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INFLUENCE OF THE MICROSTRUCTURE AND OF AN ION BEAM ETCHING ON THE DOMAIN PROPAGATION IN PZT THIN FILMS

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Abstract : $PbZrTiO_3$ (PZT) thin films have been grown by RF-magnetron sputtering and sputter etched by Argon ion beam. The topography of the bombarded material is studied by Atomic Force Microscope (AFM), several ferroelectric domains are created by applying a sufficiently high voltage between the tip of the AFM and the Ti/Pt back electrode of the PZT sample, and subsequently imaged using the AFM piezoresponse mode. The influence of the microstructure and of the ionic bombardment on the domain propagation is studied with a nanoscale resolution. It is found that the difference of cristallographic orientation between the samples has little influence on the domain propagation, except at large pulse durations. After etching, it is found that it is still possible to create and image stable domains, with no major influence of the bombardment on the propagation of the ferroelectric domains on comparable samples.

Keywords : Atomic Force Microscope, piezoresponse, PZT, ionic bombardment, domain propagation

1 INTRODUCTION

$PbZrTiO_3$ (PZT) is now used in numerous applications taking advantages of its piezoelectric and ferroelectric properties, and is likely to be found in more and more complex integrated devices. To do so, it can be necessary to use ion milling for PZT patterning. However, very few is known about the influence of the etching on the piezoelectric and ferroelectric properties of the material, and in particular on the influence of the Argon bombardment on the propagation of the ferroelectric domains. Atomic Force Microscope (AFM) piezoresponse mode has proven to be the appropriate tool to create and visualize ferroelectric domains on thin films [1] [2] [3]. To the authors'

knowledge, this technique has never been used to image ferroelectric domains on sputter-etched ferroelectric samples. In this paper, AFM piezoresponse mode is used to create nanoscale ferroelectric domains on non-bombarded and bombarded PZT thin films surface, and to subsequently measure the size of these domains as a function of the duration of the voltage pulse which has created the domain. The influence of the morphology and of the sputter-etching is investigated.

2 PREPARATION OF THE SAMPLES

Pt and Ti layers (thickness 500nm) were deposited on SiO_2/Si substrates by DC sputtering. $PbZr_{0.54}Ti_{0.46}O_3$ thin films were subsequently deposited by rf-magnetron sputtering with a thickness in the range $0.9\mu m$ to $1.2\mu m$ in the case of etched samples, $\simeq 280 - 320nm$ in the case of non-etched sample. After etching, the thickness of the etched and non-etched films is approximately the same. The sputtering conditions are given elsewhere [4]. The PZT films were annealed at $625^\circ C$ for 30 minutes to obtain the PZT perovskite phase. The samples are preferentially (110) and (111) oriented, depending on the samples, with no pyrochlore phase. Ion Beam Etching (IBE) of PZT was performed by a Veeco Microetch 3" instrument, equipped with a Kaufman type source. Argon ions are extracted by an acceleration potential (between 0.6 and 1kV), with adjustable ion intensity. A filament allows neutralising the positive charges, so that in principle only neutral elements hit the surface. More details about the experimental setup are described elsewhere [5]. The topography images shown in this paper were realised with an Atomic Force Microscope (AFM - Digital Instruments Nanoscope IIIA Multimode) in contact mode, along with the piezoresponse measurements.

3 AFM PIEZORESPONSE MEASUREMENTS

The physical basis of the AFM piezoresponse mode [6], [7], [8] and the experimental setup for the following AFM piezoresponse results can be found elsewhere [9]. Briefly, the piezoelectric information is obtained through an alternative voltage V_{ac} applied between the tip and the sample while the AFM apparatus is implemented in the normal contact mode. The amplitude of the resulting piezoelectric vibration is related to the piezoelectric coefficient d_{zz} , where z is the direction perpendicular to the sample surface. It is extracted from the topographic signal using a lock-in amplifier (Perkin-Elmer 7280). AFM piezoresponse mode allows 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 uniform polarisation and adjustable shape and size can be created this way.

