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Original Article

Local piezoresponse and ferroelectric domain of sol-gel $Pb(Zr_x,Ti_{1-x})O_3$ film

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Abstract

In this work $Pb(Zr_xTi_{1-x})O_3$ (PZT) films with different thicknesses and compositions were prepared by a sol-gel method. Surface morphology and nanoscale behavior of single domain were mainly investigated by the piezoresponse force microscopy. Island-like and sun-rays types of grain and ferroelectric domain structures were observed. Changes of local hysteresis loops and magnitudes of the piezoresponses of the PZT films with different thicknesses and at different domains were systematically investigated.

Keywords: $Pb(Zr_xTi_{1-x})O_3$, atomic force microscopy, piezoresponse, ferroelectric.

1. Introduction

Researchers and engineers have long been focusing on ferroelectric materials due to their ability to transform electromagnetic, thermal and mechanical energy into electrical charge, which has been used in a number of electronic applications such as non-volatile computer memories and microelectromechanical systems. However, the scale of interest for determining the ferroelectric properties, the grain and domain structures is now nanoscale while the science of ferroelectrics at this scale is still scarce. The development of atomic force microscopy (AFM) has allowed the routine evaluation of surface topography of these materials. In the last few years an additional technique, i.e., piezoelectric atomic force microscopy (P-AFM or PFM), has been developed for determining the ferroelectric properties of a material (Snitka *et al.*, 2006: Dunn and Whatmore, 2002). This work aims to fabricate thin films of $Pb(Zr_xTi_{1-x})O_3$ or PZT, the most common conventional ferroelectric and piezoelectric materials, using the sol-gel method. Subsequently, the PZT films are characterized by the use of a piezoelectric atomic force or piezoresponse force microscopy (P-AFM or PFM) to determine the ferroelectric domains and the local piezoelectric hysteresis (d_{33}-E) loops.

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2. Methodology and Equations

The PFM technique, in which the converse piezoelectric effect was employed, was mainly used in this work. The system comprised PFM tip in contact with the dielectric surface. The tip served as the top electrode. A weak ac voltage was applied between the conducting tip and bottom electrode to induce a local piezoelectric vibration, which is detectable by the same tip. The amplitude of the vibration signal provides information on the magnitude of the piezoelectric coefficient, while the phase signal determines the polarization direction. Due to the absence of the top electrode and consequent high resolution, one can observe the ferroelectric domains and the surface topography at the same

time and easily correlate the microstructure and the domain behavior inside individual grains (Chrisman *et al.*, 2000; Harnagea *et al.*, 2001).

A piezoelectric material will provide an additional response to an applied ac electric field due to the converse piezoelectric and electrostrictive effects. For a homogeneously polarized (in z direction), stress-free ferroelectric material its vertical displacement (Z) can be expressed as follows:

$$\Delta z = d_{33}V + \frac{M_{333}}{t}V^2 \quad (1)$$

Where V is the applied voltage, t is the sample thickness, d_{33} and M_{333} are the piezoelectric and electrostrictive constants, respectively. The second term in Eq.1 is typically much smaller than the first one in a polarized state (Jaffe *et al.*, 1971). Under the external voltage $V = V_{dc} + V\cos(\omega t)$ the surface displacement will consist of a dc component (that cannot be measured with a lock-in), the signals at first and second harmonics are respectively :

$$\Delta z_{\omega} = d_{33}V_{\omega} + 2\frac{M_{333}}{t}V_{dc}V_{\omega} \quad (2)$$

$$\Delta z_{2\omega} = \frac{1}{2}V_{\omega}^2\frac{M_{333}}{t} \quad (3)$$

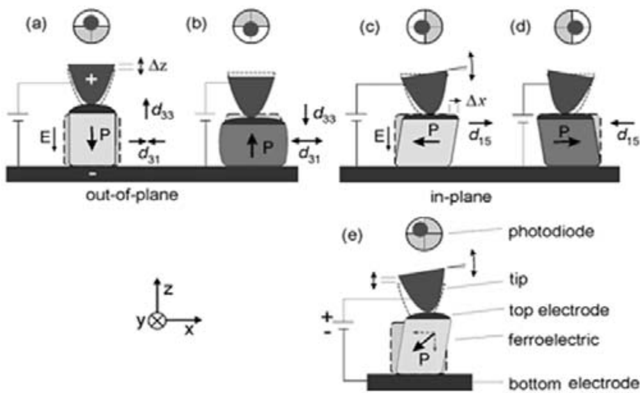


Figure 1. PFM investigation: (a) electric field aligned parallel to the spontaneous polarization leads to a lifting of the cantilever due to the d_{33} effect (out-of-plane signal). It causes additional lateral contraction of the ferroelectric via the d_{31} piezoelectric coefficient, (b) the anti-parallel alignment of the electric field and the spontaneous polarization leads to a vertical contraction and a horizontal expansion of the ferroelectric, (c) and (d) electric field applied orthogonally to the polarization results in a shear movement due to the d_{15} coefficient (in-plane signal) and (e) a grain polarized in the *x-z* plane will contribute to the in-plane as well as to the out-of-plane signal. (After Kholkin *et al.*, 2006).

