

Composition control of PZT thin films by varying technological parameters of RF magnetron sputter deposition

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Abstract. The article presents the effect of technological parameters of RF magnetron sputtering on the concentration of components of thin-film ferroelectric structures based on lead zirconate titanate PZT in the region of the morphotropic phase boundary. It is shown that by changing the distance from the target to the substrate and the pressure of the working gas mixture Ar + O₂, it is possible to vary the composition of the deposited thin layers.

1. Introduction

Solid solutions of zirconate-titanate lead are now one of the main materials of modern piezo-engineering [1]. Anomalous high values of the dielectric and piezoelectric characteristics of structures based on them are observed in the region of the morphotropic phase boundary (MPB), which separates the rhombohedral and tetragonal modifications of the ferroelectric phase (figure 1). Recently, these anomalies have been attributed to the existence of an intermediate monoclinic phase in the MPB region [2]. Particular attention is paid to the possibilities of forming thin-film structures based on PZT with extremely high piezoelectric characteristics. At the same time, the formation of such structures is associated with the need for fine-tuning the elemental composition of the PZT in the region of MPB. For practical purposes it is also important to obtain self-polarized thin films in which macroscopic polarization, comparable in magnitude to spontaneous polarization, is formed directly in the process of their formation [3–5]. In a number of works it is assumed that the appearance of a self-polarized state in thin PZT layers is associated with an excess content of lead in the form of an oxide [4–6]. The main goal of this work was to study the fine tuning of the composition of PZT films (changes in the ratio of Zr/Ti atoms and excess Pb atoms) in the region of MPB using the RF magnetron method of their formation with variation of technological parameters.

2. Experimental procedure

The studied samples of ferroelectric PZT films with a thickness of 500 to 800 nm were formed by a two-step procedure [7]. In the first stage, the films were deposited by the RF magnetron sputtering



method in an argon-oxygen atmosphere on a silicon substrate coated with a layer of platinum 80 nm thick at $\sim 150^\circ\text{C}$. Ceramic targets $(1-x)\text{PbTiO}_{3-x}\text{PbZrO}_3$ of compositions corresponding to the MPB region ($x = 0.53$ and 0.54) were used for sputtering. Variations in the composition of the deposited films were carried out by: a) changing the pressure of the working gas mixture in the range 2...8 Pa; b) changing the target-substrate distance in the range from 30...70 mm. In the second stage, the formed films were annealed in air in the range 580...600 $^\circ\text{C}$ for 1 h.

The structure of the films was determined using an optical microscope Nikon Eclipse LV150, an atomic force microscope Ntegra Prima (NT-MDT, Zelenograd) and a scanning electron microscope Zeiss EVO-40. The electron X-ray microanalyzer based on energy-dispersive analyzer INCA with the electrons energy about 12 keV was used for the composition analysis. Dielectric measurements were carried out using the E7-20 immittance and the modified Sawyer Tower scheme.

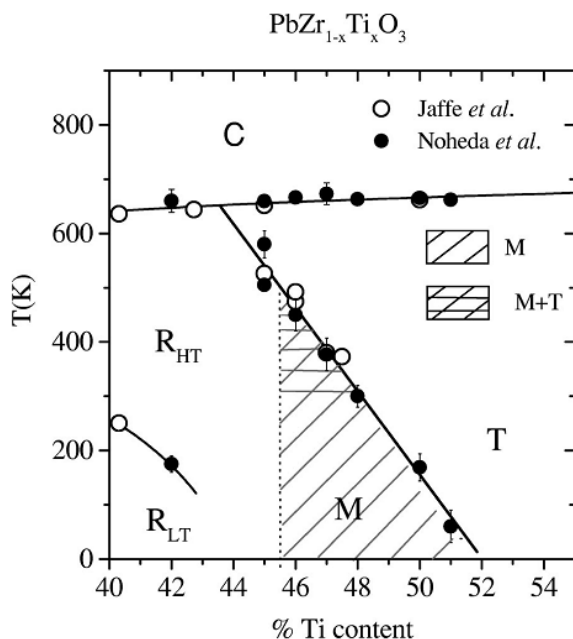


Figure 1. Phase diagram of PZT in the region of the morphotropic phase boundary: T – the region of the tetragonal phase; R – the region of the rhombohedral phase; M – the region of the monoclinic phase; C – region of the cubic phase (according to [1–2]).

