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In-Plane 90° Rotation of Lamellar Domains in $PbTiO_3$ Grains Revealed by Piezoresponse Force Microscopy

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Abstract. Nanoscale switching of the lamellar 90° domains (*a-a* domains) of $PbTiO_3$ grains in the surface of sol-gel-derived $PbTiO_3/Pb(Zr_{0.58}Ti_{0.42})O_3/PbTiO_3$ thin films is studied by three-dimensional piezoresponse force microscopy. It is demonstrated that the lamellar domain pattern in the $PbTiO_3$ grains can be rotated 90° in the plane of film by the electric field at the tip. It is found that the rotation of lamellar domain pattern involves transverse growth of the existing embedded *a-a* domain nucleus, whose domain walls are perpendicular to the surrounding ones. During the transverse growth, the existing 90° domains extend along length direction and penetrate into neighboring domain walls, while formation of new 90° domain walls was mediated by the nanoscale 45° tilted spike domains.

Keywords: scanning force microscopy, ferroelectrics, thin films, domain

1. Introduction

In the past decades, dynamics of ferroelectric (FE) domains attracts tremendous interests, because of its fundamental importance and applications on ferroelectrics-based devices, such as nonvolatile memory and MEMS [1]. The quick development of scanning force microscopy (SFM), especially the piezoresponse force microscopy (PFM), provides a powerful tool to image ferroelectric domains and study switching dynamics of ferroelectric domains in the nanoscale [2, 3]. Most of SFM investigations were concerned on the reversal of 180° domains in ferroelectric films for the development of ferroelectric memories [4–7]. Study on the rotation of 90° domains was limited, until Eng and coworkers [8–11] developed three-dimensional PFM, which enable to observe the in-plane component of the polarization. Roelofs et al proposed a method by PFM to differentiate 90° and 180° switching, but 90° domain switching was not observed at that time [12]. Later, Nagarajan et al [13] showed that the movement of 90° domain walls in a discrete ferroelectric island is possible. Loppacher et al. [14] tried to manipulate the lamellar domains (90° domains) in the non-continuous polycrystalline $PbTiO_3$ (PT) films by SFM, and found that the lamellar domain structure recovered as time elapsing. Recently, the important roles of 90° domains in the ferroelectric films were being recognized, such as influence on the nucleation during polarization reversal [15] and stabilization of 180° reversed domains [16]. However, the observation of the in-plane rotation of 90° domains in the continuous ferroelectric films at the scale of nanometer was few reported. Therefore, dynamics of 90° domain at nanoscale needs further study in the viewpoint of fundamental and applications of ferroelectric films.

In this study, switching behaviors of lamellar 90° domains in the surface of sol-gel-derived $PbTiO_3/Pb(Zr_{0.58}Ti_{0.42})O_3/PbTiO_3$ (PT/PZT/PT) films were studied by the three-dimensional PFM. It was found that these lamellar domains rotated 90° in the plane of film under electrical field of SFM tip, and the rotation was mediated by nucleation of spike domains at the domain walls.

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2. Experimental

The multi-layered PT/PZT/PT films were prepared by the sol-gel method [17]. PT and PZT mono-precursor were spin coated on the Pt/Ti/SiO_2/Si substrate, after spin coating of each layer, films are dried at 120 °C for 15 min. In order to transform the amorphous film into perovskite phase, a post-annealing at 700 °C for 30 min was carried out. The thickness of each layer was estimated about 100 nm.

