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Nucleation and growth domain limits in ferroelectric polycrystalline thin films

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Abstract—Nowadays, polycrystalline $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT) thin films are widely used in various applications such as piezoelectric actuators, sensors and Ferroelectric Random Access Memory. In this later case an important issue is the switching speed capability at low voltage of the ferroelectric domains as well as their size. The switching speed control of nano-sized domain is mandatory for the application of ferroelectric nanostructures in new more efficient devices. In the last years, many studies have been done on the switching dynamics of epitaxial PZT ferroelectric thin films via Piezoresponse Force Microscopy (PFM). PFM is a powerful technique to study ferroelectric materials at the nanoscale level as the domain structures can be controlled in a non-destructive way and the orientation of the polarization can be studied locally. We report here the switching dynamic study in polycrystalline PZT thin films with two different thicknesses on a large time scale (from 1 s down to 10^{-9} s). Both films present a similar grain size ($R_{\text{mean}} \approx 45$ nm) and allowed the observations of two different regimes for the polarization switching speed. We could evidence a tight connection of the nucleation and growth of nano-domains as well as of their success rate with the film thickness and grain structure.

Keywords—Piezoresponse Force Microscopy; granular $\text{Pb}(\text{ZrTi})\text{O}_3$; domain switching; Nucleation and growth dynamics;

I. INTRODUCTION

In the last decade, an increasing interest has emerged for the possibility to use an Atomic Force Microscopy (AFM) in order to locally polarized/erased ferroelectric nano-domains [1]. In order to do so, the polarization of a ferroelectric material is locally switched by applying a DC voltage through the aid of the AFM tip during a well-defined time. This kind of local polarization process reproduce quite well the “writing/reading” mechanism used in the ultrahigh density information storage device. In this later technology several requirements have to be targeted: small bit size, fast access times, long term data retention, data reliability and low power. One promising material for the development of Ferroelectric Random Access Memory showing better performances than the commercialized one, is the ferroelectric $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT). This material has been intensively studied in the last years for memory applications due to its high remnant polarization showing a high stability in time. A huge effort has

been done on the dynamic switching behavior understanding in epitaxial PZT thin films [2, 3]. Nevertheless, due to the industrial production needs of an easy and low cost elaboration process, polycrystalline granular nanostructures are currently widely used for many applications [4]. So far, local domain switching dynamics studies on polycrystalline PZT materials have been focused on individual and nearby grains in various composition of PZT thin films [5, 6, 7, 8, 9]. In our study, we report on the nanoscopic control of the read/write operations in two nano-granular PZT20/80 thin films with different thickness. We study the time dependence of the domain switching behavior in a large time range (from 1 s down to 10^{-9} s). The percentage of read/write success as well as the domain size for both samples is reported in the whole range of time and for hundreds of writing/reading processes.

II. EXPERIMENTAL

We studied two granular $\text{PbZr}_{0.2}\text{Ti}_{0.8}\text{O}_3$ samples showing thicknesses of 150 and 260 nm (respectively call PZT (150nm) and PZT (260nm) from now on). The granular PZT layers have been grown by sol-gel process on a Pt/Ti/SiO₂/Si(001) substrate. PZT films are polycrystalline showing a c-axis preferentially oriented along the perpendicular to the plane of the substrate (more details can be found elsewhere [10]). PFM images have been performed on a Bruker DI-3100 instrument, using gold coated tips (Multi75GB-G, Budget Sensors and 240AC-GG, Micro Cantilevers) and PtIr coated tips (SCM-PIT, NANO WORLD) with stiffnesses of 2-3 N/m and a free cantilever resonance frequency of 70-75 kHz. The frequency used for the PFM images presented below, has always been set out of the contact resonance frequency (*i.e.* around 300 kHz) and reasonably close to it, in agreement with previous studies [11]. An AC voltage of 2V maximum in amplitude has been used in order to read the PZT polarization along the c-axis (*i.e.* Vertical Piezoresponse Force Microscopy also called VPFM). In the case of the dynamic switching study we polarized a $8 \times 8 \mu\text{m}^2$ area by the application of a DC voltage (-9V of amplitude for the PZT (150nm) and -12V respectively for the PZT (260nm). These DC amplitude voltages are well above the coercive voltage of the PZT samples measured by standard polarization hysteresis cycles [10]. Afterwards, using a

