Nanoscale investigation of the ferroelectric properties of sol-gel (PbZrxTi1-x)O-3 films

B. Gautier, C. Thiebaud, D. Charraut, Jc Labrune

► To cite this version:

B. Gautier, C. Thiebaud, D. Charraut, Jc Labrune. Nanoscale investigation of the ferroelectric properties of sol-gel (PbZrxTi1-x)O-3 films. *Ferroelectrics*, 2002, 269 (1), pp.219-224. 10.1080/00150190211152 . hal-00093526

HAL Id: hal-00093526

<https://hal.science/hal-00093526>

Submitted on 15 Apr 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Distributed under a Creative Commons Attribution| 4.0 International License

NANOSCALE INVESTIGATION OF THE FERROELECTRIC PROPERTIES OF SOL-GEL ($PbZr_xTi_{1-x}$) O_3 FILMS

B. GAUTIER⁽¹⁾, C. THIEBAUD⁽²⁾, D. CHARRAUT⁽²⁾ AND J-C. LABRUNE⁽¹⁾

(1) Centre de Recherche sur les Ecoulements, les Surfaces et les Transferts (UMR-CNRS 6000), 4 place Tharradin B.P. 71427, 25211 Montbéliard Cédex.
(2) Laboratoire d'Optique Pierre-Marie Duffieux (UMR-CNRS 6603), route de Gray, 25030, Besançon cédex, France.
Institut des Microtechniques de Franche-Comté (IMFC - FRE0067 CNRS)

In this paper, nanoscale ferroelectric and piezoelectric properties (e.g. cartography of the piezoelectric coefficient after poling and polarisation direction) of sol-gel PZT thin films are studied using a modified Atomic Force Microscope (AFM). Polarisation patterns are created, and then imaged after more than one year. Hysteresis loops are recorded and it is shown that their shape and related parameters (remanent polarisation and coercitive field) are strongly dependant on the experimental conditions.

Keywords : AFM, piezoresponse, PZT, Sol-Gel, Hysteresis, Polarisation

1 INTRODUCTION

The need for the reduction of the size of ferroelectric devices such as Ferroelectric Random Access Memories (FeRAM) or Surface Acoustic Wave (SAW) devices has made mandatory the development of characterisation techniques capable of providing a nanometric resolution for the spatial repartition of ferroelectric domains and of giving local information about the ferroelectric parameters of the films (coercitive fields, remanent polarisation...). The piezoresponse mode of the Atomic Force Microscope (AFM) has already shown its capabilities in supplying reliable information with a sub-micrometric lateral resolution [1] [2] [3]. In this paper, we illustrate the piezoresponse mode's contribution in the study of the ferroelectric properties of sol-gel PZT thin films (polarisation direction, coercitive fields and remanent polarisation).

2 EXPERIMENTAL

2.1 The AFM piezoresponse mode

The piezoresponse mode of the AFM is implemented using a modified commercial AFM apparatus (Digital Instrument Nanoscope IIIA) and NT-MDT cobalt coated tips or Nanoprobe PtIr5 coated tips (force constant $\simeq 1 - 10 \text{ N.m}^{-1}$). The physical basis of the piezoresponse mode can be found elsewhere [2] [4]. Briefly, the piezoelectric information is obtained through an AC voltage V_{ac} applied between the tip and the sample while the AFM apparatus is implemented in the contact mode. The amplitude of the resulting (very weak) piezoelectric vibration, which frequency is the same as V_{ac} , is thought to be proportional to the piezoelectric coefficient d_{33} . It is extracted from the topographic signal using a lock-in amplifier and does not interfere with it, allowing the simultaneous recording of the topographic and piezoelectric image [2]. AFM piezoresponse mode allows to record a cartography of the piezoelectric coefficient d_{33} of the surface, and to modify the polarisation state of the piece of material located under the tip by applying between the tip and the sample a voltage corresponding to an electric field higher than the local coercitive field of the film. Domains with an uniform polarisation and an adjustable shape and size can be created this way. Also, local hysteresis cycles can be recorded by stopping the tip over a given point of the surface and recording the piezoelectric response with respect to a varying electric field.

2.2 Preparation of the samples

The sol-gel PZT samples were elaborated by dip-coating on Ti/Pt electrodes and Si substrate. From this elaboration technique, we expect piezoelectric thin films with a good purity, low roughness and interesting piezoelectric and ferroelectric properties [5]. The cristalline structure of the film has not been determined by X-ray diffraction due to the small size ($\simeq 5\text{mm} \times 5\text{mm}$) and thickness ($\simeq 100\text{nm}$) of the sample. However we expect a film orientation along the (001) axis, leading to a polarisation vector perpendicular to the surface of the film [6] [7]. The topographic AFM observations (not shown) show a granular morphology, with grains of diameter $\simeq 300 \text{ nm}$. Macroscopic hysteresis loops obtained on the samples (using a simple electric Sawyer-Tower setup used at 50 Hz), show a remanent polar-

FIGURE 1 : Left : Amplitude piezoresponse image after a $3\mu \times 3\mu$ square polarisation pattern has been created on the surface. Middle : phase image showing effective polarisation reversal. Right : lateral piezoresponse image.

isation $P_r \simeq 15\mu C/cm^2$ and a coercitive voltage $E_c = 150kV/cm$. The film has been uniformly poled by scanning a $5\mu \times 5\mu$ area with a constant DC voltage of +10V between the tip and the bottom electrode, then by scanning a $3\mu \times 3\mu$ area with a constant DC voltage of -10V. Finally, the amplitude, phase and lateral piezoresponse image have been recorded. The latter is obtained by recording the lateral vibration amplitude detected in the photodiode signal by the lock-in amplifier, instead of the normal vibration amplitude, and is thought to be related to the vibration of the film in the plane of the surface. The result of these images can be found in Figure 1. From these images, we can draw the following *qualitative* conclusions :

- The uniformity of the amplitude and phase images in the poled regions suggests an uniform distribution of the piezoelectric coefficient d_{33} . The opposite phase between the area poled with -10V and +10V indicates that the polarisation has been effectively switched by the applied electric field. Note that with our experimental setup, the phase information is included in the amplitude image, so that the domains which polarisation is toward the bulk (bright areas, in phase with the reference voltage) appear with a positive amplitude, and the domains which polarisation is toward the surface (dark domains, opposite phase) with a negative amplitude, although the absolute value of the amplitude is comparable for both domains.