3. Experimental results and discussion

Changes in the composition of deposited films with a variation in the pressure of the working gas and the distance between the target and the substrate are shown in figures 2 and 3. From figure 2(a) that an increase in the working gas pressure ($x = 0.46$) led to a significant change in the concentration of lead in the films (of the order of 30 %). The $\text{Pb}/(\text{Ti} + \text{Zr})$ dependence was a monotonically increasing curve, the initial value of which at 2 Pa corresponded to a composition with a strong lack of lead relative to the stoichiometric composition PZT – $\text{Pb}/(\text{Ti} + \text{Zr}) = 0.93$. Because of this, the crystallization of the perovskite phase occurred only in local regions of films islands, whose formation and growth was possible due to the migration of missing lead atoms to the interphase boundary of pyrochlore-perovskite during high-temperature annealing. At 8 Pa, the amount of excess lead was about 25 %, and the formed film was a composite structure consisting of PZT perovskite regions and PbO microinclusions. Thus, it turned out that the variation of the working gas pressure can change the relative content of lead atoms in a very wide range of concentrations.

The reason for such changes in lead content is related to the processes of scattering of sputtered target atoms in a gas plasma under conditions of a specific geometry of the mutual location of the circular zone of erosion of the ceramic target and substrate (figure 4). Analysis of literature data shows that in the investigated pressure range of the working gas medium, the so-called thermalization of lead atoms occurs when the directed motion of atomized atoms begins to be replaced by a diffusion motion characterized by an isotropic form of atom propagation [8–9].

In contrast to a strong change in the lead content with increasing working gas pressure, the ratio of $\text{Zr}/(\text{Ti} + \text{Zr})$ atoms varied in a relatively small range - no more than 2.5 % (figure 2(b)). The dependence of $\text{Zr}/(\text{Ti} + \text{Zr})$ on the pressure of the working gas was a curve with a maximum. However, such changes are sufficient to scan the composition of practically the entire expected MPB region at room temperature (figure 1). Of practical interest is the right-hand side of the curve, which corresponds to perovskite films with an excessive lead content and does not contain inclusions of the low-temperature pyrochlore phase. The presence of a maximum on the curve $\text{Zr}/(\text{Ti} + \text{Zr})$ indicates the presence of at least two different mechanisms that lead to a change in the composition of the films. The left-hand side of the curve (at low pressures of the working gas) can be connected with the final stage of the thermalization of zirconium atoms, and the right-hand side can be related to the difference in the redox potentials of zirconium and titanium atoms.

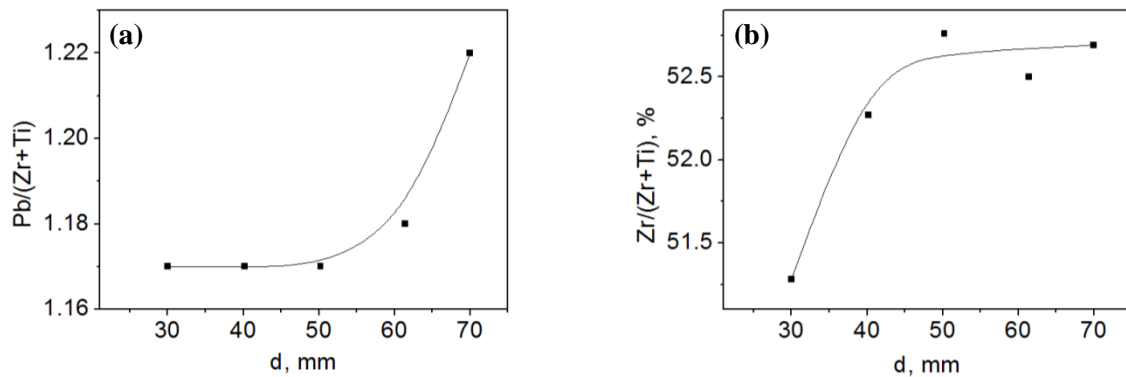


Figure 2. Graphs of the change in the ratio of the $\text{Pb}/(\text{Ti} + \text{Zr})$ (a) and $\text{Zr}/(\text{Ti} + \text{Zr})$ (b) atoms in thin PZT films prepared by sputtering a ceramic target $x = 0.46$ with the addition of 10 mol. % PbO at a pressure variation of the working gas. The film thickness is 800 nm.