Nanoscale inspection of the ferroelectric films was carried out using a commercial scanning force microscopy (SPA-300 HV, Seiko Instruments Inc.). Operation in the piezoresponse mode allows simultaneously recording topography and piezoresponses in the z (out of polarization, OPP) and y (in-plane polarization, IPP_y) directions. After 90° rotation of the sample around the film norm, the same area was re-scanned under the same experimental conditions. Thus, the piezoresponse in the x direction (in-plane polarization, IPP_x) was recorded. Comparable experimental setup can be found elsewhere [8–11]. Due to the non-planar nature of tip/FE/bottom electrode configuration and the high dielectric constant of ferroelectric films, field generated by the SFM tip is highly concentrated near the tip-sample contact area and rapidly decreases away from it [18, 19]. And therefore, PFM is a highly surface sensitive tool. For a 128 mm thick bulk barium-titanate crystal, Abplanalp and Guenter [20] calculated that the upper first 30 nm of the piezoelectric material contributes about 90% to the piezoresponse. Thus it is believed that the piezoresponse signals detected in our experiment is suitable for characterizing topmost PT layer. In our experiments, an ac voltage with amplitude of 1.5 V (peak to peak) and frequency of 10 kHz was applied between Au coated silicon tip and Pt bottom electrode, and the contact force was adjusted as low as possible (about 0.4 nN) to avoid triggering elastic switching.

In order to investigate the dynamics of 90° domains in the individual PT grains, a dc −10 voltage was applied between the tip and bottom electrode, and the scanning area was limited within the grain. After turning off the dc voltage, OPP and IPP_y images were acquired immediately. The IPP_x image was acquired after 90° rotation of the sample. The same grain can be identified by fully matching of the rotated topography image with the former one. The interval, which was needed to rotate sample and relocate tip to the same grain, was about one hour. Relaxation of the switched domains was also monitored by a series of OPP and IPP_y images, which were acquired after rotating the sample back.

3. Results and Discussion

In Fig. 1, the topography and piezoresponse images of the PT/PZT/PT films are shown, depicting the predomination of lamellar domains in $PbTiO_3$ grains. Widths of these lamellar domains range from about 10 to 60 nm, as inspected. The distinguishable thinnest lamellar is 8 nm (Fig. 1(e)). Regard to the distribution of three components of polarization, it can be confirmed that these lamellar domain pattern represent 90° domains with polarization vectors lying in the plane of the films (*a-a* domains). For example, considering the grain circled by the broken line in Fig. 1, the faint OPP image (magnified in Fig. 2(a)) indicates the polarization vector is parallel to the $x - y$ plane. The bright color zone in IPP_x image (Fig. 2b) indicates that P_x points to the negative x-direction, while bright and dark stripes in IPP_y image (Fig. 2(c)) shows P_y in each stripe point to the positive and negative y-direction, respectively. Thus the domain structure of the circled grain can be reconstructed schematically (Fig. 2(d)).

Figure 2 shows the variations of piezoresponse images of the circled grain after being switched by the electric field of SFM tip (−10 V dc biased). In the IPP images Fig. 2(c) and (f) , the domain walls in the grains before and after being switched cross perpendicularly. It is obvious that the lamellar domains pattern was rotated by 90°. The faint contrast in OPP image (Fig. 2(e)) after the switching indicates that the polarizations are switched in the plane of films. So the 90° domain switching occurred in the plane of the films. A series of OPP and IPP_y images are acquired after rotating the sample back, and rearrangement of the switched domains was not observed. Therefore, IPP_x image (Fig. 2(f)) is valid to reconstruct the domain structure after switching (Fig. 2(h)), though it was acquired about one hour later. Switching experiments on other grains with mean diameter ranging from about 700 to 200 nm is reproducible.

It is note that a head-to-head domain wall formed after switching (marked by arrow in Fig. 2(f) and (g), and magnified in Fig. 3(a) and (b). Generally, the head-to-head domain wall is charged and energetically unfavorable. It always tends to rearrange (or backswitch) as time elapsing. In our experiment, the rearrangement

