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Local switching behavior and electrical polarization of ferroelectric thin films under nanoindentation

V. Koval[a,*], J. Dusza[a], A.J. Bushby[b], M.J. Reece[b]

[a] *Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 043 53 Kosice, Slovak Republic*
[b] *Department of Materials, Queen Mary University of London, Mile End Road, E1 4NS London, United Kingdom*

Abstract

The local polarization state and switching behavior of ferroelectric thin films under external mechanical loading were investigated. A nanoindentation technique has been devised to impose local mechanical stress. The results are presented for a 700 nm thick, $Pb(Zr_{0.30}Ti_{0.70})O_3$ (PZT), film prepared by a sol–gel technique on a platinized Si substrate. A hysteric behavior was found in the local direct piezoelectric response of the ferroelectric thin films within the subcoercive stress range, and an enhanced piezoelectric activity is attributed to the effect of stress-induced domain-wall movement. Upon nanoindentation, voltage shift was observed in the Q–V hysteresis loops along the voltage axis, indicating an asymmetric switching behavior of the local polarization in the loaded films. The parameter of horizontal loop asymmetry increased and the Q–V loop shifted gradually to the positive voltage side as the indentation force increased. The changes in local switching behavior are suggested to result from a variation in residual stress state, asymmetric distribution of charged defects and asymmetric lattice distortion produced by the inhomogeneous indentation stress field.
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1. Introduction

Despite a number of advantages for the integration of ferroelectric films into microelectronic components, there are severe reliability problems that considerably hinder their full commercialization. The phenomena related to the decrease of switchable polarization with increasing cumulative switching cycles, also well known as polarization fatigue, poor retention of polarization and imprinting of the films in FeRAM capacitors during normal operation conditions, have been investigated extensively and attributed to the polarization reversal driven by the internal depolarizing fields,[1] distribution/alignment of charged defects,[2] space–charge rearrangement,[3] domain pinning[4] and by the clamping of domain walls.[5] Although it is widely accepted that the behavior of the defects is a key to the switching behavior and domain-wall processes, a full understanding of the degradation phenomena in ferroelectric thin films does not exist yet. The origin of the P–E loop deformations is considered to be an internal field due to an asymmetric space–charge distribution induced by the poling or natural alignment of spontaneous polarization during cooling, film processing and electrode patterning.[6,7] Kohli et al.[8] measured a strongly shifted hysteresis loop for sol–gel prepared PZT films after hot dc poling. A conspicuous voltage shift was also observed in as-grown heteroepitaxial $BaTiO_3$ and PZT thin films[3,6] and polycrystalline PZT films fabricated by a sol–gel deposition technology.[9,10] Theoretical and experimental studies[11,12] presented recently in literature show that the internal residual stresses[13] as well as external mechanical loading produce a homogenous stress field[14,15] or strain gradient[16,17] in the films that has a profound effect on their dielectric, piezoelectric and polarization switching behaviors.

Our previous research[18,19] on PZT thin films have demonstrated that both the dielectric and electromechanical properties are dependent on stress state in the film, which can be affected during nanoindentation. In this study, the effect of spherical nanoindentation on the local switching behavior and piezoelectric response of PZT films is reported.

2. Experimental procedure

The samples used for this study were 700-nm-thick lead zirconate (PZT) films, with a Zr/Ti molar ratio of 30/70, deposited

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* Corresponding author. Fax: +421 55 7922 408.
E-mail address: vkoval@imr.saske.sk (V. Koval).

