition. Figure 3 illustrates the piezoresponse images of the PZT52/48 films after negative and positive poling, both exhibiting some grains with polarization always opposite to the applied field. In addition, local PFM phase hysteresis loops obtained in these inversely poled grains look like mirror images of the loops measured in the normally switching regions [Figs. 3(c) and 3(d), respectively]. This switching behavior was reproducibly observed in several samples of PZT 52/48 and PZT 60/40 films.

One of the reasons for the polarization contrast opposite to the applied field can be ferroelectric imprint, which results in spontaneous backswitching to a preferred polarization state after the poling field is turned off. However, imprint cannot explain the inversion of the PFM phase hysteresis

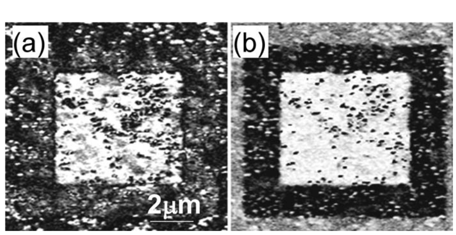

FIG. 2. (a) PFM amplitude and (b) phase images of the PZT60/40 film after dc poling. Large bright and dark areas in (b) are poled by dc biases of +10 and −10 V, respectively.

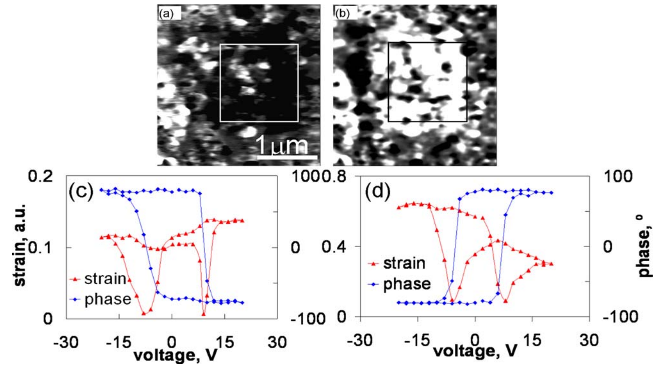

FIG. 3. (Color online) Piezoresponse images of the PZT52/48 film showing domain structures after (a) −15 V and (b) +15 V dc poling, respectively. Local piezoresponse hysteresis loops were obtained in (c) inversely poled grains and (d) in the normally switched region.

loop. The contact force during these experiments was held at the level of 1 nN, which allowed us to rule out mechanical suppression of switching as a possible reason for the inverse polarization contrast. To check if charge injection and electrostatic tip-sample interaction can be the reason for the observed effect,[13] PFM imaging through the top electrode of the PZT capacitors has been performed. In this type of imaging, neither of these effects should play a significant role due to the relatively low electric field generated in the capacitor and zero potential difference between the probing tip and the sample surface.

In the PZT20/80 capacitors, regions of abnormal polarization contrast after poling have been rarely observed (not shown here). These regions usually exhibited hysteresis loops shifted along the voltage axis, suggesting local imprint and spontaneous backswitching after poling.[15] On the other hand, for the PZT52/48 capacitors, regions with polarization direction opposite to the applied field were repeatedly observed. PFM amplitude and phase images of a PZT52/48 capacitor after application of a negative bias of −5 V are shown in Figs. 4(a) and 4(b), respectively. There are quite a few regions of positive polarization exhibiting bright phase contrast within the negatively poled matrix with dark PFM phase contrast. However, the distinctive feature of the switching behavior here is that the very same regions show negative polarization (indicated by dark PFM phase contrast) after the capacitor was poled by a positive bias of +5 V [Figs. 4(c) and 4(d)]. Note that for both switching polarities, the PFM amplitude signal of these regions is strong, suggesting complete switching. In other words, these regions exhibit polarization opposite to the field direction irrespective of the applied voltage polarity.

Furthermore, to check if this effect is due to the spontaneous backswitching after the removal of the external field, the same area of the PZT52/48 capacitor has been imaged with a dc bias of +7.5 V superimposed over the imaging ac voltage [Figs. 4(e) and 4(f)]. The applied dc bias is well above the coercive voltage of the capacitor. It can be seen that the regions of interest still exhibit polarization opposite to the applied field even in the presence of the applied field. Hence, spontaneous backswitching has been excluded as a reason for the abnormal switching behavior. Finally, the local PFM hysteresis loops measured in those regions are out-of phase by 180° relative to the loops measured in the normally switching area [Figs. 4(g) and 4(h)]. This means that under