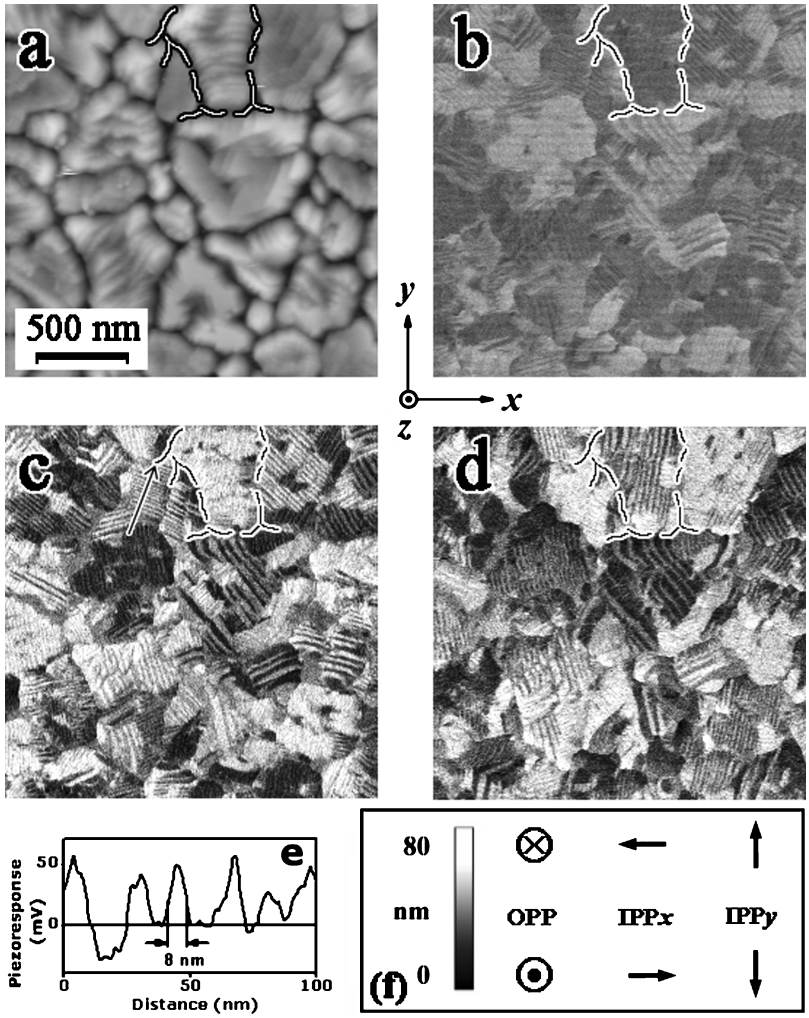

Fig. 1. Topographic (a) and piezoresponse images of the free surface of PT/PZT/PT films. Faint color in the out-of-plane polarization (OPP) image (b) indicates $Pz \approx 0$. Black in the in-plane polarization along x-axis (IPP_x) image (c) indicates Px pointing to positive direction, while black in the in-plane polarization along y-axis (IPP_y) image (d) indicates polarization on the y-axis pointing to negative y direction. It is clear that the lamellar domains pattern represents 90° domains (a-a domains). Line scan (indicated by the arrow in (c)) shows width of the distinguishable smallest domain is about 8 nm (e). Schematic diagram (f) of three-dimensional components of polarization represented by the contrasts of piezoresponse images.

(backswitching) of the head-to-head domain wall was not observed, even one week later. This could be ascribed to the presence of nanoscale spike 180° domains at the domain wall. These nanoscale spike domains with opposite polarization could provide oppositive charges to compensate the accumulated charges at the head-to-head domain wall and decrease depolarizing energy (Fig. 3(c)). Similar formation of spike 180° domains at the charged domain wall have been already observed in the early study on $BaTiO_3$ single crystal, but at the scale of micron by optical microscope [21].

In our continuous multi-layered films, the in-plane 90° rotation of lamellar domain pattern undoubtedly involves significant displacement of 90° domain walls. It is well known that the movement of 90° domains in the ferroelectric film is hampered severely by the substrate-imposed clamping stress, due to the misfit of ferroelectric film and substrate. Obvious displacements of 90° domains walls were only observed in discrete