Piezoresponse images have been realized using W_2C coated tips (from *$\mu Mash$* company) with a $\simeq 105\text{kHz}$ resonance frequency and $\simeq 2\text{N.m}^{-1}$ stiffness. Whenever it was possible, the same tip has been kept in order to compare measurements. The phase output of the lock-in amplifier is shown in the images rather than the amplitude output. Because of the sometimes complex microstructure of the sample, the domains created in the films are not always round shaped, so that it is difficult to measure a diameter of the domains efficiently. Thus, we have estimated an equivalent diameter using the following procedure : the maximum (in the case of bright domains) or the minimum (in the case of dark domains) of the signal has been measured, allowing to define a reference level corresponding to a level at half maximum (half of the difference between the maximum and the background surrounding the domain). Then, the histogram of all the levels of the pixels of the image has been realised using a commercial software ¹ and the percentage p of pixels which level is situated over (bright domains) or below (dark domains) the reference level has been calculated. The surface of the domain can be extracted from the total surface of the image multiplied by p . Eventually, an equivalent diameter of the domain has been calculated from the surface of the domain (considering the diameter of a circle which area is the same as the domain).

4 RESULTS AND DISCUSSION

4.1 Influence of the microstructure and cristallographic orientation on the domain propagation

Sputtered PZT thin films can exhibit two different microstructures afore mentionned "big grains" and "small grains", which cristallographic orientation is a little different. Left part of Figure 1 shows the morphology of the "large" grains sample and the right part of Figure 1 shows that of the "small" grains samples, as measured by AFM. The RMS roughness (measured within a $15\mu\text{m} \times 15\mu\text{m}$ square) measured on the "large grains" samples is found to be 4.1 nm RMS (in accordance with the AFM results found in ref. [5]), and 2.7 nm on the "small grains" samples. When measuring the roughness within a $800\text{nm} \times 800\text{nm}$ square, where no grains boundary is encountered for both samples, the RMS roughness becomes 1.6nm (large grains) and 1.3nm (small grains).

X-ray diffraction (RX) spectra show that the proportion of the

¹OMICRON, SCALA image processing software

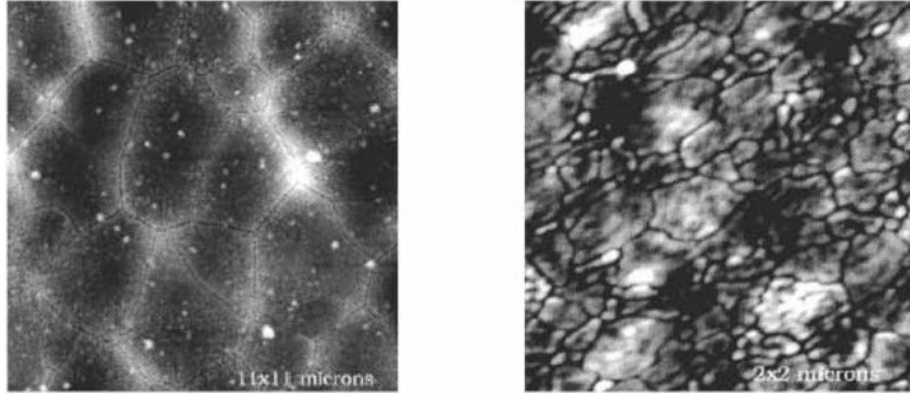


FIGURE 1 : Topography of the "big grains" PZT thin film (left - $11\mu\text{m} \times 11\mu\text{m}$) and the "small grains" PZT thin film (right - $2\mu\text{m} \times 2\mu\text{m}$).

(110) phase in the "large" grains samples is predominant, compared to the (111) phase, whereas the situation is inverted for the "small" grains samples, which are strongly (111) oriented, with still the presence of a detectable (110) phase. The samples are polycrystalline, so that we can expect a detectable piezoelectric contrast between antiparallel domains even in the case where the polarisation lies in the plane of the surface, as it may happen for the (110) regions (in this article, we record the piezoelectric vibration in a direction perpendicular to the surface, so that in the case where there is no component of the polarisation in this direction, no discrimination between antiparallel domains can be obtained).

