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# Correlation between domain evolution and asymmetric switching in epitaxial $Pb(Zr_{0.52}Ti_{0.48})O_3$ thin films

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The process-induced domain evolution and asymmetric switching in epitaxial $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) thin films have been studied by reciprocal space mapping, transmission electron microscopy, high-temperature x-ray diffraction, and the polarization-electric field hysteresis loop measurements. After annealing at reduced oxygen pressures, it was evidenced that an oxygen loss at the PZT bottom interface can occur at temperatures well below the Curie temperature $T_C$, and more importantly, the oxygen loss can induce a large positive voltage offset and drive simultaneously the polydomain formation in the PZT films. Our results indicate that the structure evolution is correlated with the coercive voltage shift, and an oxygen-loss-related internal stress at the interface would be responsible for the large internal electric field in epitaxial PZT films. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1866506]

Epitaxial growth of $Pb(Zr_xTi_{1-x})O_3$ (PZT) films on dissimilar substrates inevitably accompanies polydomain formation.[1,2] The domain evolution was explained based on the consideration of strain energy accumulation, arising mainly from the lattice and thermal expansion mismatch between film and substrate, and the phase transformation at the Curie temperature ($T_C$).[3,4] Theoretically, it is usually assumed that the lattice misfit strain is fully relaxed by misfit dislocations at the growth temperature, and during cooling the thermal expansion mismatch between the PZT and perovskite substrates like $SrTiO_3$ is small. Thus, just before the structural phase transformation at $T_C$, the films are stress-free and the internal stresses develop just below $T_C$ due to the phase transformation. In practice, however, the domain structure is found to be affected dramatically by *the unrelaxed strains at $T_C$, if any*, as has been demonstrated by Baik and co-workers, hence besides temperature the final domains could be substrate, film thickness, and cooling rate dependent,[5–10] although for PZT at the morphotropic phase boundary ($x=0.52$) the domain evolution has been rarely studied.[8] On the other hand, it is well documented that the ferroelectric properties of expitaxial PZT films such as the polarization, coercive field, and fatigue are closely linked to the domain structure.[7,10–12] Like fatigue, imprint is also one of the major degradation problems in PZT films, characterized by a preferential polarization state and an asymmetry in polarization-electric field ($P$–$E$) hysteresis loops.[13] In the past decade, the asymmetric switching has been extensively studied through macroscopic $P$–$E$ loop measurements, and was ascribed to aligned defect-dipolar complexes and/or asymmetric distribution of charged defects that possibly exist in the ferroelectric capacitors.[13–17] However, the structural aspects related to the imprint are not clear yet. Imprint in PZT films at the nanoscale was recently examined by using the local piezoresponse method, and structurally backswitching of domains was directly observed during the polarization reversal. Based on these observations, the mechanic stress in the ferroelectric thin films was also believed to be responsible for the imprint behavior.[18,19]

In this letter, the process-induced domain evolution and imprint in epitaxial PZT ($x=0.52$) films were studied and found to be highly correlated. We show evidence that *even at temperatures well below $T_C$*, an oxygen loss at the PZT interface can drive the polydomain formation, and induce simultaneously a large voltage offset in the PZT films. Our results indicate that the domain evoluation can be a manifestation of the imprint, and an oxygen-loss-related strain gradient at the PZT bottom interface would be crucial for creating the large internal electric field in epitaxial PZT films.

Epitaxial PZT/$La_{0.7}Sr_{0.3}MnO_3$ (LSMO) bilayers were grown on $(LaAlO_3)_{0.3}(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$ [LSAT(001)] substrates by the pulsed laser deposition method,[20] on which Pt or LSMO top electrodes were deposited using a shadow mask with the holes of 0.2 mm in diameter. After growing at 620 °C, the capacitors were cooled to 550–300 °C in 10 Torr of $O_2$, and then *in situ* annealed at 10 or $10^{-5}$ Torr for 30 min before being cooled to room temperature (RT) in the same annealing ambient. Some capacitors annealed *in situ* at 10 Torr were further *ex situ* annealed in a different vacuum run, with both the heating and cooling processes conducted in $10^{-5}$ Torr of $O_2$. The thicknesses of Pt, PZT, and LSMO films are about 40, 400, and 150 nm, respectively. The $P$–$E$ hysteresis loops were measured at RT using a RT66A tester.

