Structure and properties of thin PZT films with inhomogeneous composition distribution

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Abstract. The paper presents the results of studies of bilayer thin ferroelectric PZT films with a lead content variation on the films thickness, formed by the method of radio-frequency magnetron deposition at different pressures of the gas mixture. It was shown that, depending on the sequence of deposition of the layers, both the structure and the dielectric parameters of the samples change.

1. Introduction

Thin films of Pb(Zr,Ti)O\textsubscript{3} (PZT) solid solutions are widely used in various fields of microelectromechanics, infrared technology, multiferroics and in a number of other engineering areas \cite{1-3}. The most popular are films of compositions corresponding to the morphotropic phase boundary (MPB), where the electromechanical parameters of solid solutions reach maximum values. One of the serious problems that prevent the achievement of maximum film parameters is the elemental inhomogeneity, both the excess (superstoichiometric) lead content, located in the form of PbO at the interfaces and in the intercrystalline space, and the Zr and Ti atoms occupying octahedral positions in perovskite lattice. The local variation of the composition can reach several percent or more, which leads to a diffuseness of the MPB and a decrease in the dielectric and electromechanical parameters.

The amount of Pb required for crystallization of the perovskite phase and its distribution over the film thickness depends on the synthesis temperature and the location of the nucleation centers of the perovskite phase – at the interfaces or in the bulk of the film \cite{4-6}. The reason for the non-uniform distribution of Zr and Ti atoms may be related to their segregation occurring at the crystallization of the perovskite phase due to the difference in the crystallization temperatures of lead titanate PbTiO\textsubscript{3} and lead zirconate PbZrO\textsubscript{3}, which differ by more than 100 °C.

It was previously shown that by slightly varying the composition of the sol-gel PZT layers, it was possible to reduce the composition inhomogeneity and significantly increase the dielectric constant and, as a result, the electromechanical parameters \cite{7}. In \cite{6, 8}, it was shown that using the RF method of magnetron sputtering by varying the pressure of the working gas, one can change the elemental ratio of Zr and Ti and the Pb content in PZT films. In this regard, the purpose of this work was to study bilayer thin PZT films deposited in 80% Ar + 20% O\textsubscript{2} atmosphere at 4 and 8 Pa pressures and annealed at 570 °C.
2. Sample preparation and research

The films were formed both on a silicon substrate (Si) and on a substrate with a platinum electrode (Pt/TiO$_2$/SiO$_2$/Si). The composition of the ceramic target corresponded to the elemental ratio of the atoms Zr/Ti = 54/46 with the addition of 10 mol.% PbO. The bi-layer structures were made in two versions: I) the first layer (bottom) was deposited at a pressure of 4 Pa, the second layer (top) was deposited at a pressure of 8 Pa (figure 1(a)); II) the first layer (bottom) was deposited at a pressure of 8 Pa, the second layer (top) was deposited at a pressure of 4 Pa (figure 1(b)). The total thickness of the formed layers was nearly 900 nm.

![Figure 1](image)

**Figure 1.** A schematic images of bi-layer structures (I and II) deposited at different working gas pressures.

To study the change of elements across the thickness of films deposited on silicon, windows with an inclined wall were etched. The etching was performed at an angle of less than 1° by a Ga ions beam (figure 2). To study the dielectric properties of samples formed on platinized silicon, an array of platinum contact pads was applied, the size of which was 120*120 μm. The LYRA 3 scanning electron microscope (Tescan) with the X-Max 80 energy dispersive attachment (energy of the probe beam was 12 keV) and an automated complex based on the E7-20 immittance meter were used to diagnose the film surface, microstructure, composition and study of the dielectric properties.

![Figure 2](image)

**Figure 2.** SEM image window for the study of the elements changes across the film thickness.

3. Results and discussion

The results on lead content in amorphous films are presented in figure 3 and in table 1. It can be seen that the lead content in the PZT layer, deposited at 4 Pa, is slightly lower than the stoichiometric and more than 20% less in the layer deposited at 8 Pa (figure 3,a,b). The elemental ratio of Zr/Ti in the layer deposited at 4 Pa was ~ 54.2/45.8 and differed from the ratio of Zr/Ti ~ 55.8/44.2 observed in the layer deposited at 8 Pa (table 1).

Control of the phase state after perovskite formation showed that the crystallization was close to completion in both structures. In structure «I», the content of the perovskite phase reached ~ 89%, and in structure «II» ~ 99%. High-temperature annealing led to a redistribution of lead content between the layers of the structures (table 1).
Figure 3. The elemental ratio of Pb/(Zr+Ti) through the thickness of the bi-layer films. On the scale of the abscissa "0" corresponds to the free surface of the samples.

Table 1. The content of elements (in relative units) in the near-surface region of thin PZT films.

| Structure «I»       | Structure «II»       |
|----------------------|----------------------|
| amorphous phase      | perovskite phase     |
| Ti/(Zr+Ti)           | 0.458                |
| amorphous phase      | 0.442                |
| Pb/(Zr+Ti)           | 1.21                 |
| perovskite phase     | 0.44                 |
| Pb/(Zr+Ti)           | 1.07                 |
|                      | 0.99                 |
|                      | 1.02                 |

Figure 4. The reversible dependences of the dielectric constant and the dielectric hysteresis loops of the structures «I» (a), (c) and «II» (b), (d), correspondingly.
In structure «I», excess lead from the upper layer is displaced both into the lower and upper parts of the film, evaporating from the free surface. In structure «II», the displacement of lead from the lower layer mostly occurs in the upper part of the film, and thus, in the latter case, the loss of excess lead turns out to be less.

The study of the reversible dependences of the dielectric constant ($\varepsilon$-$V$) revealed some differences in the magnitudes and character of the curves (figure 4(a), (b)). In structure «I», the dielectric constant was approximately 15% higher than in structure «II». In addition, the $\varepsilon$-$V$ asymmetry of the curve, which indicates the presence of an internal field, was larger in structure «I» than in structure «II». The dielectric hysteresis loops, measured at a frequency of 1 kHz, had a character similar to the behavior of $\varepsilon$-$V$ curves. In structure «I», the hysteresis loops were almost symmetrical (figure 4(c)). In structure «II», the loops were shifted along the abscissa axis, and the internal field reached nearly 12 kV/cm (figure 4(d)). The existence of an internal field in bi-layer structure «II», and the absence of such a field in the structure «I» confirms that the excess lead oxide, localized near the bottom interface of the film, takes participation in the formation of a space charge and a polarizing field.

4. Conclusions
It was shown that during the crystallization of the perovskite phase of bi-layer PZT structures, a decrease in elemental inhomogeneity was observed as a result of diffusion of lead atoms into the lead-depleted region. The dielectric properties of the structures differ significantly depending on the sequence of layers with different lead contents.

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