The sign of the converse piezoelectric signal (first term in Eq.2) depends on the relative orientation of the polarization and applied electric field. The PFM movement and the corresponding piezoelectric coefficient are shown in Figure 1. By acquiring all three components of the piezoresponse signal it is possible to perform a reconstruction of polarization orientation of the domains.

3. Materials and Methods

$Pb(Zr_xTi_{1-x})O_3$ films with x = 0.3, 0.4, 0.52, 0.6 and 0.7 were prepared using a sol-gel method. The precursor solution process for PZT films is based on the procedure proposed by Budd *et al.* (1985) 0.6 M $Pb(Zr_xTi_{1-x})O_3$ solutions were prepared by using tetra-n propyl-orthozirconate (Aldrich, 99% purity, 70% wt. in n-propanol), tetra-iso propyl-orthotitanate (Aldrich, 99% purity), and lead-acetate tri-hydrate (Riedel-de Haen, 99% purity) as starting materials, and 2-methoxyethanl as a solvent. At first, lead acetate trihydrate was dissolved in 2-methoxyethanol and mixed for 30 minutes. Approximately 10% excess lead was added to the precursor solutions to compensate for the loss of lead during the final annealing processing. The solution was distilled until it became a white powder with increasing temperature up to 130 C. 2-methoxyethanol was then added and refluxed for 3 hours. This process was followed by the addition of tetra-n propyl-orthozirconate to the lead solution and it was refluxed during 2 hours. Finally, tetra-iso propyl-orthotitanate was added to the solution and mixed for more than 12 hours. The addition of the tetra-n propyl-orthorzirconate in the second step of the reaction and the refluxing during 2 hours were carried out in order to stabilize the solution and to avoid the formation of titanium hydroxide (Gurkovotch and Blum, 1985).

$Pb(Zr_xTi_{1-x})O_3$ films were deposited onto (111)Pt/Ti/SiO_2/Si substrates using conventional spin-coating method. The $Pb(Zr_xTi_{1-x})O_3$ solutions were dropped onto the substrate and then spun at 3000 rpm for 30 s. $Pb(Zr_xTi_{1-x})O_3$ films were dried at 230 C for 1 min and subsequently pyrolysis at 450 C. After all layers were deposited, the coated films were annealed at 600 C for 30 min. in a tube furnace by a rapid thermal process (RTP). The crystal structure and texture of the $Pb(Zr_xTi_{1-x})O_3$ films were examined by x-ray diffraction (Philips X-Pert diffractometer). The patterns were recorded at a scan rate of 3 per min for phase and texture analyses.

The topography and domain structure of PZT thin films were investigated by mean of PFM at room temperature. Experimental setup of PFM (MultiMode™ SPM, Digital Instruments) was shown in Figure 2. PFM was performed in a commercial setup Multimode and equipped with the lock-in amplifiers (SR830, Standard Research Systems) and a function generator (Yokagawa, FG-120). A commercial tip-cantilever system (NCHR Nanosensors) with spring constant of k = 40 N/m and tip apex radius less than 10 nm was used. The function generator was used to applied ac voltage of amplitude V_{ac}=5 V at f = 50 kHz and a scan speed of 1-5

