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# AFM based polarization nanolithography on PZT sol–gel films

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**Abstract**

In this work, the possibility to create the inverted domain patterns on the surface of sol–gel derived ferroelectric $PbTiO_3$–PbZrO3 (PZT) thin films are demonstrated. Surface microstructure and local piezoelectric properties were investigated by piezoresponse atomic force microscopy. Macroscopic piezoelectric properties are investigated by laser Doppler vibrometry. PZT films exhibits high $d_{33}$ (93 pm/V in unpoled and 419 pm/V in poled state). Piezoresponse atomic force microscope (AFM) measurements were carried out by applying AC voltage (frequency 25 kHz and amplitude of 2 V) coupled with DC bias voltage between the grounded tip of AFM and Pt bottom electrode of the sample, and detecting first harmonics of resulting surface vibration by lock-in amplifier. The possibility to write and read the polarization patterns on the PZT thin film by piezoresponse AFM was confirmed.
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*Keywords:* Nanolithography; Atomic force microscopy; Ferroelectric; Sol–gel

## 1. Introduction

As a high-density recording media, ferroelectric materials are considered to be superior to the ferromagnetic materials widely used at present because the domain wall thickness of typical ferroelectric materials is of the order of a few lattice spaces, far less than of ferromagnetic materials [1]. Several authors use scanning probe microscopy as a method of forming and detecting small domain dots in ferroelectric thin films [2]. On a 10–100 nm scale, ordered surface heterogeneity can be produced based on the ability of a scanning probe microscope, to mechanically or electronically "write" on a surface. Recently, PZT thin film which was polarization-patterned by conductive tip of atomic force microscope (AFM) was employed to produce nanostructures by assembly of Ag nanoparticles, suggesting a new way of nanofabrication [3,4]. These applications require thin films with specific properties, such as smooth microstructure, small grain size, high piezoelectric and electromechanical coupling coefficient, and high piezoactivity on the local scale. A number of processing methods have been used to produce ferroelectric PZT thin films, including radio frequency magnetron sputtering, metalorganic chemical vapor deposition (MOCVD), laser ablation, and sol–gel technology [5]. Sol–gel processing route has many advantages, such as fine control of stoichiometry and microstructure [6], cost-effectiveness, relatively low processing temperature, possibility to coat large areas, and reproducibility of parameters [7]. In this work, the possibility to create the inverted domain patterns on the surface of sol–gel derived ferroelectric $PbTiO_3$–PbZrO3 (PZT) thin films using probe microscopy are demonstrated.

## 2. Experimental

Our PZT thin films were deposited on commercial Pt/Ti/$SiO_2$/Si substrates by sol–gel technique using layer by layer spin coating and crystallizing at 700 °C in air. The $Pb(Zr_{0.52}Ti_{0.48})O_3$ films (PZT near the morphotropic phase boundary) were deposited, producing 700-nm thick layers. Pt top electrodes with 50 nm thickness and diameter 0.6 mm were deposited on the films by sputtering. After investigation of as-prepared films by Doppler vibrometry, they were corona poled at 250 °C and 15 kV. The surface topography of the films was investigated using a home-built atomic force microscope controlled by commercial

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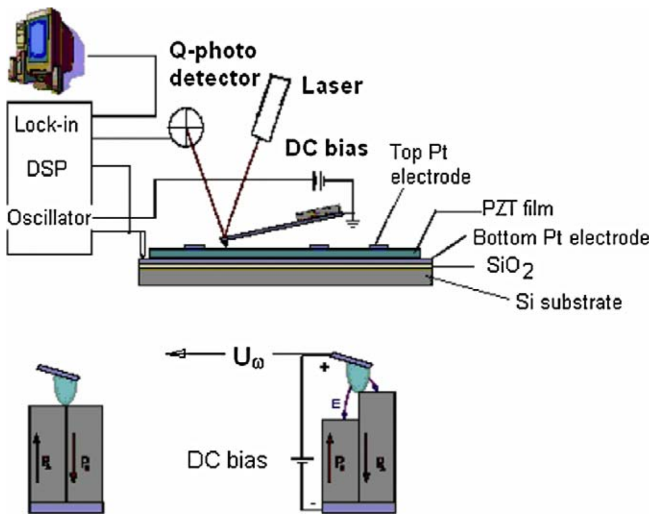


Fig. 1. AFM based experimental setup to measure local piezoresponse.