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by spin-coating on Pt/TiO_2/SiO_2/Si substrates. The ferroelectric/metal/substrate heterostructures were prepared by Cranfield University, UK. More details about the film processing are given in Ref. [20]. The (1 1 1)-oriented films without a top electrode were corona-poled by the manufacturer. The effect of external mechanical loading on the local piezoelectric response and hysteresis loop was studied using a UMIS-2000 Nanoindenter (CSIRO, Australia). This was modified to allow a conductive WC-Co indenter tip of 500 μm radius to be used as a top electrode for the electrical measurements. An electrometer (Keithley, model 6517A) and a purpose-built ferroelectric test system were used for the piezoelectric and hysteresis measurements, respectively. For the electromechanical experiments, the load was increased step-by-step up to peak load of 500 mN in 30 steps (dwell time = 0.1 s) at a loading rate of 10 mN/s. The unloading was symmetric to the loading. The electrometer was used to measure the quasi-static current generated through the piezoelectric effect across the film. The integration of current transients was carried out with respect to time to obtain the corresponding charge versus force response. An effective piezoelectric coefficient, d_{eff}, was then determined from the values of the derivative of the released charge. For the acquisition of the ferroelectric loops, sine waves of 10, 50 and 100 Hz were formed by a function generator (Agilent, model 33120A), which were then amplified by a high-voltage amplifier (TREK, model 603) up to 50 V. The amplified waveform was sent to the film and then the current passing through the indented sample was measured and converted to a voltage (Stanford Research Systems, model SR570 current amplifier). The captured input and output waveforms were sent to the computer for subsequent ferroelectric analysis. Every single loop was traced at peak load levels of 100, 200, 300, 400 and 500 mN and captured after several switching cycles (2–3 cycles). Charge–voltage (Q–V) loops were software corrected for the linear capacitance (C) and linear resistance (R) of the films. Ferroelectric parameters, negative coercive voltage $V_c(-)$ and positive coercive voltage $V_c(+)$ and remanent switching charge, $Q_r(-)$ and $Q_r(+)$ were estimated from the amplitudes of the current peaks, $i_{\max}(-)$ and $i_{\max}(+)$ and from the intersections of the saturated hysteresis loops with the charge axis, respectively. $V(+)$ corresponds to the top electrode having a positive potential.

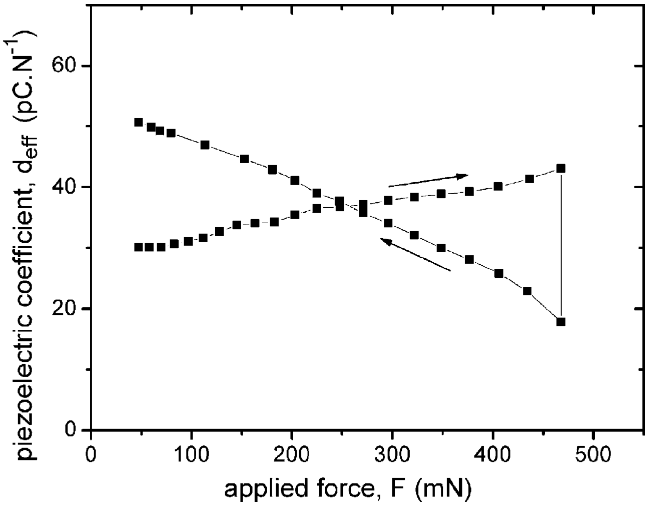

Fig. 1. The dependence of the effective piezoelectric coefficient, d_{eff}, on the indentation force in loading/unloading cycle for 700 nm thick PZT film.

3. Results and discussions

Fig. 1 shows the dependence of the effective piezoelectric coefficient, d_{eff}, on the indentation force during a loading/unloading cycle for a 700 nm thick PZT film. The electromechanical measurements in the low signals region (<100 mN) reveals that the values of the effective piezoelectric coefficient ($d_{\mathrm{eff}} \sim 30$–50 pC/N) are in rough agreement with those reported in literature for compositionally similar sol–gel PZT films measured using various techniques, including optical dual-beam laser interferometry[21] and normal load method.[22] Upon loading, the effective piezoelectric coefficient continuously increases with the applied force up to 500 mN. At a force of 500 mN, d_{eff} is about 35% higher than that of the initial value. Experimental results indicate that at subcoercive stress fields the translational displacements of the ferroelastic domain walls, generated by indentation stress during loading, considerably contribute to the increasing of the effective piezoelectric coefficient in thin PZT ferroelectric films. Upon unloading, another important observation is found in the piezoelectric response (see Fig. 1); as the indentation force is decreased to its initial value, the effective piezoelectric coefficient increases after an instantaneous drop following a different trace to that during loading. The d_{eff} coefficient after a complete cycle is even higher than its initial value, prior to the nanoindentation.