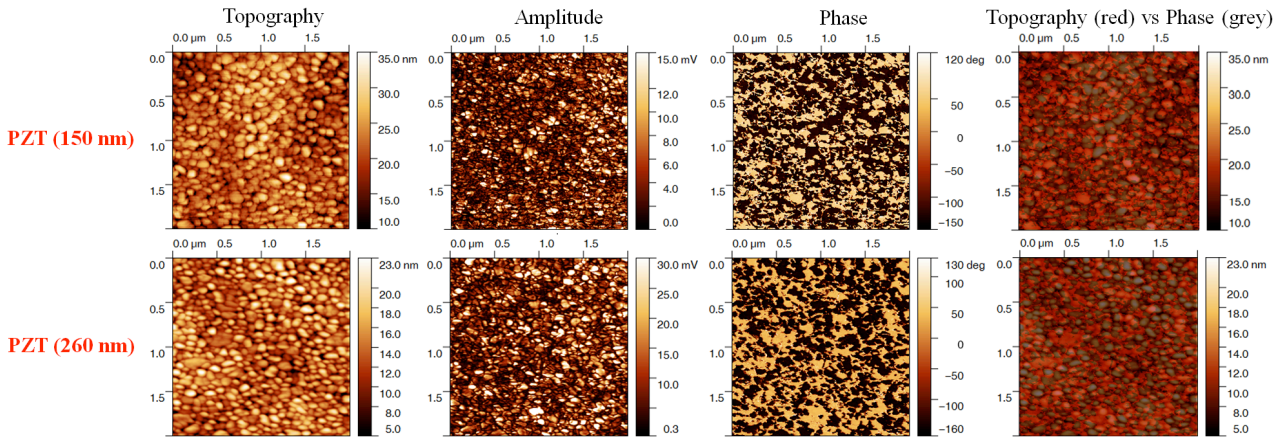


Fig. 1. $2 \times 2 \mu\text{m}^2$ intrinsic PFM images recorded on PZT (150nm) (upper images) and PZT (260nm) (bottom images) samples. First images from the left correspond to the topography images, second images are the vertical-PFM amplitude, third images are the vertical-PFM phase and the last images on the right side are the superposition of the topography and the Phase images.

homemade program the AFM tip is driven to specific positions over the pre-poled area. At each specific position (describing a net like in a battleship table), the AFM tip is stuck and a pulse of +9V of amplitude and of a defined time (between 1 s and 10^{-9} s) is applied. The distance between 2 pulses is settled at 400 nm. Once a net of 100 pulses is “written” inside the $8 \times 8 \mu\text{m}^2$ poled-area, we “read” as explained before the VPFM response.

III. NANO-GRANULAR INTRINSIC RESPONSE

A. Topography versus Intrinsic Ferroelectric Domain Distribution

Fig. 1 shows the intrinsic VPFM images obtained on the two granular PZT samples. Upper images correspond to the PFM images recorded on PZT (150nm) and bottom ones correspond to PZT (260nm). The topography images confirm the granular structures for both polycrystalline samples with an average grain size of 45 ± 5 nm. Both samples present a VPFM amplitude and phase distributions characteristics of an intrinsic opposite polarized domains. Indeed the phase difference between the dark and clear zones is of 180° confirming an intrinsic c-axis orientation of the tetragonal PZT ferroelectric domains. A slight difference of the intrinsic domain size distribution is observed between the two films, putting in evidence smaller ferroelectric domains for the PZT (150nm) sample where size down to 10 nm are observed. In order to study the connection between the ferroelectric intrinsic domain size and the nano-granular structure, we superposed the topography image on the VPFM phase one for both samples (see images on the right side of Fig. 2). In this comparison the ferroelectric domains of the PZT (260 nm) appear to be more influenced by the grain-structure than in the case of the PZT (150 nm). In thicker PZT film, in fact, the majority of grains are mostly monodomains (up or down) while in the second case there is not an evident connection

between the grain distribution and the ferroelectric domain one. This seems to suggest that the intrinsic ferroelectric domain in the thinner sample behaves more like an epitaxial PZT film.