Figure 1 shows RT x-ray diffraction (XRD, Cu $K\alpha$ radiation) $\theta$-$2\theta$ scans on the LSMO/PZT/LSMO samples *in situ* annealed at 550 °C in 10 or $10^{-5}$ Torr of $O_2$. It is seen that the LSMO electrodes are quite stable against the *in situ* annealing at reducing atmosphere, since the same LSMO(002) reflections were recorded for the two samples. However, with a large positive voltage offset (the inset), the capacitors after the $10^{-5}$ Torr anneal showed a depressed

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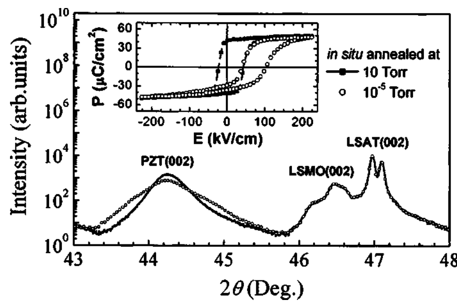


FIG. 1. XRD specular linear scans and *P–E* loops (the inset) from the LSMO/PZT/LSMO capacitors *in situ* annealed at 550 °C and in 10 (■) and $10^{-5}$ (○) Torr of $O_2$.

PZT(002) reflection, peaked at the same Bragg angle but with a much broadened width. It means that the imprint may have nothing to do with the electrode itself, and was induced by oxygen loss possibly at the PZT/LSMO interfaces. As the annealing temperature is decreased, for the capacitors annealed at $10^{-5}$ Torr, both the width of the PZT(002) reflection and the voltage offset in the *P–E* loops decrease, and after annealing *in situ* at temperatures lower than 400 °C, no broadening of the PZT(002) reflection and, moreover, no voltage shift was observed (not shown). To fully characterize the structural changes observed for the PZT layer, the reciprocal space around the PZT(002) reflections was mapped using Cu $K_{\alpha 1}$ radiation for the two samples *in situ* annealed at 550 °C. After annealing at 10 Torr, as shown in Fig. 2(a), the PZT film showed almost a single *c*-domain structure. After annealing at $10^{-5}$ Torr, however, according to Fig. 2(b), apart from the diffuse intensity contours along the 00*l* direction, the PZT(200) and PZT(020) reflections appeared,[1] indicating that the oxygen loss has induced a large-scale strain gradient along the growth direction,[5] and at the same time, generated 90° domains in the *c*-domain matrix. This is in good agreement with the cross-sectional transmission electron microscopy images, as shown in Figs. 2(c) and 2(d). Compared with the 10 Torr annealed sample, the PZT film annealed at $10^{-5}$ Torr showed clearly the *a*/*c*/*a*/*c* polydomain structure,[8,13] where the *a* domains have width of only about 10 nm, resulting in the elongated PZT(200) and PZT(020) relrods in Fig. 2(b).[1]

In order to understand the domain evolution during the reducing annealing, we performed a high temperature XRD study on the 10 Torr annealed Pt/PZT/LSMO capacitors.

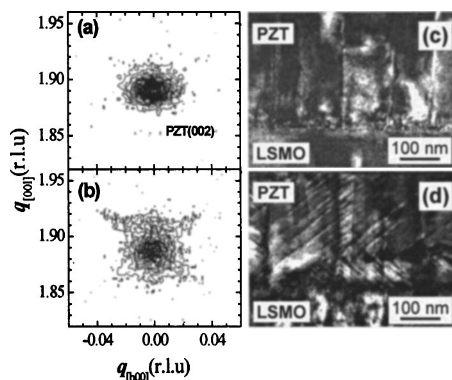


FIG. 2. XRD contour maps of partial reciprocal space of the *hl* plane [around the PZT(002) reflection] and cross-sectional TEM images showing the domain structure of the epitaxial PZT thin films *in situ* annealed in 10 [(a), (c)] and $10^{-5}$ [(b), (d)] Torr of $O_2$.

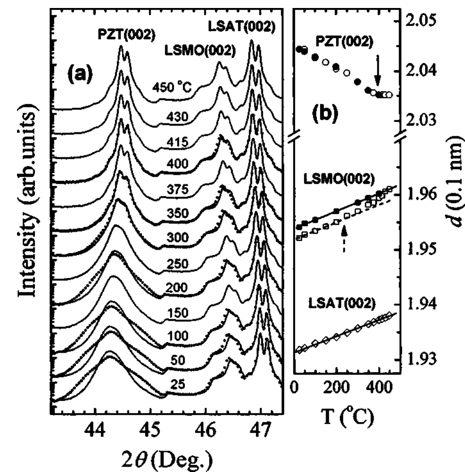


FIG. 3. (a) High temperature XRD specular linear scans on the Pt/PZT/LSMO capacitor after *in situ* annealing at 10 Torr. The PZT(002) reflections show the domain evolution as a function of temperature during the heating (solid line) and cooling (dotted line) in $10^{-5}$ Torr of $O_2$ ambient. For clarity, during cooling some data are omitted. (b) The *d* values corresponding to the reflections recorded during heating (open symbol) and cooling (solid symbol). The solid and dashed arrows indicate $T_C$ and the temperature at which the bottom LSMO electrode begins to loss oxygen.