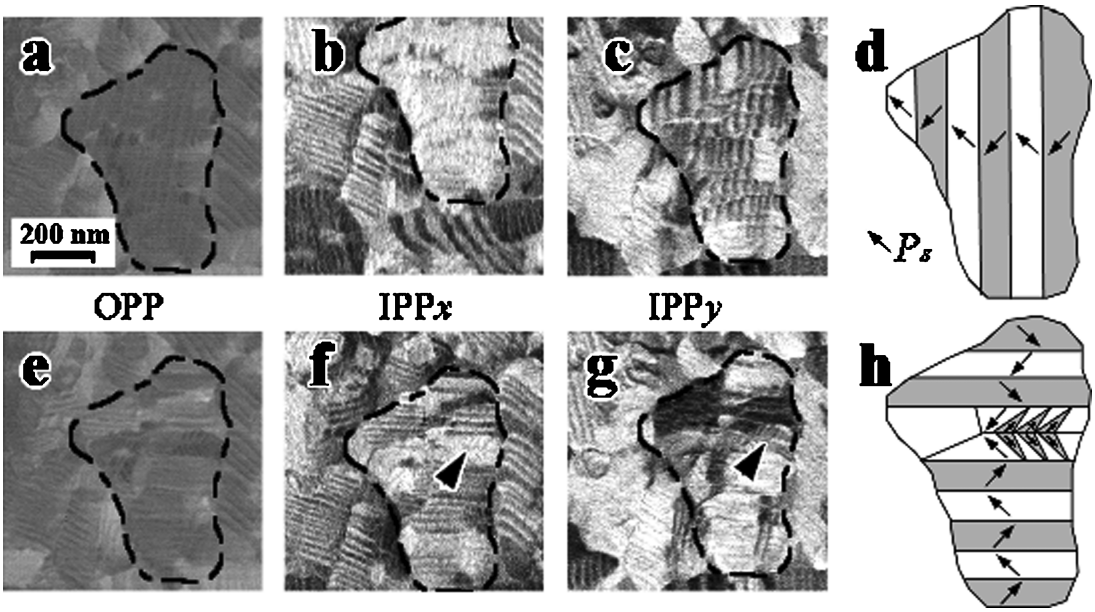

Fig. 2. Three-dimensional piezoresponse images of the inspected grain before (*a-c*) and after (*e-g*) switching demonstrate in-plane 90° rotation of the lamellar domain pattern. From left to right, OPP, IPP_x , and IPP_y images are presented respectively. Corresponding domain structures are reconstructed schematically in (d) and (h). The head-to-head domain wall is indicated by triangles.

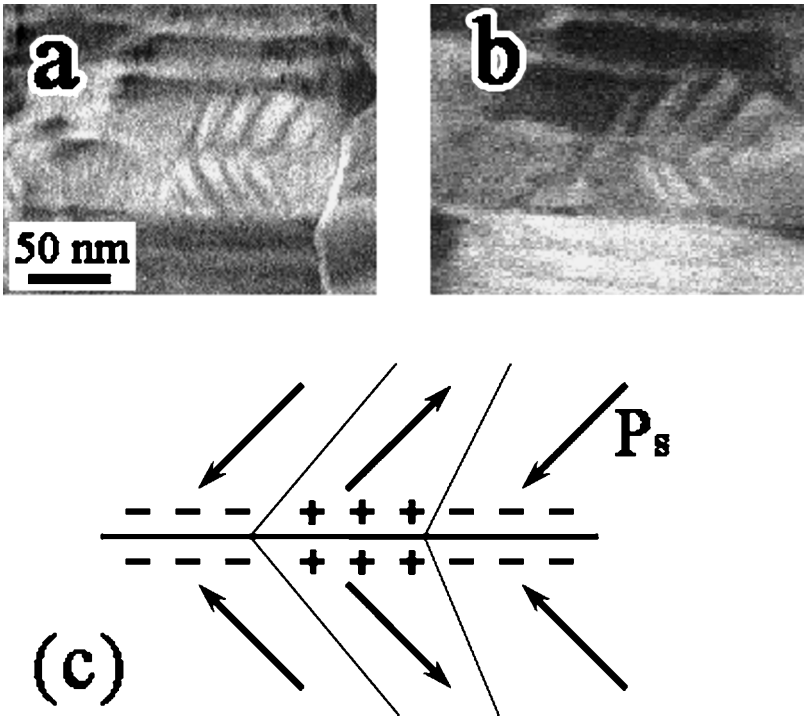

Fig. 3. High resolution IPP_x (a) and IPP_y (b) images the head-to head domain wall, which formed after switching. Schematically shown in (c), the nanoscale spike 180° domains provide positive local charge charges to compensate the negative charges accumulated at the head-to-head domain wall, and decreasing the local electrostatic energy.

