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High-temperature ferroelectric domain stability in epitaxial PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films

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Using high-resolution atomic force microscopy, we have shown extremely high stability of linear ferroelectric domains in epitaxial PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films heated up to 735 °C, a significant advantage for technological applications. An elevated transition temperature $\sim$785 °C is observed even in relatively thick (91 nm) films, despite relaxation of in-plane film-substrate lattice-mismatch-induced strain. We also demonstrate the negligible role of the film surface in determining the written domain-wall configuration, both by direct comparison of the surface roughness with domain-wall position at successive thermal cycles, and by measurements of domain-wall dynamics before and after heating. © 2006 American Institute of Physics.

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The diverse electronic and mechanical properties of ferroelectric perovskites make them particularly interesting for multifunctional devices in which their piezoelectric and pyroelectric properties, as well as their switchable ferroelectric polarization, can be exploited. In addition, local control of polarization by atomic force microscopy (AFM), combined with oxide growth techniques by which epitaxial tric polarization, can be exploited. In addition, local control of pyroelectric properties, as well as their switchable ferroelectric perovskites make them particularly interesting interactions, within the theoretical framework developed for random bond disorder and dipolar interactions. In such systems, domain-wall dynamics before and after heating. © 2006 American Institute of Physics.

In this letter we report the high stability of linear ferroelectric domains in epitaxial PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films up to temperatures as high as 735 °C, well above the bulk ferroelectric transition temperature ($T_c$). We also show that surface deterioration during successive thermal cycles has no significant effect on the static and dynamic behavior of domain walls, demonstrating the high thermal robustness of this system. Finally, $T_c \sim$785 °C, directly measured as the temperature at which domains were observed to have disappeared, is observed in both thinner (50 nm) and thicker (91 nm) films, in spite of the relaxation of in-plane compressive strain, suggesting that high stability of domains and of the ferroelectric phase can be obtained even in thicker films grown in a similar fashion, an important consideration for future devices.

The tetragonal PbZr$_{0.2}$Ti$_{0.8}$O$_3$ films used in the study were grown on metallic Nb-doped single-crystal (001) SrTiO$_3$ substrates by off-axis radio-frequency magnetron sputtering, as detailed in (Ref. 12). To investigate thermal nonlinear response is possible even for subcritical forces. However, the induced domain-wall velocity decreases exponentially as the driving force goes to zero. For ferroelectric domain walls, this driving force is due to either externally applied or internal electric fields, or to line tension of domain walls with nonzero curvature, all promoting domain-wall motion and thus the growth or decay of domains. For linear domains like those used in the prototype PIT-SAW device, with essentially “straight” domain walls, high stability even at elevated temperatures can be expected in zero field. However, thermal fluctuations can also induce domain-wall roughening, which could affect the performance of devices requiring sharp definition of the domain structure. We have previously demonstrated high stability at room temperature of both linear domains and of nanoscopic circular domains in dense arrays, which remain unchanged over observation periods of one month. In contrast, studies of thermal domain evolution in PbZr$_x$Ti$_{1-x}$O$_3$ showed an Arrhenius-type decay of domain size. Thermally activated decay of naturally occurring domains in cleaved triglycine sulfate single crystals was also studied at room temperature and under heating, with independent observation of random-bond disorder-governed behavior.

In this letter we report the high stability of linear ferroelectric domains in epitaxial PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films up to temperatures as high as 735 °C, well above the bulk ferroelectric transition temperature ($T_c$). We also show that surface deterioration during successive thermal cycles has no significant effect on the static and dynamic behavior of domain walls, demonstrating the high thermal robustness of this system. Finally, $T_c \sim$785 °C, directly measured as the temperature at which domains were observed to have disappeared, is observed in both thinner (50 nm) and thicker (91 nm) films, in spite of the relaxation of in-plane compressive strain, suggesting that high stability of domains and of the ferroelectric phase can be obtained even in thicker films grown in a similar fashion, an important consideration for future devices.