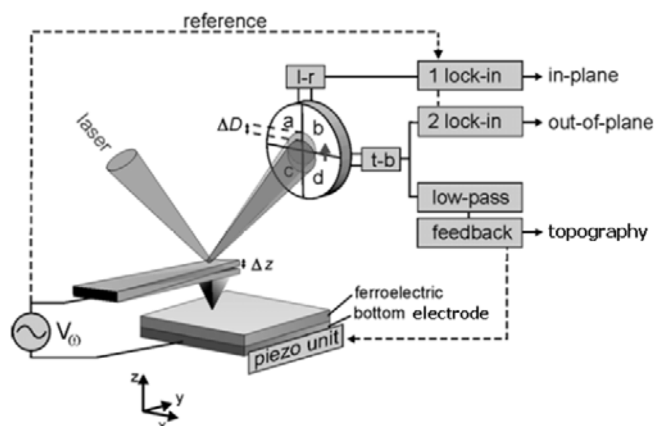


Figure 2. Schematic diagram of the PFM experimental setup

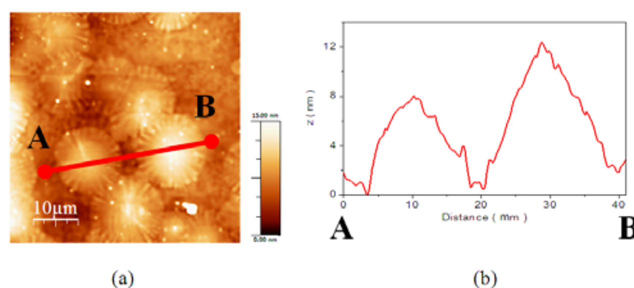
mm/s between the tip and the bottom electrode. A sinusoidal voltage was passed between the tip and the back electrode of the PZT sample, usually held at ground. The voltage-induced cantilever deflection is detected by a reflected laser beam on a four quadrant photodiode. The two signals: (a+c)-(b+d) and (a+b)-(c+d) are demodulated with two lock-in amplifiers representing the in- and out-of plane signals, respectively. The average force on the cantilever during the scanning process is kept constant by a feedback loop. During the experiment the scan size was set to 0 nm in order to remove any topographic variation from the z-axis displacement with a scan rate to 0.1 Hz. The displacement of the sample surface due to the applied field was directly int1erpreted from the z-axis scale of the microscope (Digital Instruments 3000 systems). The variation in the z-axis displacement was plotted against the applied voltage and can be interpreted as a typical strain/field plot for the sample. Great care was taken during the electroding of the tips to ensure that they were free of stress.

4. Results and Discussion

The XRD patterns of $Pb(Zr_xTi_{1-x})O_3$ thin films on $(111)Pt/TiO_2/SiO_2/Si$ substrates show the film to be a single perovskite phase. The typical *P-E* hysteresis loop of the PZT x=0.52 was observed. The film shows a well defined ferroelectric hysteresis loop with a typical remanent polarization value and optimized coercive field as presented in the previous report (Khaenamkaew *et al.*, 2007).

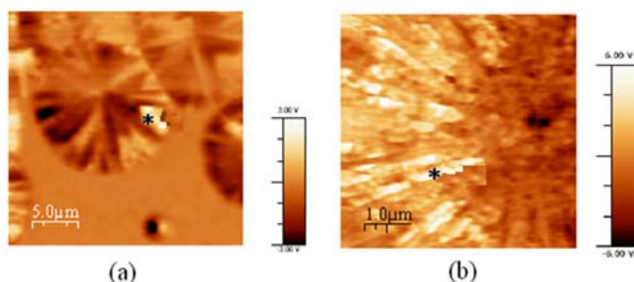
Topographies and Grain structures

The PZT film with single deposition (referred as monolayer hereafter) was AFM observed at a relatively high magnification to reveal its island-like texture as shown in Figure 3a. When the film was cross sectionally scanned, the height of the circular pattern was in a range of 8-15 nm as seen in Figure 3b. When the film became thicker, the ferroelectric domains became sun-rays type structure (Figure 4).



(a) (b)

Figure 3. AFM images of monolayer PZT film. (a) topography and (b) cross-section along AB.



(a) (b)

Figure 4. Out-of-plane PFM signals for (a) monolayer and (b) multilayers (10 layers) (* are referred to the AFM-tip position for local hysteresis loop measurement)

Each central point was the origin of the domains oriented along the radius of the circle. These patterns have been reported as an the ideal grain shape in the growing process of the films (Alexe and Gruverman, 2004).

From Figure 4a, the grains were separated on the free film substrate. While the ten-layered film image (Figure 4b), domains with same polarization are present on separate rays of sun. Radial oriented symmetry of grain positions is correlated with ferroelectric domain structure (Figure 5). It is possible to assume radial symmetric process of film growth with distance between initiated grains about 10 mm.

Figure 6 shows a topography and a piezoresponse of PZT film with x = 0.52. It can be seen that the polarization distribution of the grain is arbitrary and random. The variation of grain size with composition ratio was also observed in previous work (Khaenamkaew *et al.*, 2007). The grain sizes of PZT films strongly depended on the composition ratio. The films with higher Ti content have smaller nucleation energy as reflected in smaller grain in the film with x = 0.7 (Zeng *et al.*, 2003: Zeng *et al.*, 2005: Kuffer *et al.*, 2000: Shvartsman *et al.*, 2005).

Ferroelectric hysteresis characteristics

For all of the PZT samples, a typical open-hysteresis loop was observed. A strong dependence of the piezoresponse was also observed which is consistent with *P-E* behavior. In addition, large differences between initial and final polarization states were depended on the composition

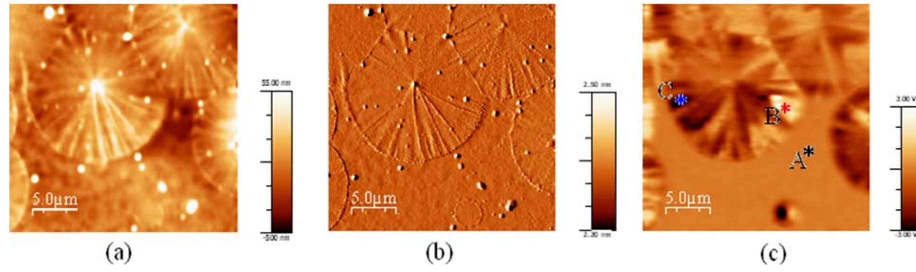


Figure 5. Out-of-plane PFM signals for monolayer PZT detected at (a) topographic image; (b) deflection (dz/dx) image and (c) PFM image.