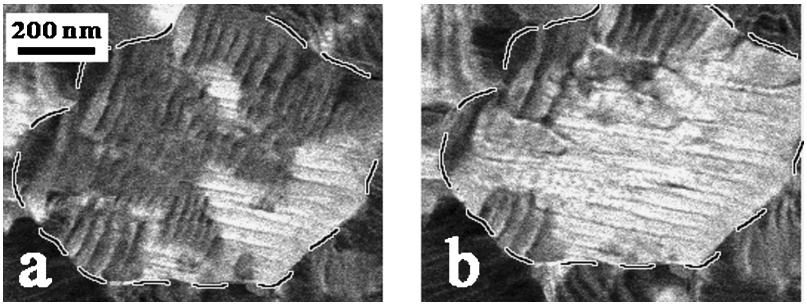

Fig. 4. The existing *a-a* domains (bright contrast) in a large grain (a) were triggered expanding transversely and merging into a big *a-a* domain (b), when being scanned by a dc −10 V biased SFM tip. The grain boundary is circled by dash lines.

ferroelectric islands [16] and discontinued ferroelectric films [14], in which the clamping stress has been reduced. Therefore, it is believed that the topmost PT layer is less clamped. The modification of clamping is likely attributed to the PT/PZT/PT sandwich structure [17]. In the multi-layered films, the insetting PZT mid-layer introduced two PT/PZT interfaces. Like the PT/Pt interface, the PT/PZT interface results thermal misfit stresses during the crystallization process, due to the different thermal expansion coefficients. Generally, the thermal misfit stress (S_m) can be expressed as $S_m \approx (\alpha_b - \alpha_0)\Delta T$, where ΔT is the temperature difference, and α_b and α_0 are thermal expansion coefficients of the substrate and the film prototypic cubic phase, respectively [22]. Taken the thermal expansion coefficients of PT ($\alpha_0 \approx -5.5 \times 10^{-6} K^{-1}$), PZT ($\alpha_0 \approx 6 \times 10^{-6} K^{-1}$) [23], and Pt ($\alpha_0 = 8.9 \times 10^{-6} K^{-1}$) [24], it is clearly that the thermal stress of PT/PZT interface ($S_m \approx 7.7 \times 10^{-3}$) is less than that of PT/Pt interface ($S_m \approx 9.7 \times 10^{-3}$), when films suffer the same thermal process ($\Delta T = 675K$). Moreover, PT/PZT interfaces can provide sites for structural defects to accommodate local strain (or stress). As a consequence, the clamping stress in the multi-layered films could be significantly altered, though the whole FE films suffers the platinum-substrate-imposed clamping stress. It is reasonable that PT grains in the topmost layer is less clamped, compared to traditional mono-layered FE/Metal films, in which displacement of 90° domain walls has seldom been observed.

How the *a-a* domain switching proceeded is an interesting question. It is noticed that the domain structure of these PT grains is seldom of a simple *a-a* domain state. There are always some embedded nucleus of $a-a$ domains with theirs domain walls perpendicular to surrounding ones (Fig. 4(a)). In the energetic viewpoint, rotation of 90° domain pattern in PT grains via lateral expansion of these existing nucleus is less costly than that via forming new nucleus and consequent growth. Experimentally, it was found that the transverse growth of existing *a-a* domains can be easily achieved in a large grain (about 750nm in mean diameter) by applying the electric field of SFM tip (Fig. 4(b)).

