High-temperature ferroelectric domain stability in epitaxial $PbZr_{0.2}Ti_{0.8}O_3$ thin films

Paruch, Patrycja; Triscone, Jean-Marc

How to cite

PARUCH, Patrycja, TRISCONE, Jean-Marc. High-temperature ferroelectric domain stability in epitaxial $PbZr_{0.2}Ti_{0.8}O_3$ thin films. In: Applied physics letters, 2006, vol. 88, n° 16, p. 162907. doi: 10.1063/1.2196482

This publication URL: https://archive-ouverte.unige.ch//unige:31050
Publication DOI: 10.1063/1.2196482

APPLIED PHYSICS LETTERS **88**, 162907 (2006)

High-temperature ferroelectric domain stability in epitaxial $PbZr_{0.2}Ti_{0.8}O_3$ thin films

P. Paruch[a] and J.-M. Triscone
DPMC, University of Geneva, 24 Quai Ernest Ansermet, 1211 Geneva 4, Switzerland

(Received 21 November 2005; accepted 10 March 2006; published online 20 April 2006)

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 ~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*.
[DOI: 10.1063/1.2196482]

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 single-crystal quality thin films of these materials can be grown on numerous substrates,[1,2] including silicon,[3] allows significant gains to be envisaged in application parameters, such as frequency or information density. An important consideration for devices is thermal stability. For example, in surface acoustic wave (SAW) frequency filters, thermal effects are a primary cause of device failure, and there is great interest in developing temperature-compensated systems.[4] Recently, a prototype SAW filter was fabricated using ferroelectric domain structures in $PbZr_{0.2}Ti_{0.8}O_3$ as 1–4 GHz range "piezoelectric interdigitated transducers" (PIT) (Ref. 5). This material, unlike many standard piezoelectrics, shows a positive temperature coefficient of delay of the transverse vibrational mode resonant frequency. Its use in combination with a negative-temperature-coefficient-of-delay substrate could thus allow compensation of quasistatic thermal effects, provided the ferroelectric domain structures remain stable in the −20–100 °C range particularly important for applications. Investigating the effects of heating on ferroelectric domains in epitaxial thin films is thus of obvious practical importance. To understand these effects at the nanometer scale required for miniaturized devices, such studies should focus in particular on domain walls, whose static and dynamic behavior determines the stability and growth of domains in ferroelectric materials.

We have recently shown that ferroelectric domain walls in epitaxial thin films are well described as elastic interfaces in the presence of random bond disorder and dipolar interactions,[6] within the theoretical framework developed for elastic objects in random media.[7] In such systems, domain walls are pinned by disorder, although a thermally activated 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[6] and of nanoscopic circular domains in dense arrays,[8] which remain unchanged over observation periods of over one month. In contrast, studies of thermal domain evolution in $PbZr_xTi_{1-x}O_3$ showed an Arrhenius-type decay of domain size.[9] 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.[10,11]

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

---

[a] Present address: Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, NY 14853; electronic mail: patrycja.paruch@cornell.edu

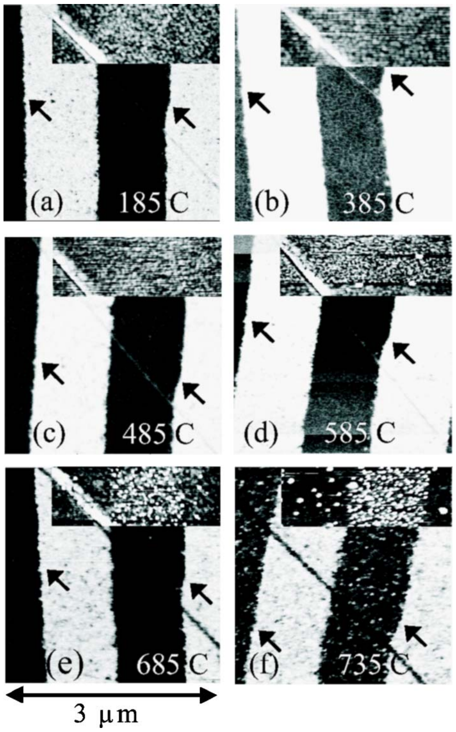

FIG. 1. (Color online) (a)–(f) PFM images of line domains taken at room temperature in a 50-nm thick $PbZr_{0.2}Ti_{0.8}O_3$ film after heating to the indicated temperatures, with insets showing the topographical image for the corresponding area of the sample, all at the same 5-nm grayscale. The arrows indicate nanoscale features which remain stable in spite of the heating cycles, and increasing deterioration of the surface quality [inset (e), (f)]. Small scale thermal roughening of domain walls is visible especially after heating close to $T_c \sim 785$ °C. The different orientations of the images are a result of the manual positioning of the sample in the AFM and scanner drift.

