Stress-induced depolarization of (Pb,La)TiO$_3$ ferroelectric thin films by nanoindentation

M. Algueró, A. J. Bushby, and M. J. Reece

Department of Materials, Queen Mary University of London, Mile End Road, London E1 4NS, United Kingdom

R. Poyato, J. Ricote, M. L. Calzada, and L. Pardo

Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco 28049, Madrid, Spain

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Electrical depolarization has been observed in lanthanum-modified lead titanate ferroelectric thin films stressed by nanoindentation. A spherical metallic indenter was used as a top electrode to locally pole the films and then to measure the depolarization current intensity. The current intensity had distinctive maxima at given indentation forces. These are related to the stress thresholds for the depolarization mechanism, which is probably 90° domain wall movements. Knowledge of the depolarization stresses is necessary for the design of microelectromechanical systems that include a ferroelectric layer. © 2001 American Institute of Physics. [DOI: 10.1063/1.1418258]

Microelectromechanical systems (MEMS) sensors and actuators can use a range of mechanical to electrical, and vice versa, transduction mechanisms, among which the piezoelectric effect is especially suitable at high frequencies. Examples of MEMS that use piezoelectric active layers are the force sensor for atomic force microscopy and the ultrasonic micromotor. Ferroelectric oxides with the perovskite structure, such as lead zirconate titanate or lanthanum-modified lead titanate (PTL), are the preferred materials when high piezoelectric coefficients are required. Films of these compositions often need to be poled to obtain a significant and reproducible electrical polarization and then useful piezoelectric coefficients. The stability of this electrical polarization during the device operation is a key factor in determining the reliability of the microdevice.

Stresses induce depolarization by ferroelastic, non-180°, domain wall movements in ceramics, but this phenomenon has not been studied for films. The stability of the polarization of a film under stress depends on whether there are ferroelastic domains in the film, and if so on the mobility of their domain walls. It has been shown that ferroelastic domains exist in ferroelectric thin films. The mobility of the walls during polarization switching at electric fields above the coercive field has been questioned. The walls are maintained throughout the contact. The poling field was a subsequent indentation test at the same location.

The results are presented for two single phase PTL films of Pb$_{0.88}$La$_{0.08}$TiO$_3$ composition, as monitored by Rutherford backscattering spectrometry and 250 and 700 nm thickness. They were prepared by a diol-based sol-gel process with a rapid thermal annealing on Pt/TiO$_2$/Si substrates. The tetragonal perovskite structure was tailored to show a strong mixed (001), (100) preferred orientation, which fixed the orientation of the 90° domain walls relative to the indentation axis to ~45°. Quantitative texture analysis of x-ray pole figures was used to characterize this orientation. A texture index of 7.9 and 9.6 m.r.d. (multiple of a random distribution) was obtained for the films of 250 and 700 nm thickness, respectively. The relative contribution to the global texture of the (100) and (001) components was similar, ~50%, for both films.

The films were tested without being poled, and small depolarization current intensity transients were recorded (2–4 pC). Therefore, a spontaneous electrical polarization existed in the films. This is in agreement with the spontaneous piezo- and pyroelectric activity found in the films. The sign of the current intensity indicated that the polarization vector pointed to the surface.

Films were poled by using the spherical indenter as a top electrode. The poling was accomplished during an indentation contact with a 10 mN s$^{-1}$ force rate, 500 mN maximum load, and 60 s dwell at maximum load before unloading. The electric field was switched on before mechanical contact, and maintained throughout the contact. The poling field was a train of square pulses with a nominal height of 150 kV cm$^{-1}$ and a frequency of 200 Hz. This field was sufficient to saturate the induced polarization for the 700 nm film ($E_c$ = 50 kV cm$^{-1}$, $P_r$ = 16.6 µC cm$^{-2}$), but was not sufficient to do the same for the 250 nm film ($E_c$ = 136 kV cm$^{-1}$, $P_r$ = 16.6 µC cm$^{-2}$). The effects of positive, parallel to the initial polarization, and negative, antiparallel, electric fields were investigated.