B. Clamping Effect

In order to study the influence of the nano-granular structure on the reversal mechanism of the ferroelectric domains in our samples and thus the clamping effect usually observed in this systems [12] we perform the polarization process presented in Fig. 2. In this figure we report the results of the application of a DC voltage of -9 Volt (upper images) and of +9 Volt (bottom images) in two different non-poled zone of $400 \times 400 \text{ nm}^2$ for the PZT (150nm) sample. In both cases the starting ferroelectric state is the intrinsic one observed in Fig.1 (*i.e.* opposite oriented ferroelectric domains are randomly distributed). In Fig.2 we can see that the application of a higher voltage than the critical one [10] do not succeed in flipping all the area and non-reversed domains are left behind. Thus in the case of a negative applied voltage (upper images) few positive oriented domains/grains still exists as well as in the case of positive applied voltage (bottom images) few

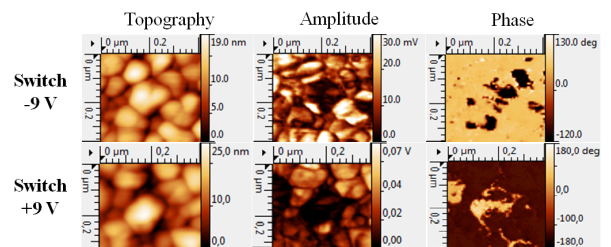


Fig. 2. $0.4 \times 0.4 \mu\text{m}^2$ VPFM images of PZT (150nm) sample recorded after the application of -9 Volt (upper images) and +9 Volt (bottom images) in 2 different areas. First images on the left correspond to the topography images, the second one to VPFM amplitude images and third one to VPFM phase images.

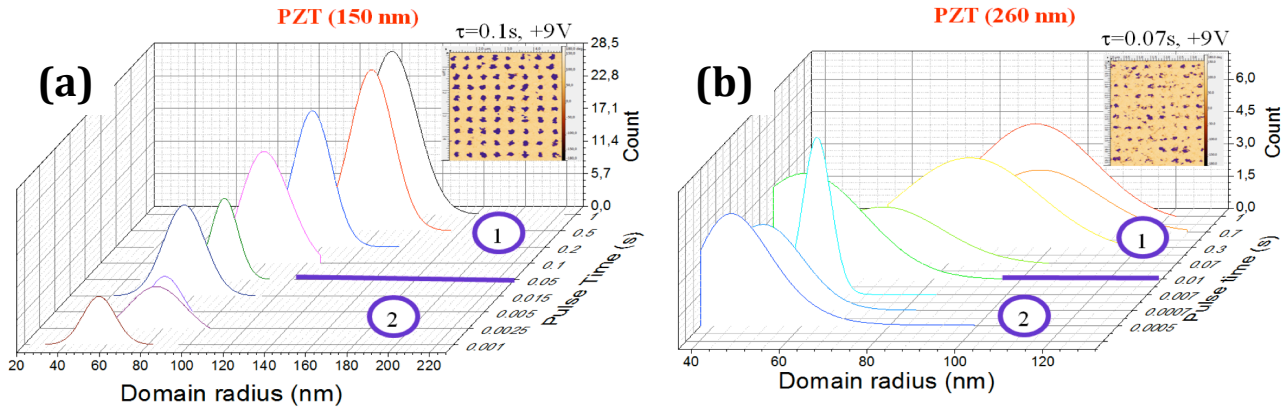


Fig. 3. Pulse time dependence of the 3D statistical domain size distribution for PZT (150nm) (a) and PZT (260nm) (b); insets show the the VPFM phase images of the net of positive pulses applied in the 8x8 μm² negative poled-area..

domains/grains are still clamped in down direction. This clamping effect has been observed also in the PZT (260 nm) (not shown here) revealing a grain-pinning influence on the local reversal mechanism of the ferroelectric domains for polycrystalline PZT thin films. In the following paragraphs we will discuss how this effect can disturb the “writing/reading” local polarization information technology.

IV. TIME DEPENDENCE OF THE FERROELECTRIC DOMAIN AND DISTRIBUTION SUCCESS

As explained in paragraph II, using a homemade program, we locally polarized ferroelectric domains by simulating the “writing/reading” process of the recording devices. The insets of Fig. 3 (a) and (b) show the VPFM phase images of the net of pulses applied in the 8x8 μm² poled-area. In both cases the amplitude of the applied pulse is +9 Volt while the time of the pulse changes (in fig. 3 insets is respectively of 0.1 s for the thinner film and 0.7 s for the thicker one). In both cases clamped area are visible as positive orientated nano-zones (black areas) observable outside the net of polarized zone at a crossing point between virtual rows and columns. These clamped zones are obviously not taken into account in the analysis of the ferroelectric domains radius distributions measured as function of the pulse time. In Fig. 3 (a) and (b), we show 3D graphs reporting the statistic distribution of the ferroelectric domain radius recorded at different times for both samples. As it can be observed, the mean radius can go from 140 nm at high pulse time down to 46 nm at low pulse time for PZT (150nm) while it goes from 88 nm down to 44 nm for PZT (260nm) respectively from high to low pulse time applied. Two main common results come up from this study: (i) the shift towards the low domain radius as function of the decreasing pulse time for both the statistical distributions