domain stability, the samples were first patterned to define specific areas which could be reliably located using the optical positioning system of the AFM. In these areas multiple 10×10 μm^2 arrays of linear domains with 1 μm linewidth were written by alternate application of ±12 V while scanning a metallic AFM tip in contact with the surface of the ferroelectric film, and imaged by piezoforce microscopy (PFM). The samples were then heated to progressively higher temperatures in air at atmospheric pressure. For each heating step, the tube oven used was first stabilized for 1 h to ±2.5 °C precision, before the sample was placed inside and heated for 3 h, then quenched to room temperature on a large copper block.[16] High-resolution images of the domain structures were acquired at room temperature after each heating step to measure any domain evolution.

As can be seen in Fig. 1, showing a series of PFM images of the line domains in a 50-nm film taken after successive heating steps, we found that domain structures remained stable and well defined after being heated well above the bulk ferroelectric-paraelectric transition temperature of ~460 °C. In fact, even relatively fine features of the domain configuration, such as the 10-nm lengthscale kink and the 100-nm lengthscale shoulder indicated by the arrows in each image, remain clearly visible between successive heating steps. This high stability of the ferroelectric domains is even more remarkable when the film surface deterioration during the 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 nm root-mean square (rms) over 3×3 μm^2] for moderate temperatures (up to ~635 °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 °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 °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 °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 the absence of size effect satellite peaks suggests deterioration of the crystal itself.

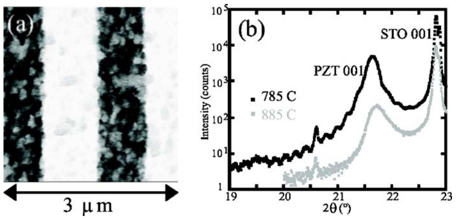

FIG. 2. (Color online) (a) The sample remains ferroelectric, allowing well-defined domain structures to be written, in spite of significant deterioration of surface quality after heating beyond $T_c \sim 785$ °C. (b) θ–2θ x-ray diffraction around the $PbZr_{0.2}Ti_{0.8}O_3$ 001 reflection reveals finite size effect peaks, demonstrating continued high-crystalline quality after heating to 785 °C (black points), which disappear after the sample is heated beyond 885 °C (gray points). The difference in intensity is a result of different acquisition times.

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 7.5×7.5 μm^2 region in the sample after the 735 °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,

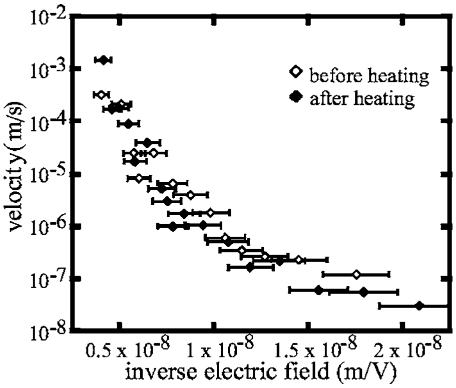

FIG. 3. Domain-wall speed as a function of the inverse applied electric field for the 50-nm $PbZr_{0.2}Ti_{0.8}O_3$ thick film, as measured prior to the heating experiments, and after heating to 735 °C. The dynamical exponent μ governing the observed creep behavior $v \sim \exp[-R/k_BT(E_0/E)^{\mu}]$ decreases negligibly from 0.59 to 0.54 after heating (R is a characteristic energy and E_0 a critical electric field).

with negligible difference in the values of the dynamical exponent μ, governing the observed creep relation between the domain-wall velocity and electric field ($v \sim \exp[-R/k_BT(E_0/E)^{\mu}]$ with R a characteristic energy and E_0 a critical electric field), extracted prior to (0.59) and after (0.54) heating over the same electric-field range, suggesting little change in the disorder potential governing the observed creep process. Thus, it is more probable that defects within the body of the thin film (such as oxygen vacancies) or at the substrate-film interface provide a dominant contribution to the disorder potential.

