Applied Physics Letters

Mechanical stress effect on imprint behavior of integrated ferroelectric capacitors

Cite as: Appl. Phys. Lett. **83**, 728 (2003); https://doi.org/10.1063/1.1593830
Submitted: 16 December 2002 • Accepted: 30 May 2003 • Published Online: 22 July 2003

A. Gruverman, B. J. Rodriguez, A. I. Kingon, et al.

Mechanical stress effect on imprint behavior of integrated ferroelectric capacitors

A. Gruverman,[a)] B. J. Rodriguez, A. I. Kingon, and R. J. Nemanich
North Carolina State University, Raleigh, North Carolina 27695

A. K. Tagantsev
Ceramics Laboratory, EPFL, CH-1015 Lausanne, Switzerland

J. S. Cross and M. Tsukada
Fujitsu Laboratories, Atsugi 243-0197, Japan

(Received 16 December 2002; accepted 30 May 2003)

Stress-induced changes in the imprint and switching behavior of (111)-oriented $Pb(Zr,Ti)O_3$ (PZT)-based capacitors have been studied using piezoresponse force microscopy. Visualization of polarization distribution and d_{33}-loop measurements in individual 1×1.5-μm^2 capacitors before and after stress application, generated by substrate bending, provided direct experimental evidence of stress-induced switching. Mechanical stress caused elastic switching in capacitors with the direction of the resulting polarization determined by the sign of the applied stress. In addition, stress application turned capacitors into a heavily imprinted state characterized by strongly shifted hysteresis loops and almost complete backswitching after application of the poling voltage. It is suggested that substrate bending generated a strain gradient in the PZT layer, which produced asymmetric lattice distortion with preferential polarization direction and triggered polarization switching due to the flexoelectric effect.
[DOI: 10.1063/1.1593830]

It is a well-known fact that mechanical stresses have a profound effect on the ferroelectric and piezoelectric behavior of $Pb(Zr,Ti)O_3$ (PZT) thin films. Accommodation of the misfit strain between a substrate and a thin film in epitaxial heterostructures results in multidomain pattern formation and in significant size dependence of dielectric properties.[1,2] It has been proposed that the misfit strain can lead to the appearance of phases forbidden in bulk samples.[3] Mechanical clamping of non-180° domain walls by a substrate has been suggested to account for the significant difference between the piezoelectric properties of thin films and bulk ceramics.[4,5] In tetragonal PZT films, external stress can generate ferroelastic switching via the 90° rotation of a polarization vector.[6] Significant changes in hysteresis loop behavior under external stress have also been observed.[7,8] In addition, the recently reported size effect on the piezoelectric response of nanoscale ferroelectric structures has been attributed to the decrease in internal stress and constraint.[9] In another report, the same effect has been explained by reduction in the number of *a*-domains due to less thermal mismatch stress in nanoscale capacitors.[10] Recently, Stolichnov *et al.*[11] reported an anomaly in polarization distribution of 2×3-μm^2 (111)-oriented PZT capacitors, which was discussed in terms of strain-induced phase transition. These effects indicate that mechanical stress can be an important factor in determining the switching behavior of PZT films, which are being intensively investigated for application in nonvolatile ferroelectric random access memory (FRAM) devices.[12]

In this letter, stress-induced changes in the imprint and switching behavior of etched 1×1.5-μm^2 (111)-oriented PZT capacitors are reported. It has been shown that reliability of FRAM capacitors can be drastically affected by mechanical stress. Characterization of switching behavior of the FRAM capacitors has been performed by means of piezoresponse force microscopy (PFM), which has become one of the major tools for characterization of ferroelectric materials at the nanoscale.[13,14] Development of the PFM method opened a possibility of testing the switching behavior of individual submicrometer capacitors.[11,15,16]

The (111)-oriented Ca-, Sr-, and La-doped PZT layers with Zr/Ti ratio of 40/60 have been sputtered on the Pt bottom electrode on the 0.5-mm-thick Si substrate. The thickness of the PZT layer was 200 nm. Reactive ion etching has been used to fabricate 1×1.5-μm^2 capacitors with 50-nm-thick IrO_2 top electrodes on the PZT surface. In this study, visualization of domain patterns has been performed on individual capacitors by applying a modulation (imaging) voltage to the capacitor's top electrode using a conductive PFM tip. The same tip was used to detect the mechanical displacement of the surface due to the converse piezoelectric effect. The top electrode did not conceal the domain structure, which has been imaged with a lateral resolution of less than 30 nm. This approach[17] allows one to circumvent the problem of inhomogeneous electric field distribution generated by the probing tip in a ferroelectric film without a top electrode, and to exclude possible contribution of Maxwell stress to the piezoresponse signal.[18] During imaging, the film was scanned with an oscillating tip bias of 0.8 V rms at 10 kHz. Polarization reversal in individual capacitors was induced by applying voltage pulses to the top electrodes using the same probing tip. The local hysteresis loop measurements were performed by positioning the PFM tip at various sites on the