electronics (NT-MDT Co, Russia). Macroscopic piezoelectric properties of the films were evaluated by laser Doppler vibrometry and local piezoelectric properties – by piezoresponse atomic force microscopy [8]. Doppler vibrometer setup consisted of Polytec OFV 353 sensor head and OFV 3001 vibrometer controller, DSP lock-in amplifier (AMETEK 7225), waveform generator (HP 3325 A), and voltage source (Keithley 2410). Doppler vibrometry measurements were taken applying 5 kHz ac voltage coupled with dc bias voltage between the top and bottom electrodes. Laser beam was focused on the center of top electrode. AFM cantilevers with stiffness 5.5 N/m, resonant frequency 150 kHz and tip curvature 35 nm (as reported by manufacturer) coated with conductive TiN layer (NSG11/TiN, NT-MDT Co., Moscow, Russia), were used for surface imaging and piezoresponse AFM. Piezoresponse AFM measurements were carried out by applying ac voltage (frequency 25 kHz, amplitude 4 V peak-to-peak) coupled with dc bias voltage between the grounded tip of AFM and Pt bottom electrode of the sample, and detecting first harmonics of resulting surface vibration by lock-in amplifier. Generator and lock-in amplifier built into AFM controller were used. The experimental setup to measure local piezoresponse is presented in Fig. 1.

## 3. Results and discussion

Grain size and roughness of the films have an essential importance for nanoresolution patterning of the surface. To minimize the polarization line distortions on the grain boundaries, grain size should be less than the wide of polarization line. Roughly estimating the diameter of AFM cantilever 10 nm (specification of NT-MDT Co.), the patterns line wide in the range of tenth of nanometers can be realized on the planar crystal surface. The grain size and roughness of the deposited PZT and Sm doped (PSZT) films were investigated by AFM. The images of investigated films are shown in Fig. 2. Main roughness parameters, calculated from 1 μm$^2$ scans after applying plane fitting correction, are given in Table 1 see (Fig. 2).

Table 1
Roughness parameters found from AFM measurements

| Sample (nm) | PSZT | PZT | PST/ PSZT |
|---|---|---|---|
| Roughness average | 2.3 | 2.89 | 0.389 |
| Root mean square | 2.78 | 3.52 | 0.646 |
| Estimated grain size | 60 | 200 | 70 |

Main roughness parameters, calculated from 1 μm$^2$ scans after applying plane fitting correction were average roughness 2.89 nm and root mean square 3.52 nm. The piezoelectric coefficients of the films calculated from vibrometer measurements were $d_{33} = 93$ (pm/V) for unpoled samples and $d_{33} = 419$ (pm/V) for poled samples. Poling considerably increased $d_{33}$ for all films. Poled PZT film exhibits very high $d_{33}$ of 419 pm/V. While this value is much higher than reported in many sources, it correlates well with 400 pm/V reported in the work [9]. Such high piezoelectric response in PZT near the morphotropic rhombohedral–tetragonal phase boundary has been attributed to elongation along the direction associated with monoclinic distortion [10].

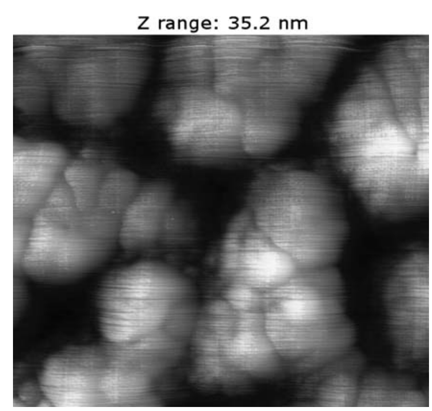


Fig. 2. AFM image of surface microstructure of the PZT film ( scan area: 1 × 1 μm$^2$).

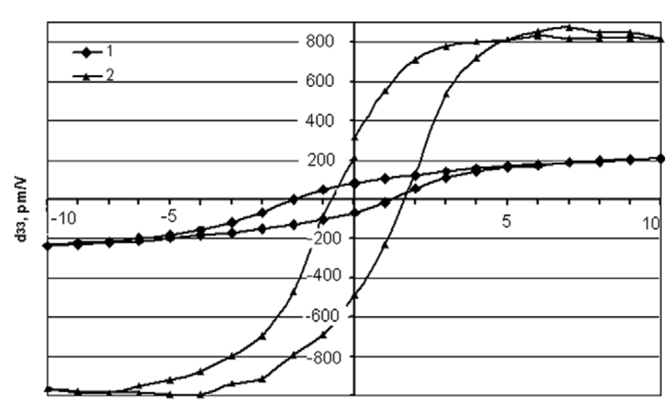


Fig. 3. Piezoelectric coefficient $d33$ hysteresis loops of PZT film measured by Doppler vibrometer: (1)–unpoled; (2)–poled.