High resolution scanning at the location where two *a-a* domain patterns meet shows that the transverse growth of existing 90° domain nucleus is resulted from complex interactions between new domain walls and original ones, and is mediated by nanoscale spike domains. During the experiments, the conductive tip was located at the region where the 90° domain walls met perpendicularly (marked by a cross in Fig. 5(a)). Then a −10 V pulse of 10 seconds was applied. Immediately after that, the corresponding piezoresponse image (Fig. 5b) were first recorded without any dc bias. It is clearly that the 90° domains (indicated by numbered arrows) extended in length and penetrated into the neighboring 90° domain wall, forming a zigzag boundary (white lines). Most remarkable, nanoscale 45° tilted spike domains is found nucleated at the newly formed domain wall. The lengths of these spike domains ranged from 65 to 20 nm, with thickness about 10 nm. In the second scanning, the corresponding piezoresponse image (Fig. 5(c)) was record with a −5 V dc bias applied to the tip. Here the scanning direction is from left to right, then from bottom to up. The nanoscale spike domains were found being shrunk or shifted. And another new 90° domain formed and penetrated into the neighboring perpendicular domain wall like previous ones (indicated by the arrow 3 in Fig. 5(c)). As the stress and strain always accompany with 90° switching, the

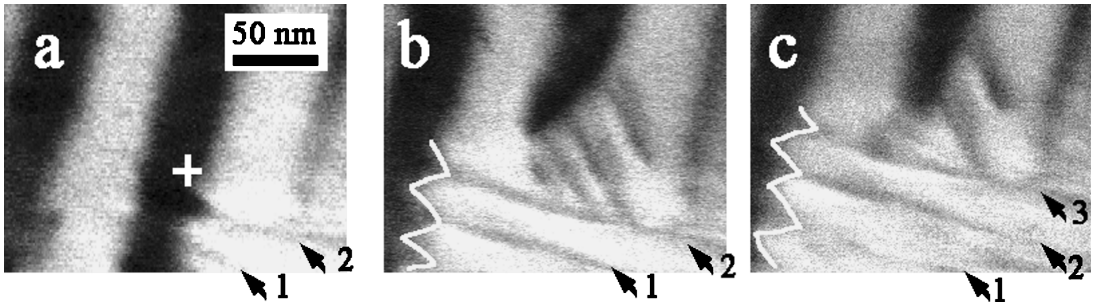

Fig. 5. When applying a dc −10 V pulse at the region two perpendicular lamellar patterns meets (marked by a cross in (a)), the existing 90° domain walls (marked by numbered arrows) extend in length and penetrate into neighboring domains, forming a zigzag boundary (b), and nanoscale 45° tilted spike domains is found nucleate, connecting two perpendicular domain walls. Scanned by a −5 V biased SFM tip, the spike domains shrink or shift, and a new 90° domain forms (indicated by the arrow 3 in (c)).

effect of electric and elastic fields is far more complicated. Nevertheless, the experiment itself shows that the formation of 45° tilted spike domains is a energetically favorable way for 90° switching under a relative lower dc voltage bias (−5 V).

As discussed above, a reasonable scenario for in-plane rotation of lamellar 90° domain patterns could be summarized. Most surface PT grains of the multilayered films contain nucleus of $a - a$ domains with their domain walls perpendicular surrounding ones. Due to the less clamping stress in the surface layer of the sandwich PT/PZT/PT structure, these nucleus would be facilitated to extend transversely when triggered by the electric field of SFM tip. The existing 90° domain walls tend to extend in length and penetrate into neighboring domains. And the formation of new 90° domain walls is mediated by the nanoscale 45° tilted spike domains. As dc biased SFM tip moving around the whole grains, these nucleus continuously expand and merged into each others, finally the new lamellar domains overcome the whole grain. Therefore, the original *a-a* domain pattern seems like being rotated about 90° in the plane of films.

4. Conclusion

In conclusion, the switching of ferroelectric domains in the surface PT layer of PT/PZT/PT thin film is studied by the three-dimensional PFM. It is found that the lamellar 90° domain (*a-a* domain) pattern, which are predominant in PT grains, can be rotated 90° in the plane of the film under electric field of the SFM tip. The facilitation of 90° switching is ascribed to the sandwich PT/PZT/PT structure, which is plausible to reduce substrate-imposed clamping in the topmost PT layer. High resolution scanning shows that the rotation of 90° domain pattern is proceeded by the transverse growth of existing *a-a* domain nucleus, which are embedded perpendicularly into the surrounding *a-a* domains, with the mediation of forming nanoscale 45° tilted spike domains.

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