[a)]Electronic mail: alexei_gruverman@ncsu.edu

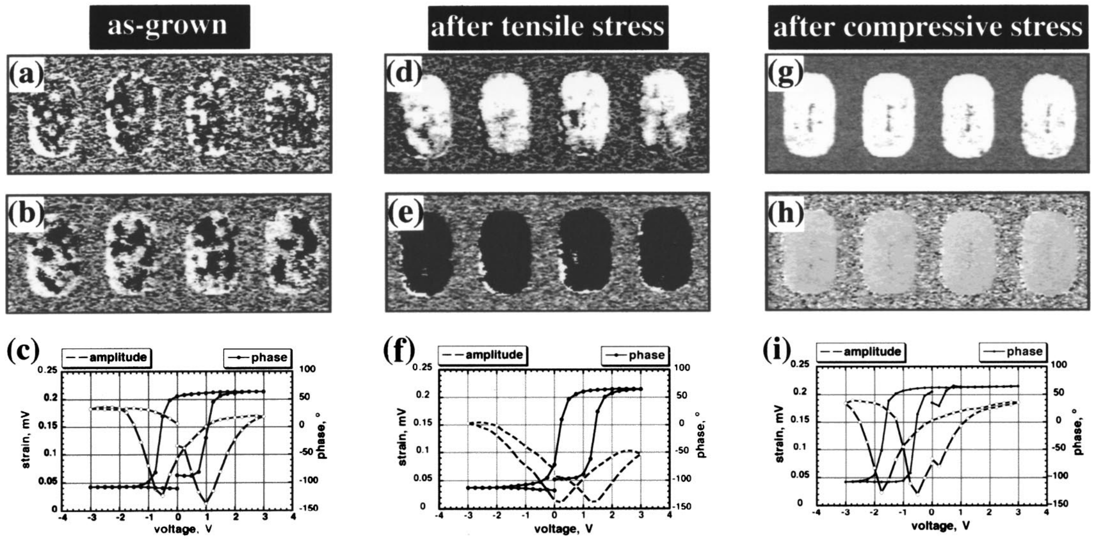

FIG. 1. PFM images illustrating the impact of stress on polarization and switching behavior of the (111)-oriented PZT capacitors. (a)–(c) Before stress application: PFM amplitude (a) and phase (b) images of as-grown capacitors and a local hysteresis loop (c) measured near the edge of one of the capacitors. (d)–(f) After tensile stress application: PFM amplitude (d) and phase (e) images of the same capacitors and a hysteresis loop (f) measured in the same site. (g)–(i) After compressive stress application: PFM amplitude (g) and phase (h) images after application of compressive stress and a hysteresis loop (i) measured near the edge of one of the capacitors.

top electrode and by measuring the PFM signal as a function of a dc voltage superimposed on the imaging voltage. The dc voltage was changed by a 0.25-V increment with a 1-s delay in the range from -3 to 3 V.

Figures 1(a) and 1(b) show PFM amplitude and phase images, respectively, of the array of as-grown 1×1.5-μm^2 capacitors. The phase image [Fig. 1(b)] shows dark and light regions, which represent regions with opposite normal components of polarization: dark (oriented upward) and light (oriented downward). Hereafter, dark regions in the phase image will be referred to as ‘‘negative’’ domains and light regions as ‘‘positive’’ domains. In the amplitude image [Fig. 1(a)], the domain boundaries appear as dark lines due to the reduced piezoresponse signal as a result of the mutually compensating contribution from the opposite domains.

The effect of mechanical stress on imprint and switching properties was studied by inducing compressive and tensile stress in the PZT layer by bending the Si substrate (with a curvature radius R of about 30 cm). PFM imaging and loop measurements of the capacitors have been performed in non-stressed capacitors before and after stress application. The total stress has been estimated as $\sigma \cong cU \cong c(h/2R) \cong 0.1$ GPa, where c is the elastic constant of PZT, U is uniaxial in-plane strain, and h is the substrate thickness. This stress can produce a noticeable domain rearrangement, as has been well-documented in bulk PZT.[19] Its impact should be comparable to the effect of the electric field $E_{eq} = \sigma U_s / P_s \cong 100$ kV/cm ($U_s \approx 0.03$ and $P_s \approx 0.3$ C/m^2 are typical values of the spontaneous strain and polarization in PZT films), which is of the order of the coercive field of the PZT thin films. Indeed, the obtained results, presented in Figs. 1(d)–1(i), show a remarkably strong effect of mechanical stress on domain structure and switching behavior of FRAM capacitors. These results can be summarized as follows.