Both the heating and cooling were conducted in $10^{-5}$ Torr of $O_2$ and the process can be regarded as an *ex situ* annealing. In Fig. 3(a), as the temperature is increased from RT to 450 °C, 13 scans were recorded and each one was taken at a fixed temperature. With increasing temperature, the PZT(002) peak shifts gradually to higher Bragg angles, holding at a fixed position for sample temperatures above 400 °C; its width decreases and at 300 °C it begins to split in Cu $K_{\alpha 1}$ and $K_{\alpha 2}$ reflections. These data and features indicate that $T_C$ of the film is about 390 °C, comparable to that of bulk PZT.[8] During cooling and at the fixed temperature, XRD scans were also recorded. It is seen that at above 400 °C, the PZT(002) reflections are exactly the same as those recorded in the heating process. However, after being cooled to just below $T_C$, they begin to further broaden, and as the temperature decreases, they become more and more widened and depressed than the peaks recorded during heating. These observations indicate that it is just after the phase transformation that the oxygen loss begins to induce strain gradient in the *c*-domains and generate 90° domains in the *c*-domain matrix as well.

Figure 3(b) shows the calculated *d* values corresponding to the PZT(002), LSMO(002), and LSAT(002) reflections recorded during the heating and cooling processes. It was noted that the LSMO electrode is not as stable as that during the *in situ* annealing, although the difference is not clearly understood at present. At about 230 °C, as implied by the fast increase of *d* value (the dashed arrow), an oxygen loss from the electrode has occurred. We speculate that this will inevitably induce oxygen loss at the PZT interface, thus affecting the structural and switching properties of PZT films. In Fig. 4, the capacitors were *ex situ* annealed at 150, 250, and 350 °C in $10^{-5}$ Torr of $O_2$, respectively. It is seen that after annealing at 150 °C, almost no further broadening of the PZT(002) reflection and no coercive voltage shift in the *P–E* loops were observed (the inset). For the capacitors annealed at 250 °C, however, due to the oxygen loss from the bottom electrode and therefore the PZT/LSMO interface, the broadening of PZT(002) reflection and positive voltage shift in the

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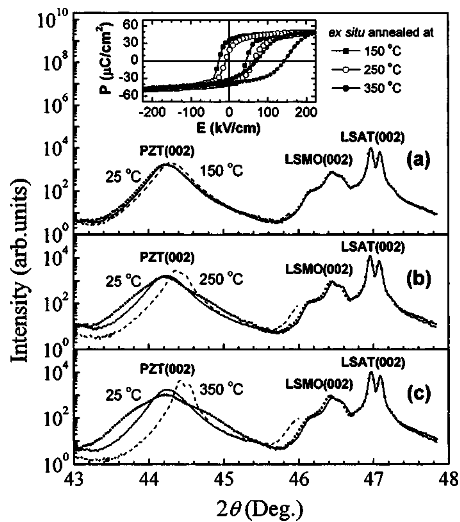


FIG. 4. RT XRD specular linear scans on the Pt/PZT/LSMO capacitor before (solid line) and after (dotted line) *ex situ* annealing at (a) 150, (b) 250, and (c) 350 °C and in $10^{-5}$ Torr of $O_2$ for 30 min. The dashed lines were recorded at the annealing temperature as indicated, and for clarity the data from the electrodes and substrate are omitted. The inset shows *P–E* loops from the capacitors *ex situ* annealed.

*P–E* loops were simultaneously observed. As the capacitors was annealed at a higher temperature of 350 °C, they showed a much broadened and depressed PZT(002) reflection, and at the same time a more pronounced voltage shift in the hysteresis loops. Clearly, like the case for *in situ* annealing, where the LSMO electrode is very stable and therefore the oxygen loss at the PZT interface can occur only at temperatures higher than 400 °C, the domain evolution and voltage offsets induced by oxygen loss at the PZT/LSMO interface are highly correlated. Moreover, it is striking that the domain evolution can be controlled at temperatures well below $T_c$ by the oxygen loss, a factor that has not been discussed previously.[5–10] As has been pointed out, the domain evolution is closely linked to the strain energy accumulation arising primarily from the internal stress at the interface, thus we believe that the internal electric field was created by the oxygen-loss-related strain gradient at the PZT interface. Since for both Pt and LSMO top electrodes the same changes were observed, it is reasonable that the oxygen loss is taken place mainly at the PZT/LSMO bottom interface, where the lattice misfit dislocations could facilitate oxygen diffusion during the annealing processes.[20] The oxygen vacancies at the PZT bottom interface would enlarge the lattice spacing there and induce tensile stress in the PZT films, and therefore result in an upward internal field in the capacitors.[18]

In summary, the process-induced domain evolution in epitaxial PZT films with composition at the morphotropic phase boundary has been studied and found to be highly correlated with the imprint effect. It is demonstrated that even at temperatures well below $T_C$, an oxygen loss at the PZT bottom interface can drive the polydomain formation, and induce simultaneously a large positive voltage offset in the PZT films. Our results suggest that the domain evolution can be a manifestation of the imprint, and an oxygen-loss-related strain gradient at the PZT interfaces would be crucial for creating the internal electric field in epitaxial PZT films.

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