Ferroelectric domains of various sizes have been created on each sample by application of a voltage pulse of duration in the range $10\mu\text{s} - 50\text{s}$ (amplitude 10V) using the tip of the AFM, the back electrode being grounded. Before creating these domains, an uniform area of several micrometers square has been polarised in the opposite direction. Some examples of the resulting piezoreponse images of the resulting domains are shown in Figure 2 for both samples. It must be pointed out in the case of the small grains sample that the domains have been created inside the biggest grains so that the grain boundaries do not play any role in the domain propagation (see the right image of Figure 2).

Results of the measurement of the diameter of the domains created by the voltage pulses can be found on Figure 3.

From these results, and within the measurements errors, there seems not to be a significant difference between both samples for the small durations of the voltage pulse. In particular, the smallest domain created in the "small grains" sample is $\simeq 53\text{nm}$ whereas it is $\simeq 47\text{nm}$ for the "large grains" sample. At longer application times,

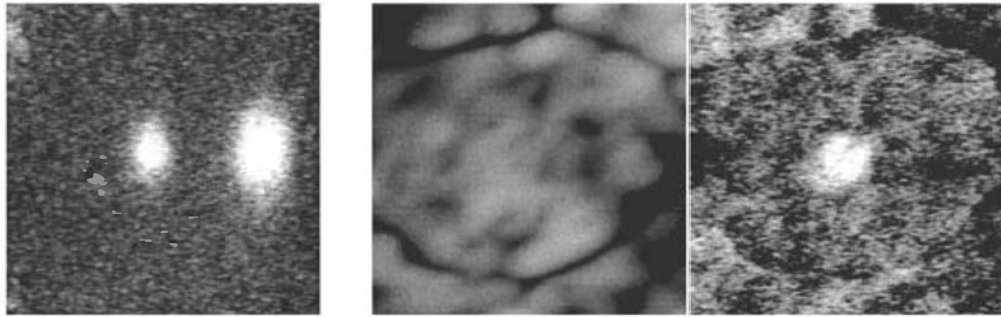


FIGURE 2 : Creation of voltage pulses on the large grains sample (left, $1\mu\text{m} \times 1\mu\text{m}$, 50s, 10V) and the small grains sample (right, $400\text{nm} \times 400\text{nm}$, 1ms, 10V. The topography is also shown).

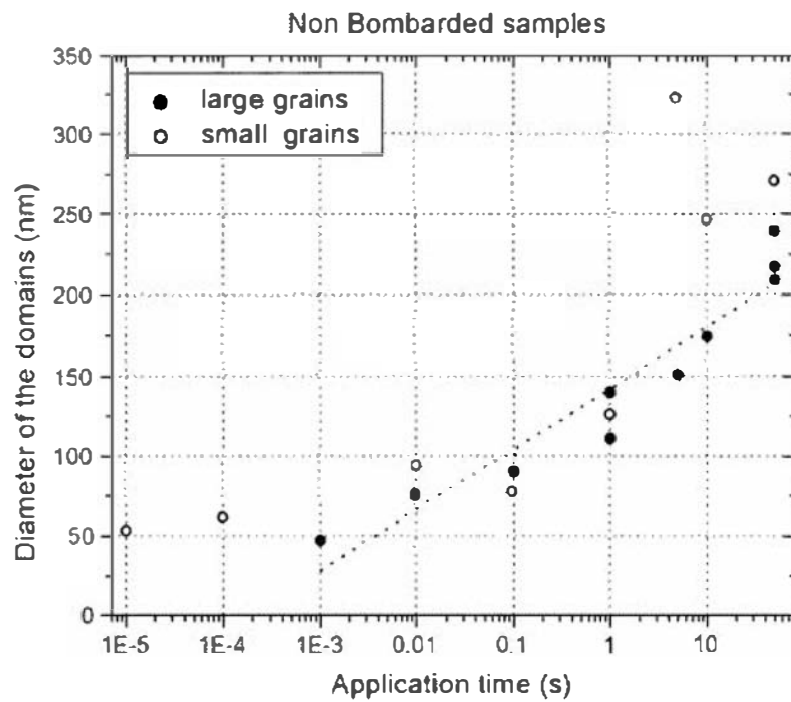


FIGURE 3 : Domain size comparisons with various pulse length : influence of the morphology. A logarithmic fit of the data from the big grains sample is given to guide the eye

the size of the domains created on the "large" grains samples tends to be smaller than in the case of the "small" grains samples.