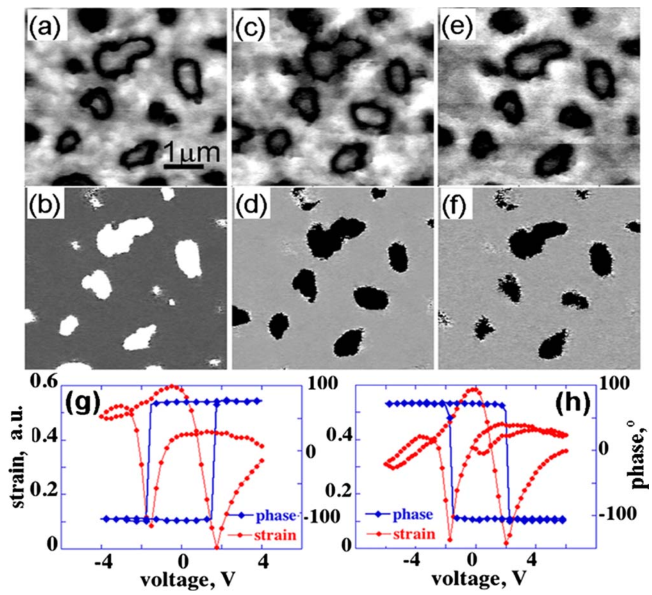

FIG. 4. (Color online) [(a), (c), and (e)] PFM amplitude and [(b), (d), and (f)] phase images of the PZT52/48 capacitor acquired through the top electrode after application of [(a) and (b)] −5 V and [(c) and (d)] +5 V poling field. (e) Piezoresponse amplitude and (f) phase images of the same film area obtained while applying +7.5 V dc bias after +5 V poling. Local PFM amplitude and phase hysteresis loops were measured in the PZT52/48 capacitor in normally (g) switching areas and (h) areas exhibiting abnormal switching. Note inversion of phase loops in (g) and (h).

application of the external field these regions indeed align in the direction opposite to the applied field and stay this way after the field is turned off.

As has been mentioned above, neither imprint nor charge injection nor tip-induced mechanical stress can explain the abnormal switching effect, which has been observed only in rhombohedral PZT films or in films with morphotropic phase boundary (MPB) composition but not in tetragonal PZT. Coexistence of rhombohedral and tetragonal phases in MPB PZT films is well documented.[16,17] This leads us to believe that the abnormal switching is due to the specific nature of polarization reversal in certain PZT grains with rhombohedral composition. All PZT films used here exhibit a (111) texture, which for rhombohedral films implies the presence of domains parallel to film normal and oblique domains with polarization tilted at 71° and 109° to it.[5] Domains of the latter type possess a small component of polarization normal to the substrate and a large in-plane polarization component.[18,19] Due to the tensile effect of the substrate,[18] the poled rhombohedral PZT films contain mostly oblique 71° and 109° domains. Electrical switching between the oblique and normal domains is usually constrained due to high mechanical stress associated with this type of switching.[8] However, given eight possible polarization directions in rhombohedral grains versus six directions for tetragonal grains, additional possibilities for switching without overcoming mechanical stress exist in rhombohedral grains. Thus, we propose that the abnormal switching effect can be explained by switching between oblique domains in rhombohedral grains, where the final orientation of the out-of-plane polarization component is determined by the charge compensation at the grain boundaries. While switching along the applied field occurs in surrounding tetragonal grains, in some rhombohedral grains switching along the field will be mechanically constrained. At the same time, charge redistribution at the grain boundaries may result in in-plane polarization switching with the normal component of polarization oriented opposite to the applied field. This mechanism can be further promoted by electric conductivity along the grain boundaries due to the higher concentration of oxygen vacancies.[20] Lateral PFM imaging could have shed more light on this mechanism should it be possible to perform it through the top electrode of large (~500 μm) dimension. It should be mentioned that mechanical shear stress gradients resulting from inhomogeneous elastic field distribution between different crystallographic phases might act as an additional driving force for the abnormal domain switching.

In summary, the true abnormal domain switching behavior is reported in PZT thin film capacitors with certain composition. The abnormal switching is characterized by formation of domains with the out-of-plane polarization opposite to the applied field irrespective of the applied voltage polarity. The observed effect is different from the previously reported data as the abnormal domains align opposite to the applied field not just after the field is off but actually in the field presence. The imprint and charge injection mechanisms were excluded as the possible reasons for the abnormal switching. It is suggested that the observed behavior is due to the combination of charge compensation and mechanical stress effects in the grains with rhombohedral structure.

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