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Hysteresis loops of piezoelectric coefficient $d_{33}$ (estimated as ratio of displacement and driving voltage) PZT films are presented in Fig. 3. Poled PZT film exhibits large displacement, reaching the saturation at relatively low bias (approximately 75 kV/cm). Local hysteresis loops obtained with piezoresponse AFM are shown in Fig. 4. PZT film has a clear hysteresis curve on the submicron scale, suggesting possibility to use it as a template for polarization patterning. The possibility to write and read the polarization patterns on the PZT film by piezoresponse AFM was confirmed by conducting the following experiment. First 1500 $nm^2$ area of the film was scanned in contact mode with −10 V bias applied to the conductive tip of AFM, inducing orientation of ferroelectric domains with polarization vector pointing upward ($c+$). Then 750 $nm^2$ area in the center of previous scan was scanned with +10 V bias, inducing reorientation of domains in opposite direction ($c-$). After this, piezoresponse AFM image of larger area was taken with zero bias. Fig. 5 shows the phase of the piezoresponse signal, revealing areas of different polarization in the film. Non-piezoelectric pyrochlore matrix inclusion is seen on the phase image. Fig. 6 demonstrates the possibilities of the method to create and read complex patterns on the PZT sol–gel films by piezoresponse AFM. The pattern was created by conductive probe AFM writing the word "micro" by probe electric field and read by piezoresponse AFM. Such polarization patterned surface may be used as a template for nanoengineering of substances which exhibit different chemical or physical properties in the presence of different surface charge.

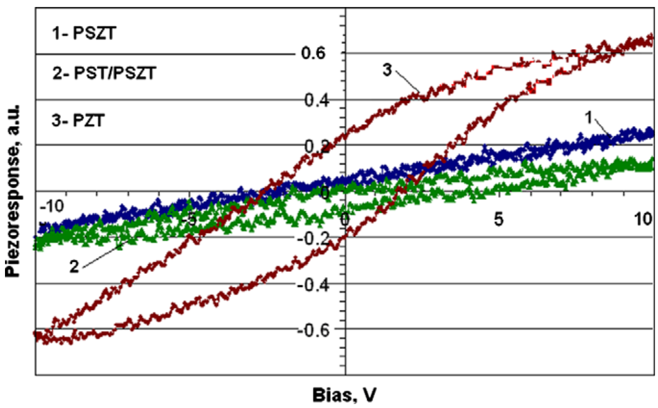


Fig. 4. Piezoresponse AFM hysteresis loops: (1)–unpoled; (2)poled.

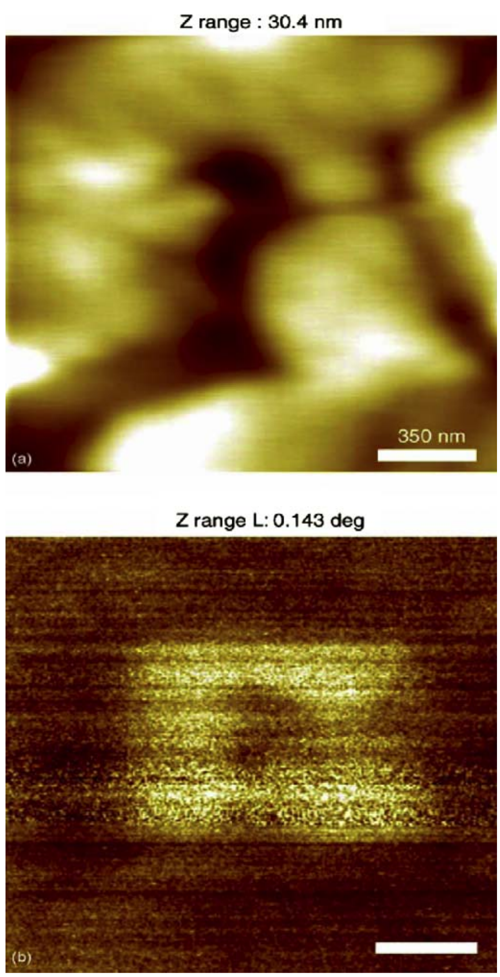


Fig. 5. Piezoresponse AFM images of polarization patterned PZT film: (a) topography, (b) phase of the piezoresponse signal. Non-piezoelectric pyrochlore region is visible in the center of patterned area. Bar = 0.35 μm.

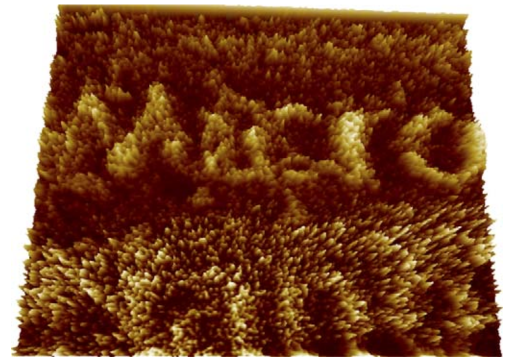

Fig. 6. Polarization-patterned PZT film with complex patterns in the form of written words "micro, nano" ( scan area: 1 × 1 $\mu m^2$).

## 4. Conclusions

Zr doped $PbTiO_3$ films were deposited using sol–gel method. Zr doped samples have high piezoelectric coefficient up to 600 pm/V for poled PZT and show promise for applications as memory devices. Local piezoelectric hysteresis on submicron scale was obtained, and polarization patterns were written on PZT film using Scanning probe microscopy technique.

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