The evolution of the size of the domains in Figure 3 depends logarithmically on the writing time, as pointed out in previously published data (see reference [1] and [10]), although the values for the diameter of the domains presented in this work are smaller than in reference [10], and larger than reference [1] (which is not surprising since the experiments in [1] are conducted on epitaxial PZT). A logarithmic fit is presented as a guide for the eye in Figure 3. Note that the size of the tip may play a non-negligible role in the smallest domains which will be created with very short pulses. Note also that it has been possible to create $\simeq 40\text{nm}$ diameter domains with 5 Volts pulses, 1s (instead of 10V, 1s).

Figure 4 shows a closer look at the "large" grains sample microstructure where an evident sub-structure can be detected thanks to the vertical sensitivity of the AFM. This "nanostructure", which covers a large percentage of the total surface beside regions with smaller roughness, stops the progression of the domains (see the right part of Figure 4) and may help to get smaller domains with equivalent pulse lengths when the size of the domains become larger.

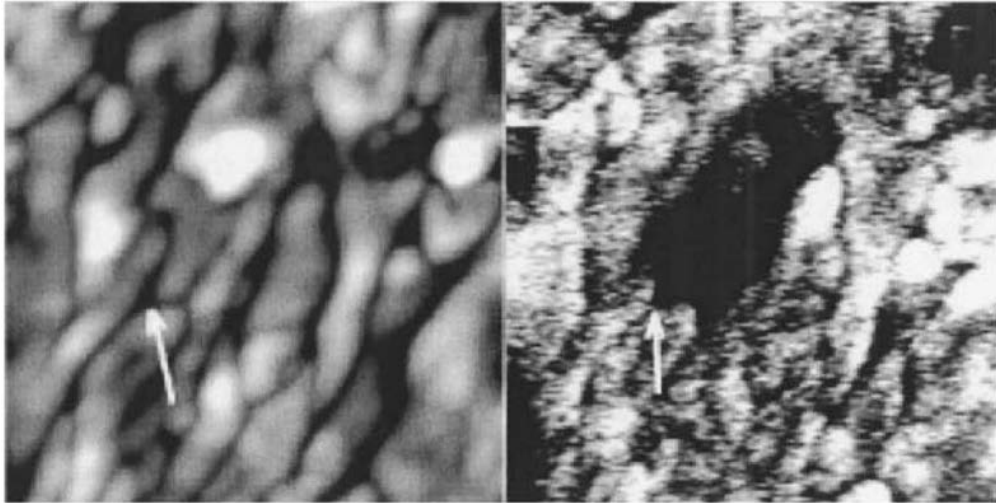


FIGURE 4 : 800nm \times 800nm piezoresponse image of a domain created by a short pulse on the "large" grains film. A closer examination of the surface of this sample shows a rather complicated microstructure. Here, the propagation of the domain has been clearly stopped by the topography of the surface (The propagation of the domain has been stopped at the place indicated by the white arrows)

From these measurements, it must also be outlined that domain creation and visualisation *is possible* for the large grains samples, in spite of the predominance of the (110) phase in RX spectrum. The

observed contrast is *not* due to the presence of surface charges created by the voltage pulse since the domains are still clearly visible one day after their creation, as the sample has been left in air for more than 12 hours. Moreover, remnant hysteresis cycles have been performed (not shown) with the AFM tip as a top electrode, and show two different stable polarisation states. The same sample has been tested macroscopically and shows hysteresis loops too. The polycrystalline state of the sample, where many regions of different cristalline orientation coexist, among which the (111) direction which exhibits a polarisation component along the z-axis, may be responsible for this behaviour.

We could expect in the case of the "large grains" sample that the size of the domains resultant from the application of the field is smaller because the propagation of the domains is stopped by the presence of a lot of (110) oriented parts of the surface. From our measurements, this seems to be true only for the largest durations of the voltage pulse.

Below 1ms, the size of the domains seems not to decrease any more in the case of the small grains sample. Note that it has not been possible to create domains on the "large grains" samples with pulse durations shorter than 1ms, which is far more than previously published data obtained on epitaxial PZT [1] or (111) MOCVD samples [10]. Maybe the presence of a large amount of (110) cristallo-graphic orientation, and the roughness of the samples (which leads to a poorer signal to noise ratio as compared with piezoresponse images performed on almost perfectly flat surfaces) is responsible for those long pulse durations needed to create stable domains on the surfaces.