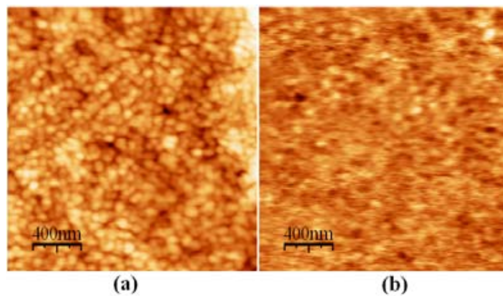


Figure 6. PFM images (a) topography and (b) piezoresponse of PZT film (x=0.52).

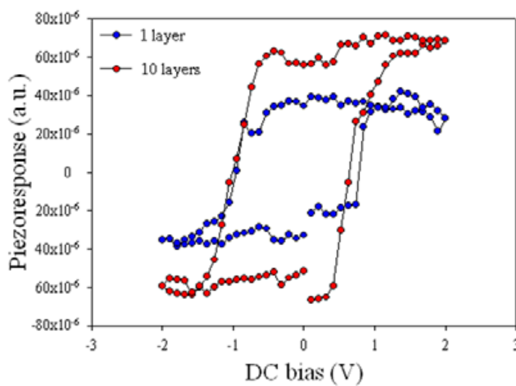


Figure 7. Local hysteresis loops for monolayer and ten-layered PZT films with x=0.52.

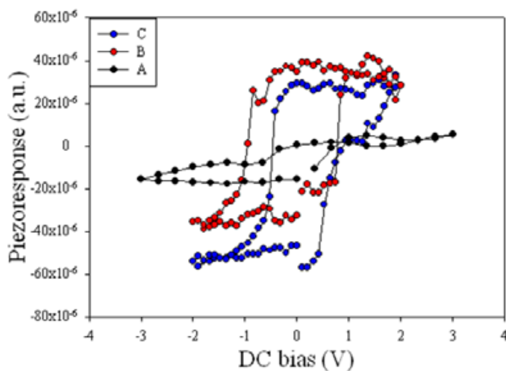


Figure 8. Local hysteresis loops of the PZT films x=0.52 detected at different domains (A, B and C are indicated in Figure 5c).

of PZT films and domain size. This is due to fine domains and their merging upon switching by PFM tip. As is evident, in the initial state, the domains in neighboring grains compensate each other. In the polarized state all domains are oriented along the applied electric field and the PFM signal should increase as observed in the hysteresis loop (Dunn, 2003).

Local hysteresis loops of the PZT films (Figure 7) with different thicknesses shown different maximum magnitudes of piezoresponse signals after full switching. The * symbol in Figure 4a and Figure 4b are the AFM-tip positions during the local hysteresis loop measurement. For ten-layered film, the piezoresponse signal is higher than that of monolayer film. This is because the tip position in Figure 4b has stronger domain polarization than that in Figure 4a and these two points have different ferroelectric domain states (Kalinin and Bonnell, 2002).

Figure 8 shows the local hysteresis loops of the film detected at different points, i.e., A, B and C as indicated in Figure 5c. For **A** points, each point is placed on the substrate in a PZT-free area, therefore, there was no piezoresponse signal. For the domain along a z-direction which was referred as **B** points, the hysteresis loop characteristics was symmetry. This is an out-of-plane polarization (OPP) signal from the PFM measurement. For the domains along a small-angle shifted z-direction or **C** points, the hysteresis loop was shifted downward. This is an in plane-polarization (IPP) signal as illustrated in Figure 1b and Figure 1e. This shift was due to incomplete switching during the process for obtaining loops and presented the non-switching part in piezoresponse signals. This means that the films have additional self polarization effect and additional internal positive electric field (Roelofs *et al.*, 2000).

5. Conclusion

Sol-gel derived $Pb(Zr_xTi_{1-x})O_3$ thin films with different thicknesses were fabricated and characterized locally by the piezoelectric atomic force microscopy. The island-like and sun-rays type domain structures were observed. Maximum magnitudes of piezoresponse signals after full switching of the film strongly depended on the thickness of the film. Changes of local hysteresis loops of the films with different domains were caused by different orientation of the

domain, in-plane and out-of-plane polarization states. Asymmetric positions of local hysteresis loops pointed out the self-polarization effect in the PZT films.

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