Investigation of microstructure and piezoelectric properties of Zr- and Sm-doped PbTiO₃ nanostructured thin films derived by sol–gel technology

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Available online 16 April 2005

Abstract

Pb₁₋₀.₈5Sm₀.₀₅(Zr₁₋₀.₈T₁₀.₈)O₃ (PSZT), PbSm₀.₀₅TiO₃ (PST), Pb(Zr₁₋₀.₈T₁₀.₈)O₃ (PZT) and heterostructure PST/PSZT thin films were deposited by sol–gel technique and investigated with emphasis on suitability for specific applications. Macroscopic piezoelectric properties are investigated by laser Doppler vibrometry, and surface microstructure and local piezoelectric properties by piezoresponse atomic force microscopy. Sm-doped films have smooth microstructure with grain 60–90 nm and piezoelectric coefficient \(d₃₃\) 7–62 pm/V. Poling induced large polarization imprint in these films. PZT film exhibits high \(d₃₃\) (93 pm/V in unpoled and 419 pm/V in poled state), but is susceptible to aging in unpoled state. Local piezoelectric hysteresis loop is obtained, and polarization patterning is demonstrated for PZT film.

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Keywords: PZT; Piezoelectric properties; Atomic force microscopy

1. Introduction

PbTiO₃–PbZrO₃ (PTO) solid solutions constitute an important class of materials known for their excellent ferroelectric and piezoelectric properties. Numerous applications of these materials in thin film form are being investigated, including surface acoustic wave (SAW) and bulk acoustic wave resonator devices [1], sensors and actuators in microsystems technology, submicron random access memory devices [2], etc. 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].

These applications require thin films with specific properties, such as smooth microstructure, small grain size, high piezoelectric and electromechanical coupling coefficient, high piezoelectricity on the local scale. A number of processing methods have been used to produce ferroelectric PZT thin films, including radio frequency magnetron sputtering, metal–organic chemical vapour deposition (MOCVD), laser ablation, and sol–gel technology [4]. Sol–gel-processing route has many advantages, such as fine control of stoichiometry and microstructure [5], cost-effectiveness, relatively low processing temperature, possibility to coat large areas, and reproducibility of parameters [6].

Sm-doping of PZT ceramics [7] and thin films [8] has been used to reduce lattice anisotropy and obtain ceramics characterized by a relatively large thickness electromechanical coupling coefficient and a small planar electromechanical coefficient [7].

In this work, we investigated surface microstructure and piezoelectric properties of sol–gel-derived Zr- and Sm-modified PTO thin films with emphasis on their suitability for specific applications.

2. Experimental

Our PTO thin films were deposited on commercial Pt/Ti/SiO₂/Si substrates by sol–gel technique using layer by layer spin coating and crystallizing at 700°C in air (see

The following films were produced: Pb_{1-x}Sm_{x}Zr_{0.52}Ti_{0.48}O_3 (PSZT), PbSm_{x}TiO_3 (PST), Pb(Zr_{0.52}Ti_{0.48})O_3 (PZT near the morphotropic phase boundary) and heterostructure PST/PSZT. Eight layers (4+4 in the case of heterostructure) were deposited, producing 700 nm thick films. Pt top electrodes with 50 nm thickness and 3 mm diameter were deposited on the films by sputtering through a shadow mask. 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 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 (see [9] for discussion of piezoresponse AFM method). Computer-controlled

![AFM images of surface microstructure of the films: (a) PST; (b) PSZT; (c) PZT; (d) PST/PSZT (bar = 0.25 μm).]
Doppler vibrometer setup consisted of Polytec OFV 353 sensor head and OFV 3001 vibrometer controller, DSP lock-in amplifier (AMETEK 7225), waveform generator (HP 3325A), and voltage source (Keithley 2410). Vibrometer 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.

3. Results and discussion

Grain size and roughness of the films have an essential importance for SAW applications. To minimize SAW energy losses due to scattering on the grain boundaries, grain size should be much less than the wavelength of SAW. Roughly estimating, grain size of less than \( \frac{3}{H} \) mm is required to achieve SAW frequencies above 200 MHz. AFM images of investigated films are shown in Fig. 1. Main roughness parameters, calculated from \( \frac{1}{H} \) nm² scans after applying plane-fitting correction are given in Table 1.

Sm-modified films have uniform and smooth fine grain microstructure. Crystallization of PZT has produced non-uniform film with rosette structure grains embedded into pyrochlore matrix and connected into lamellar structures. Rosette grains appear to be composed of the smaller grains. We refrained from estimating the size of smaller grains, since main scattering would occur on the boundaries of large lamellar structures. Therefore, suitability of such film for SAW devices is questionable. On the other hand, introduction of Sm into PT system enables to produce films with low roughness and grain size, showing promise for high-frequency applications.