The ferroelectric hysteresis loops of PZT film mechanically loaded at 100 mN steps up to a maximum indentation force of 500 mN are shown in Fig. 2. A conspicuous shift of the Q–V loop towards positive voltages can be seen with increasing indentation force. This effect only translated the whole loop further to the positive side, since the resulting loop width, also known as the total coercive voltage, $V_c(+) + V_c(-)$, did not show any significant change within the force range used in the indentation experiments. The effect of spherical nanoindentation on the

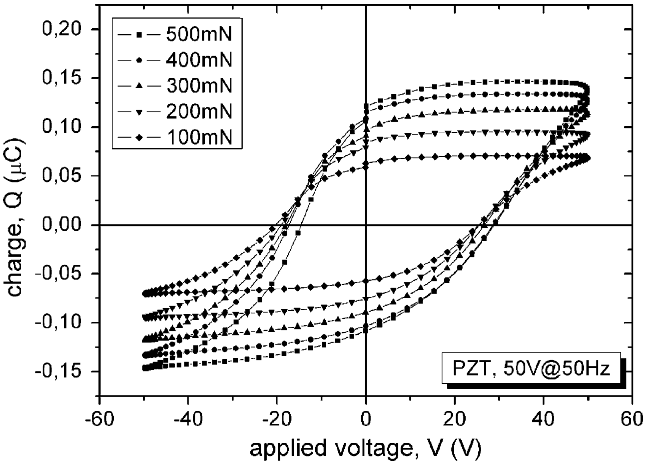

Fig. 2. Q–V hysteresis loops of PZT film mechanically loaded at 100 mN indentation steps up to 500 mN.

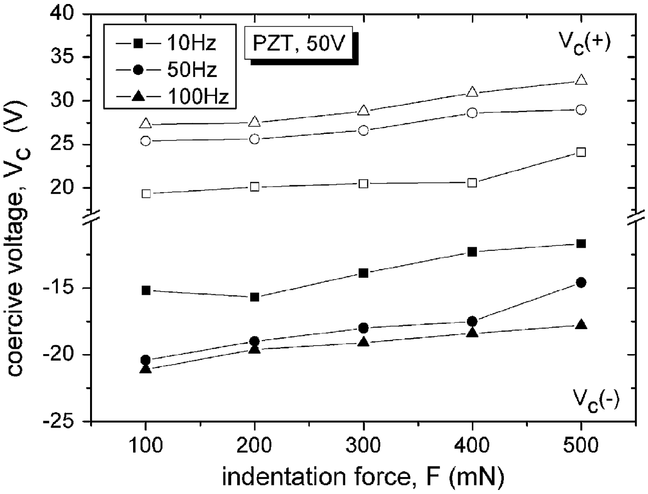

Fig. 3. Indentation force dependency of the negative and positive coercive voltages of PZT film at 10, 50 and 100 Hz with a 50 V drive voltage.