4.2 Etched samples

It must be mentionned that **only the so-called "large grains" samples have been etched**. Moreover, the etched sample is not exactly the same as the non-etched sample (which would have been subsequently etched), but has been elaborated in the same conditions, and present similar RX spectra.

A macroscopic study of the influence of the etching is presented elsewhere [5]. To summarize its conclusions, it has been found that after etching, the dielectric and ferroelectric properties had changed, as well as the topography of the samples. In particular, the permittivity is reduced, the maximum polarisation decreases whereas the remnant polarisation is not strongly modified, the average coercitive field increases and eventually the internal field remains almost unchanged. To explain those phenomena, the authors suggest that the bombardment leads to the formation of a top disturbed, amor-

phous layer which may not be ferroelectric and which roughness is far more severe than before bombardment. Indeed, left part of figure 5 shows the topography of the film after etching : a severe increase of the roughness is evident (the RMS value of the roughness on a $15\mu m \times 15\mu m$ square is found to be 31.4nm - and 4.1nm before etching).

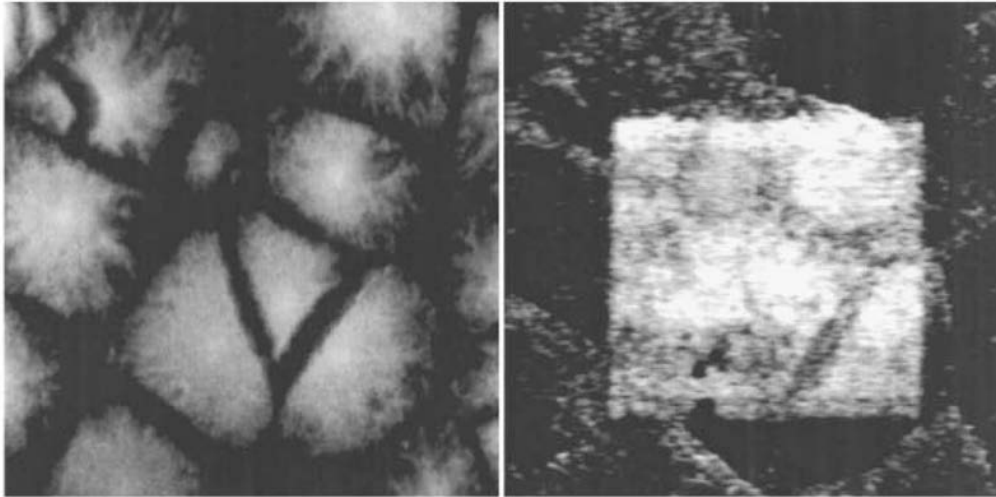


FIGURE 5 : Topography (left, $8\mu \times 8\mu$) and piezoresponse image of a sample after etching, creation of a $5\mu \times 5\mu$ square domain and creation of the domains of opposite polarisation shown in Figure 7, which are visible at the bottom of the bright square.

Moreover, it seems that the grains boundaries are more severely sputtered than the rest of the surface. This is in accordance with the observations of reference [5]. The severe roughness of the surface after etching makes the piezoresponse measurements far more difficult than in the case of non bombarded samples. However, although the influence of the topography is present in the piezoresponse image (which should not be the case in the ideal piezoresponse measurement) the creation and imaging of the domains is still possible with a lower signal to noise ratio (see for example the right part of Figure 5 where the topography and the piezoresponse image are shown, after the creation of an uniformly polarised square domain, and Figure 7 where domains are created with various pulse length). Although the top surface of the ferroelectric film may not be ferroelectric any more, it is still possible to create and inverse ferroelectric domains using the AFM tip, to image them several hours later and to perform hysteresis loops on the films.

The same experimental procedure as in the previous paragraph has been followed in order to create domains on the bombarded surface. The resulting equivalent diameters of the domains can be found

on Figure 6. It can be seen that the etching has apparently little influence on the size of the final domains. Once again, the evolution of the size of the domains is logarithmic with time, even though it is not possible to decrease the size of the domains below 1ms pulse duration (it has not been possible to create domains with pulse duration shorter than 1ms for the etched sample too).