<table>
<thead>
<tr>
<th>Sample</th>
<th>PST</th>
<th>PSZT</th>
<th>PZT</th>
<th>PST/PSZT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roughness average (nm)</td>
<td>1.32</td>
<td>2.3</td>
<td>2.89</td>
<td>0.389</td>
</tr>
<tr>
<td>Root mean square (nm)</td>
<td>1.37</td>
<td>2.78</td>
<td>3.52</td>
<td>0.646</td>
</tr>
<tr>
<td>Estimated grain size (nm)</td>
<td>90</td>
<td>60</td>
<td>70</td>
<td>-</td>
</tr>
<tr>
<td>( d_{33} ) unpoled samples (pm/V)</td>
<td>16</td>
<td>7</td>
<td>93</td>
<td>10</td>
</tr>
<tr>
<td>( d_{33} ) poled samples (pm/V)</td>
<td>7</td>
<td>62</td>
<td>419</td>
<td>35</td>
</tr>
</tbody>
</table>

Fig. 2. Displacement of the film surface as a function of amplitude of driving voltage measured using Doppler vibrometer. Open symbols denote samples in unpoled state. (a, b) PST; (c, d) PST/PSZT; (e, f) PSZT; (g, h) PZT.

Fig. 2 shows the amplitude of piezoelectric displacement as a function of amplitude of driving voltage at zero bias measured by the vibrometer. Piezoelectric activity is confirmed for all films. Data for all films can be approximated by linear distribution reasonably well. Effective piezoelectric coefficient \( d_{33} \) calculated from these fits is given in Table 1. It must be mentioned that repeated measurements showed a decrease of \( d_{33} \) for unpoled PZT film. This is presumably caused by fatigue, stress-induced depolarization, and other aging effects.

Poling considerably increased \( d_{33} \) for all films except PST. 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 by Lefki and Dormans [10]. 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 [11].

Hysteresis loops of piezoelectric coefficient \( d_{33} \) (estimated as ratio of displacement and driving voltage) for Sm-doped and PZT films are presented in Figs. 3 and 4. Anomalous shape of hysteresis loop for PST sample is caused by high leakage current. Poling of PST sample resulted in charge injection into the film and dramatic increase in leakage current,
leading to negligible piezoelectric response. For PSZT and PST/PSZT samples, poling induced significant shift of the hysteresis loops towards negative values, indicating large polarization imprint. Warren et al. attributed such shifts to the role of oxygen vacancy-related defect dipoles \[12\]. 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. 5. Only PZT film showed a clear hysteresis on the submicron scale, suggesting possibility to use it as a template for polarization patterning. For PST sample, high conductance of the film results in negligible variation of the AFM cantilever response. For PSZT and PST/PSZT structures, piezoelectric response is similar or smaller than capacitive force acting between the bottom electrode and AFM cantilever.

It is interesting to note that best AFM piezoresponse signal was obtained, when positioning conductive AFM tip over the film and not over the top electrode. It is in contradiction with expected decrease in capacitive force due to screening by the top electrode. The reason could be the relatively high contact resistance between the top electrode and conductive AFM tip, which could be higher than effective film resistance between the top and bottom electrodes.

Possibility to write and read the polarization patterns on the PZT film by piezoresponse AFM was confirmed by conducting following experiment. First, 1.5 \(\mu\)m\(^2\) area of the film was scanned in contact mode with $-10$ V bias applied to the bottom electrode, inducing orientation of ferroelectric domains with polarization vector pointing upward (\(c^-\)). Then, 0.75 mm\(^2\) 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. 6 shows the surface topography and phase of the piezoresponse signal, revealing areas of different polarization in the film. Non-piezoelectric pyrochlore matrix inclusion is seen on the phase image.

4. Conclusions

Sm- and Zr-doped PbTiO3 films were deposited using sol–gel method. Sm-doped films have smooth microstructure with estimated grain size of 70–90 nm and show promise for high-frequency acoustic applications. Poling induced significant polarization imprint in Sm-doped films, leading to almost complete suppression of polarization switching. Zr-doped samples have high piezoelectric coefficient (up to 60 pm/V for poled PSZT and 419 pm/V for poled PZT at zero bias), which makes them excellent candidates for low-frequency acoustic or microactuator applications. Local piezoelectric hysteresis on submicron scale was obtained, and polarization patterns were written on PZT film.

Acknowledgements

This work was supported in part by Lithuanian Scientific Priority Program “Functional nanostructures and molecular mechanisms” through Lithuanian Science Foundation and Program “Nanostructured thin films: investigation and application potential” through German and Lithuanian Ministries of Science and Education (WTZ Joint Project LTU02/05).

References


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