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cycles, and increasing deterioration of the surface quality. The rows indicate nanoscale features which remain stable in spite of the heating. Corresponding areas of the sample, all at the same 5-nm grayscale. The arrows indicate nanoscale features which remain stable in spite of the heating close to $T_c \sim 785 \, ^\circ C$. The different orientations of the images are a result of the manual positioning of the sample in the AFM and scanner drift. As can be seen in Fig. 1, showing a series of PFM images of line domains taken at room temperature in a 50-nm thick PbZr$_{0.2}$Ti$_{0.8}$O$_3$ film after heating to the indicated temperatures, with insets showing the topographical image for the corresponding area of the sample, all at the same 5-nm grayscale. The arrows indicate nanoscale features which remain stable in spite of the heating steps. This high stability of the ferroelectric domains is even more remarkable when the film surface deterioration during thermal cycling is taken into account. As shown in the inset topographical images for the corresponding region of the domain structures (each topographical scan mapped at the same 5-nm grayscale), the surface roughness remains relatively unchanged $[0.4–0.5 \, \text{nm root-mean square (rms)}$ over $3 \times 3 \, \mu m^2]$ for moderate temperatures (up to $\sim 635 \, ^\circ C$), but increases significantly (1.1–1.7 nm rms) for high temperatures. In addition, multiple small particles become apparent once the sample is heated beyond 635 °C, and congregate on the surface of the “up-polarized” domains (polarization vector directed towards the film surface), possibly due to the surface charge redistribution which takes place during heating as a result of the pyroelectric properties of the material. In spite of this, the ferroelectric domain structure appears to be largely unaffected, with only a small scale increase in the domain-wall roughness. After heating to $785 \, ^\circ C$, further surface deterioration was observed, giving a surface roughness of 7.1 nm rms, and the line domains were observed to have disappeared. However, the sample itself was still ferroelectric after cooling back to room temperature, and allowed well-defined domain structures to be written, as shown in Fig. 2(a). X-ray analysis of the film after heating to $785 \, ^\circ C$ revealed the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ 001 reflection with multiple size effect satellite peaks, demonstrating the continued high-crystalline quality of the sample [see Fig. 2(b)]. After heating to $885 \, ^\circ C$, the sample quality deteriorated (surface roughness of 15.1 nm rms) to the point at which we were unable to write and image ferroelectric domains clearly. Although the surface layer appeared largely paraelectric, PFM response and switching could be detected in between surface particles. X-ray analysis showed the continued existence of the PbZr$_{0.2}$Ti$_{0.8}$O$_3$ 001 reflection, and no other phases, but increases significantly (1.1–1.7 nm rms) for high temperatures. 

The observed high stability of linear domain structures fulfills a crucial requirement for their use in devices. Additionally, the absence of strong correlation between the film surface quality and the exact position of the domain walls suggests that the surface plays a relatively small role in determining the random variations in the potential landscape which can pin domain walls. As a further test, we uniformly polarized a $7.5 \times 7.5 \, \mu m^2$ region in the sample after the $735 \, ^\circ C$ heating step, inside which we wrote arrays of circular domains with voltage pulses of different durations, allowing us to extract domain-wall velocity as a function of the electric field applied at the AFM tip (as described in Ref. 13) and compare it to similar measurements carried out in the sample before heating. As can be seen in Fig. 3, the room-temperature dynamic behavior of the domain walls before and after the heating cycles appears remarkably similar.
electric information storage, nanoscale circular domains are of particular interest. In this configuration, the relative importance of line tension versus disorder pinning can have significant effects on domain stability, which should be studied in detail, and appropriately taken into account for different device applications.

In conclusion, we have shown extremely high stability of linear ferroelectric domain structures in epitaxial PbZr$_{0.2}$Ti$_{0.8}$O$_3$ thin films up to temperatures as high as 735 °C, a significant advantage for applications. The increased $T_c$~785 °C measured in the films is observed in spite of partial relaxation of in-plane strain, suggesting that these results may be extended to even thicker films.

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16. The nominal oven temperature settings were found to be consistently 15 °C higher than the actual temperature, as measured with a thermocouple at the location of the sample.