(a) Upon application of tensile stress to the substrate, all as-grown capacitors were switched into the single-domain negative polarization state and became negatively imprinted, as is indicated by the hysteresis loops shifted to positive voltages [Figs. 1(d)–1(f)]. Application of a positive poling voltage (up to 7 V) did not produce stable positive polarization as capacitors apparently switched back after voltage application. This behavior is remarkable since the electric-field-induced poling of the virgin samples usually induces no appreciable imprint effect.

(b) Compressive stress also resulted in complete switching but into the positive polarization state. Hysteresis loops of capacitors after compressive stress exhibited a significant shift to negative voltages, indicating strong positive imprint in all capacitors [Figs. 1(g)–1(i)].

Two additional features should be emphasized here. (1) Stress-induced single-domain polarization states were not stable and showed slow relaxation with characteristic times in the range from several hours to several days. (2) There were significant variations of relaxation patterns as a function of a capacitor location in the capacitor array suggesting inhomogeneous distribution of elastic fields and possible mechanical coupling between neighboring capacitors (Fig. 2).

We suggest that the observed stress-induced poling in (111)-oriented PZT capacitors can be attributed to the so-called flexoelectric effect, which is a linear polarization response to the strain gradient. It can be assumed that the substrate bending generates a strain gradient across the film thickness, which creates a preference for a certain polarization state and results in polarization switching in the capacitors. The flexoelectric effect is described by a fourth-rank tensor allowed in materials of any symmetry and can be estimated in the framework of the lattice dynamics theory.[20,21] In our geometry the strain gradient is normal to the film plane and equals $\partial U/\partial z = \pm 1/R$ (with the sign depending on the upward or downward bending). The normal component of the strain-induced polarization can be written in a scalar form as $P = f(\partial U/\partial z)$, where f is a corresponding compo-

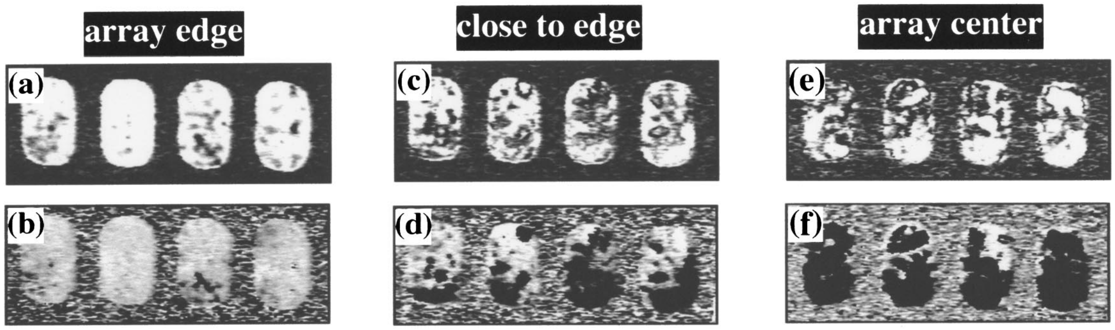

FIG. 2. PFM images illustrating variations in relaxation patterns in FRAM capacitors 10 days after compressive stress was applied. (a), (c), (e) Amplitude images. (b), (d), (f) Phase images. Right after stress application, the phase images of all capacitors were light in contrast, indicating a positive polarization state.

nent of the flexoelectric coefficient and z is the coordinate along the film thickness. An order-of-magnitude estimate of the flexoelectric coefficient $f=(\varepsilon/4\pi)(e/a)$ (where ε is a relative dielectric permittivity, e is the charge of the electron, and $a\approx 4\times 10^{-10}$ m is the lattice constant of the material) is consistent with a number of experimental observations. To assert the effect of the substrate bending, we estimated the value of the effective electric field, which would produce the same polarization as the strain gradient: $E_{\mathrm{eff}}=(f/\varepsilon\varepsilon_0)(\partial U/\partial z)=(e/4\pi\varepsilon_0 a)(1/R)\approx 10$ V/m. Obviously this value is too small to cause any switching effect and is not comparable with the field value that can be obtained from the voltage shift of the hysteresis loop. However, it should be noted that this consideration addresses only the lattice contribution to the effect. We cannot exclude that, in the case of the polydomain PZT capacitors, we are dealing with another, much stronger contribution to the flexoelectric effect. For example, Ma and Cross[22] reported a ε-dependence of the flexoelectric response essentially different from $(\varepsilon/4\pi)/(e/a)$, whereas Zheludev *et al.*[23] reported the flexoelectric coefficient of three orders of magnitude larger than our estimation.