asymmetric switching behavior in the films is, however, clearly observable in Fig. 3, which compares the force dependence of the negative and positive coercive voltage at different measurement frequencies. For a representative measurement at 50 V and 50 Hz, $V_c(+)$ increased from 25 to 29 V as the imposed force increased from 100 to 500 mN. In comparison, $V_c(-)$ gradually decreased from −20.5 to −14.5 V. The higher positive coercive field implies that nanoindentation makes it more difficult to switch the negative polarization state to the positive one. To quantify the asymmetric hysteresis behavior in the films and measure the asymmetry of the ferroelectric hysteresis loops, we define a parameter δ as follows:

$$\delta = \frac{|V_c(+)| - |V_c(-)|}{|V_c(+)| + |V_c(-)|} \qquad (1)$$

Fig. 4 displays the dependence of the asymmetry parameter δ as a function of the indentation force for the PZT thin film at different measuring frequencies. Upon increasing the indentation force to 500 mN, the δ-parameter at 50 V/50 Hz increased almost linearly by an increment of about 5×10^{-4} /100 mN.

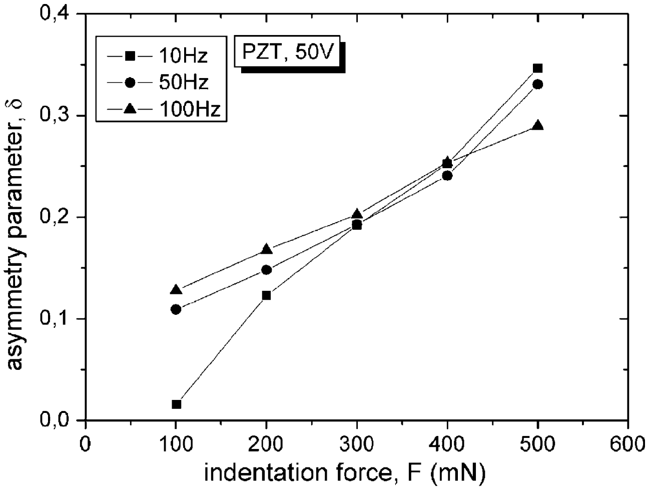

Fig. 4. The dependence of the loop asymmetry parameter δ, on indentation force for PZT film traced at 10, 50 and 100 Hz with a 50 V drive voltage.

The results indicate a considerable effect of spherical indentation on the local domain structure and switching behavior of PZT-based ferroelectric films at a micrometer scale. Upon application of combined electrical voltage and indentation load, at least two mechanisms may act in parallel on domain-wall movement and contribute to the voltage shift phenomena: (i) defect-dipole realignment and concurrent space–charge rearrangement, both driven by oxygen vacancy diffusion in the oxygen octahedron[2,4] and (ii) variation of the internal stress and reduction of the clamping effect on domains followed by irreversible translational movement of ferroelastic active DWs.[16,17] The later mechanism is consistent with the results reported by Gruverman et al.[23] on the stress-induced poling and imprint behavior of (1 1 1)-oriented PZT-based capacitors upon bending the Si substrate.

4. Conclusions

Mechanical stress effects on the local switching behavior and piezoelectric response of 700 nm thick sol–gel prepared $Pb(Zr,Ti)O_3$ ferroelectric thin films with a Ti/Zr = 70/30 were investigated using spherical nanoindentation. A non-linear and hysteric behavior was found in the electromechanical response of the loaded film within the subcoercive stress range and was attributed to ferroelastic domain-wall movement. Indentation-liberated displacements of the 90° domain walls upon loading and switching back of the ferroelectric/ferroelastic domains during unloading resulted in a new domain configuration, which was characterized by a higher polarization state than that prior to the indentation. An enhanced polarization state in the loaded film was evidenced by an increase of the effective piezoelectric coefficient of about 35% of its initial value for the thin films at maximum force of 500 mN.

Hysteresis loop measurements showed that the instrumented indentation has pronounced effect on the switching behavior of ferroelectric thin films. It is suggested that a variation of the residual stress state as well as the defect dipole realignment and consequent space–charge rearrangement during the simultaneous application of a driving voltage and an indentation load are the most probable mechanisms for affecting the built-in potential in loaded films. The built-in potential screens the applied electric field, thereby influences its effect in the ferroelectric layer and causes the polarization reversal to be asymmetrical.

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