observed, show two speed-regimes (*i.e.* namely 1 and 2 regime in the figure 3 (a) and (b)) and (ii) the success of the reversal mechanism (*i.e.* the number of local polarized domains per 100 applied pulses) depends on the pulse time applied. A main difference between the two samples is that in the case of the PZT (150nm), the decreasing of the mean domain radius as function of the pulse time is faster (almost linear) than in the case of the PZT (260nm). Thus the linear behavior observed in the case of the thinner film is in good agreement with the one observed for nanometric epitaxial PZT thin films in which a linear decreasing of the domain radius was previously observed in the time range of 1 s to 10⁻⁵ s [13]. In the regime 2, both samples show a fast decreasing mean domain radius down to 50 nm, which is equal to the nano-grain mean value of both polycrystalline PZT films. Thus in polycrystalline films the grain-pinning effect prevents to reach the inferior domain limit equal to the size of the AFM tip (20 nm) usually observed in the epitaxial PZT films [2]. Critical time for switching from one regime to the other depends on the thickness of the film as well as the nucleation and growth process. Finally, also the statistical distribution width of the ferroelectric domain size strongly dependent on the thickness of the film, showing a wider distribution in the case of the thicker one. In order to study the reliability of the domain writing process, we report in Fig. 4 the Success Rate of Domain Switching (SRDS) for both PZT (150 nm) and PZT (260 nm). This SRDS percentage simply corresponds to the number of written domains over a 100 of applied pulses. As shown in Fig. 4, both PZT samples exhibit a decreasing behavior for the SRDS as function of the decreasing time putting in evidence a limit for the fast writing process. Thickness dependence is also observed. While in the PZT (260nm), the SRDS goes under 80 percent very quickly (*i.e.* it linearly decreases between 1 s and 0.1 s), in the case of the PZT (150nm), the SRDS goes under 80 percent much slowly (*i.e.* it decreases logarithmically between 1 s and 1x10⁻³ seconds).

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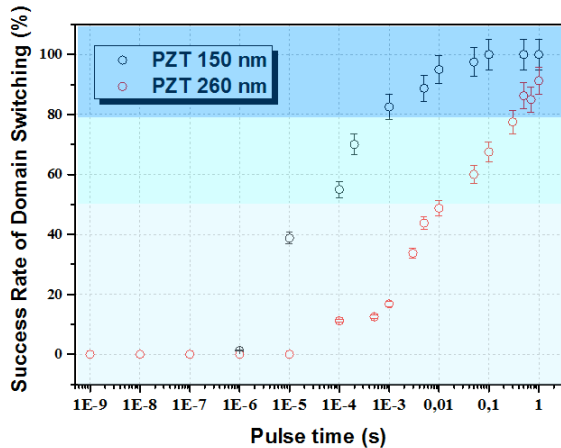


Fig. 4. Statistics of writing success at +9 voltage for PZT (150nm) and PZT (260nm).

This results suggest that thinner polycrystalline PZT samples are more suited for nanoscopic read/write operations due to their higher SRDS at smaller time pulses applied.

V. CONCLUSION

In summary, we have studied the dynamic of the domain switching behavior in PZT polycrystalline thin films presenting a nano-granular structure. Both samples show a very similar granular distribution and mean size and have different thicknesses. Our results put in evidence that the intrinsic ferroelectric domain distribution, the reversal mechanism and the ferroelectric pinning effect, strongly depend on the nano-granular and thicknesses properties of the PZT films. We also demonstrated that the statistical distribution of the domain size as function of the time pulse used for polarization as well as the success of the writing domain process of the ferroelectric domain are strongly influenced by the thickness of the film. In the frame of our experimental conditions, we could not observe any polarized ferroelectric domain below the size of a grain. This suggests that domains switching and stabilization is strongly linked to the granular PZT structure. This opens some interesting perspective for the use of these polycrystalline ferroelectric thin films for nanoscopic read/write operations. Controlling the size of the grain and the stabilization of the ferroelectric domain inside it, may open the way to very stable memory device not influenced by the size of the AFM tip.