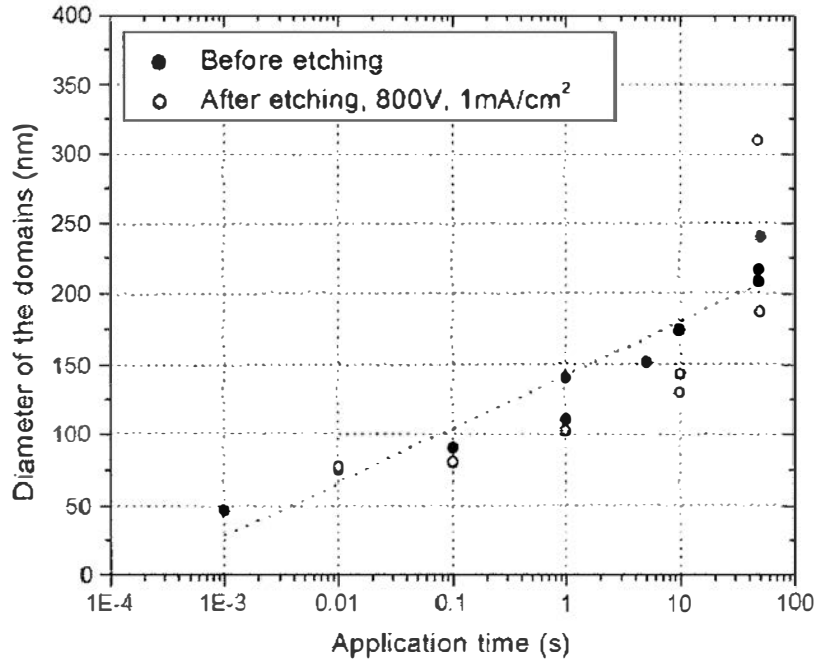


FIGURE 6 : Domain size comparisons with various pulse length : influence of the ion etching. A logarithmic fit of the data from the non-etched sample is given to guide the eye

5 CONCLUSION

In this paper the piezoresponse imaging has been used to measure the size of ferroelectric domains created by the application of a voltage pulse of various duration. The measurements indicate that there seems not to be a major difference between (110) oriented and (111) oriented samples, except at long pulse duration where the domains extension is higher for (111) samples. After etching, it is still possible to create and image ferroelectric domains although the top surface of the sample may not be ferroelectric anymore because of the ionic bombardment, and we observe the same propagation behaviour of the domains.

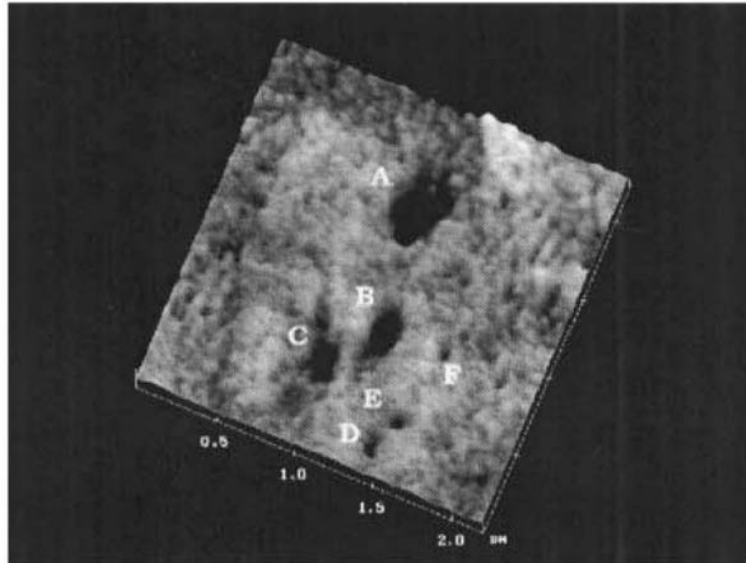


FIGURE 7 : Domain creation on the surface of a bombarded PZT thin films with various pulse length. Letters indicate the position of the domains. A : 50s, B and C :10s, D :1s,E :100ms, F :10ms

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