Finally, the disappearance of domain structures after heating to 785 °C provides a direct measurement of the high T_c in the epitaxial thin films studied. We note that elevated T_c (as compared to that of the bulk material) was observed in other perovskites epitaxially grown on rare-earth scandates,[2,14] where lattice mismatch between the film and the substrate leads to significant in-plane compressive strain for films below a critical thickness for relaxation. Following Ref. 15, the $PbZr_{0.2}Ti_{0.8}O_3-SrTiO_3$ lattice mismatch would provide 1.15% strain in unrelaxed films, giving $T_c \sim 760$ °C by extrapolating the phenomenological prediction for the related perovskite ferroelectric $PbTiO_3$. However, we observe a separation between the films and substrate (113) peaks in x-ray Q-space mapping of both the thicker (91 nm) and thinner (50 nm) films, with a measured lattice mismatch of 1.5%, suggesting that other factors are contributing to stabilize the ferroelectric phase.

This result has important consequences for applications, allowing similarly high T_c and domain stability to be reasonably expected even in the relatively thick films used for devices, epitaxially grown in the same manner.

We also note that the very high stability demonstrated in these studies was observed for "straight" domain walls, interesting for the PIT-SAW or related applications. For ferroelectric 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 $T_c \sim 785$ °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.

The authors would like to thank T. Giamarchi, S. Ballandras, C. Ahn, and X. Hong for useful discussions, S. Gariglio for his help with the x-ray diffraction, and N. Stucki for measuring the oven stability. This work was supported by the Swiss National Science Foundation through the National Center of Competence in Research "Materials with Novel Electronic Properties-MaNEP" and Division II. Further support was provided by the New Energy and Industrial Technology Development Organization (NEDO) and the European Science Foundation (THIOX).

[1] C. H. Ahn, S. Gariglio, P. Paruch, T. Tybell, L. Antognazza, and J.-M. TrisconeScience **284**, 1152 (1999).

[2] K. J. Choi, M. Biegalski, Y. L. Li, A. Sharan, J. Schubert, R. Uecker, P. Reiche, Y. B. Chen, X. Q. Pan, V. Gopalan, L.-Q. Chen, D. G. Schlom, and C. B. Eom, Science **306**, 1005 (2004).

[3] A. Lin, X. Hong, V. Wood, A. A. Verevkin, C. H. Ahn, R. A. McKee, F. J. Walker, and E. D. Specht, Appl. Phys. Lett. **78**, 2034 (2001).

[4] N. Dewan, M. Tomar, V. Gupta, and K. Sreenivas, Appl. Phys. Lett. **86**, 223508 (2005).

[5] A. K. S. Kumar, P. Paruch, J. M. Triscone, W. Daniau, S. Ballandras, L. Pellegrino, D. Marré, and T. Tybell, Appl. Phys. Lett. **85**, 1757 (2004).

[6] P. Paruch, T. Giamarchi, and J.-M. Triscone, Phys. Rev. Lett. **94**, 197601 (2005).

[7] T. Nattermann, J. Phys. C **16**, 4125 (1983).

[8] P. Paruch, T. Giamarchi, T. Tybell, and J.-M. Triscone, J. Appl. Phys. (to be published); e-print cond-mat/0411178.

[9] T. Hidaka, T. Maruyama, I. Sakai, M. Saitoh, L. A. Wills, R. Hiskes, S. A. Discarolis, J. Amano, and C. M. Foster, Integr. Ferroelectr. **17**, 319 (1997).

[10] V. Likodimos, M. Labardi, and M. Allegrini, Phys. Rev. B **61**, 14440 (2000).

[11] V. Likodimos, M. Labardi, and M. Allegrini, Phys. Rev. B **66**, 024104 (2002).

[12] T. Tybell, C. H. Ahn, and J.-M. Triscone, Appl. Phys. Lett. **72**, 1454 (1998).

[13] T. Tybell, P. Paruch, T. Giamarchi, and J.-M. Triscone, Phys. Rev. Lett. **89**, 097601 (2002).

[14] J. H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y. L. Li, S. Choudhury, W. Tian, M. E. Hawley, B. Craigo, A. K. Tagantsev, X. Q. Pan, S. K. Streiffer, L. Q. Chen, S. W. Kirchoefer, J. Levy, and D. G. Schlom, Nature (London) **430**, 758 (2004).

[15] N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, Phys. Rev. Lett. **80**, 1988 (1998).

[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.