The depolarization current intensity was measured dur-
ing a subsequent indentation test with a different force profile. The force was increased in 30 steps to 500 mN, and then decreased to zero also in 30 steps. The force was held constant at each step for 0.1 s. This enabled the penetration and electrical current intensity to be determined as a function of force. Examples of the current intensity during the indentation test are shown in Fig. 1 for the two films. The current intensity for negative poling increased with the indentation force during loading, and then reversed sign during unloading. This sign reversal on unloading indicated the presence of a significant piezoelectric contribution to the current transient. The absolute values of the intensity were higher during loading than during unloading. This indicated that depolarization had occurred during loading. The current intensity was still increasing at 500 mN, and therefore the depolarization was not saturated at that indentation force. The current intensity showed a very different behavior for positive poling. It did not increase continuously during loading, but produced distinctive maxima at given forces. The current intensity produced two maxima at indentation forces of 68 and 310 mN for the 700 nm film, and only one at 252 mN for the 250 nm film, for the examples shown. The intensity did not reverse sign during unloading but vanished slowly. Depolarization during loading was then much more severe for positive than for negative poling. The maxima in the curves correspond to forces at which the depolarization rate was a maximum. If depolarization occurs by 90° domains wall movements, these maxima must be associated with the stress thresholds for their movement. To turn these force values into compressive stresses or resolved shear stresses at the walls, the indentation stress field must be analyzed. A first approximation may be to work with the stress field for the Hertzian elastic contact of a sphere on a flat, homogenous, isotropic body. For this case, it can be shown that the uniaxial stress component along the indentation axis, \( \sigma_z \), in cylindrical coordinates, is nearly constant along \( z \) in the first micron under the contact area, which is the volume contributing to the electrical signal, but not along the radial direc-

tion. The problem is more complicated when anisotropy and piezoelectricity, and the effect of the substrate, are considered. This analysis is out of the scope of this letter. The presence of two maxima in the depolarization data for the thinner film suggests the presence of two sets of domain walls with different threshold stresses for their movement. The planar stresses exerted by the substrate can partially clamp the 90° domain walls. The effect is stronger in the grains next to the substrate than for those near the surface of the film for fine grained PTI films, similar to those studied here.

The integration of the current intensity provides the electrical charge-indentation force relations as shown in Fig. 2. The depolarization charge was 8.2 and 17 pC for the 250 and 700 nm films, respectively, for negative poling, and -15.6 and -27.3 pC for the same films and positive poling. These values can be turned into actual depolarization (surface charge density) if the contact area at maximum force is evaluated. This was achieved by assuming an elastic contact. This was a sensible approximation as can be seen in Fig. 3, where the loading-unloading penetration is shown. Hardly any hysteresis was observed. Absolute depolarization values of 3.8 and 7.2 \( \mu C/cm^2 \) for the 250 and 700 nm films, respectively, for negative poling, and 7.2 and 11.5 \( \mu C/cm^2 \) for the same films and positive poling, were obtained. Therefore, more depolarization occurred for the thicker film and for positive poling, which is likely a consequence of an initially higher electrical polarization. The depolarization charge increased for the thinner film when the poling field was increased to 200 and 250 kV cm\(^{-1}\), which supported the former explanation. Electrical breakdown occurred at 300 kV cm\(^{-1}\), and so saturation of the induced polarization, which is said to occur at 3\( E_c \), was not achieved.

The dispersion in the depolarization at 500 mN for different areas of the films was around 20%. Current intensity maxima as a function of force were observed all across the films, though the corresponding forces and magnitude of the maxima varied. This variation was a consequence of the high spatial resolution of the technique (the radius of contact at

![FIG. 1. Electrical current intensity as a function of the indentation force for the PTL film of 250 nm thickness poled at (△) 150 kV cm\(^{-1}\) and (△) \(-150 kV cm\(^{-1}\), and for the film of 700 nm thickness poled at (●) 150 kV cm\(^{-1}\) and (○) \(-150 kV cm\(^{-1}\).](image1)

![FIG. 2. Force-electrical charge relation during an indentation test for the PTL film of 250 nm thickness poled at (△) 150 kV cm\(^{-1}\) and (△) \(-150 kV cm\(^{-1}\), and for the film of 700 nm thickness poled at (●) 150 kV cm\(^{-1}\) and (○) \(-150 kV cm\(^{-1}\).](image2)
500 mN was about 9 μm and possible local fluctuations in the perovskite structure orientation or in the stress at the film-substrate interface.

We have shown that PTL fine grained films showed stress-induced depolarization during nanoindentation. The depolarization current intensity had distinctive maxima with the indentation force. These are related to the stress thresholds for the depolarization mechanism, which is probably 90° domain wall movements. The nanoindentation technique opens then the possibility of studying non-180° domain wall dynamics of films, and defining depolarization thresholds for MEMS design.

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