- The absence of contrast in the lateral image suggests that the direction of the polarisation is indeed normal to the plane of the surface, with no or little component in the plane of the surface.

3 RESULTS AND DISCUSSION

3.1 Remanent polarisation

In order to position the tip over the same area of the sample at different moments, we have engraved 9 "L"-shaped patterns using a Focused Ion Beam (FIB - Gallium source, impact energy : 30 keV). The size of each patterns was about $20\mu \times 3\mu$ and the depth of each pattern, as measured by AFM $\simeq 25\text{nm}$. Left part of Figure 2 shows optical images of the resulting patterns. These patterns, easily visible, are used as a guide to position the tip and to create different polarisation patterns using the tip. The precision of the AFM positioning allows to create any polarisation patterns with a high possible lateral resolution. Moreover, a long time after the creation of the polarisation patterns, it has been possible to position the tip exactly at the same place to check whether it had remained at the surface of the film.

FIGURE 2 : From left to right : L-shaped pattern created by FIB - Closer view of a single pattern - Polarisation patterns realized using the AFM tip.

The left part of figure 3 shows exactly the same area as the right part of Figure 2 imaged 80 days after its first polarisation. The patterns are still easily detectable with a comparable signal to noise ratio. Figure 3 (middle and right) shows the same polarisation pattern at two different moments separated by 373 days, showing that it has remained identical. However, the signal to noise ratio is lower and some domains have flipped back. This results illustrate the piezore-sponse mode's ability to image the antiparallel ferroelectric domains and study their remanent polarisation in terms of spatial repartition after a certain amount of time. Quantitative comparisons are now needed to evaluate the devices' ability to retain information.

FIGURE 3 : Left : the polarisation patterns of Figure 2 are still detectable after 80 days. Size of the image : $40\mu \times 40\mu$. Center and right : polarisation pattern imaged at two different moments separated by **more than one year** (373 days). The bigger white square's size is $10\mu \times 10\mu$.

3.2 Hysteresis cycles

Information about the very local coercitive fields and remanent polarisations may be needed to understand the fatigue and imprint phenomena in very thin films. Different authors have recorded hysteresis loops using different experimental protocols. Harnagea et al. [3] suggest to wait a least 2 seconds after the application of a voltage pulse in order to avoid any electrostatic interaction between the tip and the bottom electrode. However, using this method, only the *remanent* piezoelectric coefficients d_{33} are accessible. Eng [1] applies a voltage ramp and the resulting loops exhibit very different shapes than those from [3]. We have tried both methods. In all cases, a AC voltage (1V, 15.8kHz) was used for piezoelectric measurements. In the first case, a voltage ramp (5mHz) was applied while measuring the piezoresponse. In the second case, a voltage pulse was applied and the piezoresponse was measured immediatly after the end of the pulse. In the last case, the response was measured 3 seconds after the application of the pulse. Results can be seen in Figure 4.

Depending on the experimental conditions, the shape of the loops and the parameters measured from these loops are very different. The positive and negative remanent d_{33} and coercitive fields show a variation of more than 100% from one loop to another. However, the loops recorded without the presence of the DC voltage exhibit the same E_c whereas the remanent d_{33} remain different. This suggests the presence of surface charges when the DC voltage is not switched off before measuring the piezoelectric response as suggested before [3]. A more complete study of the dynamic electrostatic interactions between the tip, the surface and the bottom electrode is needed to achieve a complete understanding and quantification of the loops

FIGURE 4 : Local hysteresis loops obtained on PZT films. Dotted line : voltage ramp. Dashed line: Measurement just after the application of a DC voltage. Plain line : measurement 3 seconds after the application of the DC voltage.

provided by the piezoresponse mode.

4 CONCLUSION

The piezoresponse mode of the AFM is becoming an important tool for the nanoscale characterisation of ferroelectric thin films because it is able to provide local information about the direction of polarisation, the local piezoelectric coefficient d_{33} and the remnance of thin films. It is possible to record hysteresis cycles but the exact experimental conditions are still to be discussed and the involved phenomena understood for a really quantitative information to be accessible through this method.

The authors would like to thank M. Spajer for the FIB patterning of the samples.

REFERENCES

- [1] L. Eng. *Nanotechnology*, (10):405–411, 1999.
- [2] A. Gruverman *et al.* *Integrated Ferroelectrics*, 19:49–83, 1998.
- [3] C. Harnagea *et al.* In *NATO Advanced Research Workshop*, Predeal - Romania, May 24-27 1999.
- [4] G. Zavala *et al.* *Journal of Applied Physics*, 81(11):7480–7491, 1997.
- [5] R. Schwartz *et al.* *Integrated Ferroelectrics*, 7:259–277, 1995.
- [6] E. Defay *et al.* *Materials Science and Engineering*, B55:123–129, 1998.
- [7] A. Gruverman *et al.* *Applied Physics Letters*, 69(21):3191–3193, 1996.