It should be noted that the stress-induced poling results in a much stronger imprint than the electric-field poling. A plausible reason for the strong stress-induced imprint effect can be a change in the in-plane polarization component of the (111) tetragonal PZT film. This change may induce an appreciable depolarizing field. Compensation of this field, which involves accumulation of the free carriers at the border between the FRAM capacitor and the PZT matrix with their subsequent entrapment, can lead to the polarization imprint. On the other hand, for the electric-field-induced switching of the out-of-plane polarization component, the electrodes provide a very effective way of screening, which results in much less pronounced imprint.

In summary, PFM mapping of polarization distribution as well as local $d_{33}-V$ loop measurements allowed direct assessment of mechanical stress effect on polarization state and switching behavior of PZT capacitors. It has been demonstrated that mechanical stress, generated by the substrate bending, can lead to polarization switching of ferroelectric capacitors with the sign of the applied stress governing the resulting polarization direction. This behavior is consistent with the so-called flexoelectric effect. After the substrate is released the resulting polarization state is strongly imprinted. Further in time, relaxation of the single-domain patterns occurs as governed by the internal electric field and residual mechanical stress distribution. The observed strain-gradient induced poling is too strong to be attributed to the lattice contribution to the flexoelectric effect. It is believed that observed phenomenon is associated with the domain-related contribution to this effect. Although mechanical stress of such magnitude as used in the present study is unlikely to be generated in real devices, there is a possibility that local stress variations in a PZT layer, for example, due to defect microstructure, may increase capacitor-to-capacitor variability of imprint and switching behavior.

The authors acknowledge financial support of Fujitsu Limited and Swiss National Science Foundation.

[1] J. S. Speck, A. Seifert, W. Pompe, and R. Ramesh, J. Appl. Phys. **76**, 477 (1994).
[2] W. Pompe, X. Gong, Z. Suo, and J. S. Speck, J. Appl. Phys. **74**, 6012 (1993).
[3] N. A. Pertsev, A. G. Zembilgotov, and A. K. Tagantsev, Phys. Rev. Lett. **80**, 1988 (1998).
[4] R. Bruinsma and A. Zangwill, J. Phys. (France) **47**, 2055 (1986).
[5] F. Xu, F. Chu, and S. Trolier-McKinstry, J. Appl. Phys. **86**, 588 (1999).
[6] D. Berlincourt, J. Acoust. Soc. Am. **70**, 1586 (1981).
[7] S. B. Desu, J. Electrochem. Soc. **140**, 2981 (1993).
[8] T. Kumazawa, Y. Kumagai, H. Miura, M. Kitano, Appl. Phys. Lett. **72**, 608 (1998).
[9] L. Roytburd, S. P. Alpay, V. Nagarajan, C. S. Ganpule, S. Aggarwal, E. D. Williams, and R. Ramesh, Phys. Rev. Lett. **85**, 190 (2000).
[10] S. Buhlmann, B. Dwir, J. Baborowski, and P. Muralt, Appl. Phys. Lett. **80**, 3195 (2002).
[11] I. Stolichnov, E. Colla, A. Tagantsev, S. Bharadwaja, S. Hong, N. Setter, J. S. Cross, and M. Tsukada, Appl. Phys. Lett. **80**, 4804 (2002).
[12] O. Auciello, J. F. Scott, and R. Ramesh, Phys. Today **1998**(7), 22 (1998).
[13] A. Gruverman, O. Auciello, and H. Tokumoto, Annu. Rev. Mater. Sci. **28**, 101 (1998).
[14] S. Hong, J. Woo, H. Shin, J. Jeon, Y. E. Pak, E. L. Colla, N. Setter, E. Kim, and K. No, J. Appl. Phys. **89**, 1377 (2001).
[15] C. S. Ganpule, A. Stanishevsky, Q. Su, S. Aggarwal, J. Melngailis, E. Williams, and R. Ramesh, Appl. Phys. Lett. **75**, 409 (1999).
[16] M. Alexe, A. Gruverman, C. Harnagea, N. D. Zakharov, A. Pignolet, D. Hesse, and J. F. Scott, Appl. Phys. Lett. **75**, 1158 (1999).
[17] O. Auciello, A. Gruverman, and H. Tokumoto, Integr. Ferroelectr. **15**, 107 (1997).
[18] S. V. Kalinin and D. A. Bonnell, Phys. Rev. B **65**, 125408 (2002).
[19] B. Jaffe, W. R. Cook, and H. Jaffe, *Piezoelectric Ceramics* (R.A.N. Marietta, OH, 1971).
[20] A. K. Tagantsev, Phys. Rev. B **34**, 5883 (1986).
[21] A. K. Tagantsev, Phase Transitions **35**, 119 (1991).
[22] W. Ma and L. E. Cross, Appl. Phys. Lett. **79**, 4420 (2001).
[23] I. S. Zheludev, Yu. S. Likhacheva, and N. A. Lilleyeva, Kristallografiya **14**, 514 (1969).