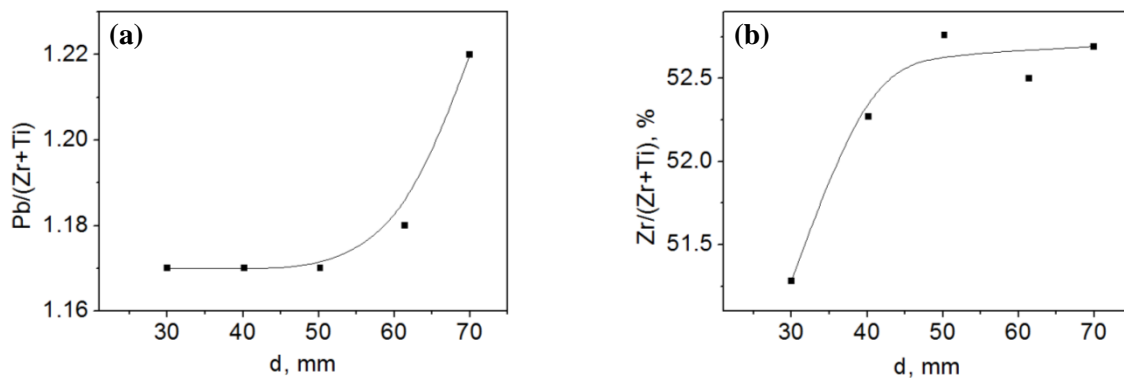


Figure 3. Graphs of the change in the ratio of the $\text{Pb}/(\text{Ti} + \text{Zr})$ (a) and $\text{Zr}/(\text{Ti} + \text{Zr})$ (b) atoms in thin PZT films prepared by sputtering a ceramic target $x = 0.47$, 500 nm thick from the distance (d) between the target and the substrate. Working gas pressure is 8 Pa.

On the basis of the approach on the thermalization of sputtered atoms of the ceramic target PZT, it was assumed that the composition of the deposited films can vary with a change in the distance (d) from the target to the substrate. In figure 3 presents the averaged results of the change in the composition of PZT layers deposited at a working gas pressure of 8 Pa, varying the distance from the target to the substrate in the range $d = 30\text{--}70$ mm. To reduce the lead content, a ceramic target of the stoichiometric composition PZT with $x = 0.47$ was used. In the process of high temperature annealing, single phase perovskite films with a thickness of ≈ 500 nm were obtained.

It is seen that with increasing d , the content of lead atoms $\text{Pb}/(\text{Ti} + \text{Zr})$ increased by approximately 5 %, from 1.17 to 1.22 (figure 3(a)). The behavior of the curve indicates that the atomic thermalization

process is not complete for lead atoms, while a slight increase in the $\text{Zr}/(\text{Ti} + \text{Zr})$ atoms content by $\approx 1\%$ (figure 3(a)) is determined, apparently, by diffusion processes in the gas plasma of titanium atoms.

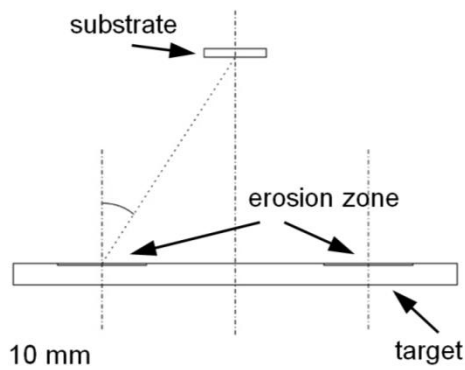


Figure 4. Diagram of the mutual arrangement of the substrate and the erosion zone of the target in an RF magnetron sputtering installation.

In films deposited from a target with a stoichiometric composition ($x = 0.47$), volt-capacitive characteristics and dielectric hysteresis loops were studied, and according to the asymmetry (the value of the internal electric field), one can judge qualitatively the degree of unipolarity of the formed films (figure 5). Preliminary results indicate that a unipolar state was observed in all the samples studied, and the value of the internal field was 17–25 kV/cm. However, in order to obtain an unambiguous regularity, additional research is needed.

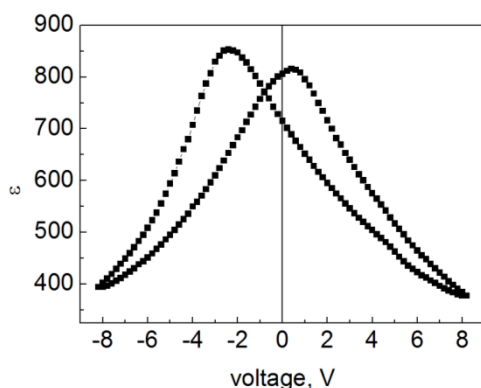


Figure 5. Voltage-capacitor (ϵ -V) curve for thin-film composition $x = 0.47$ ($d = 30$ nm).

The crystalline structure analysis of annealed PZT films by the scattered electrons diffraction method in the scanning electron microscope showed the presence of monoclinic phase in the films with the concentration increasing with the decrease of working gas pressure and the decrease of target-template distance.

4. Conclusions

The conducted studies showed that the change in the technological parameters of the RF magnetron sputtering (by varying the working gas or the distance between the sputtered target and the substrate) can, within a wide range (several tens of percent), change the lead content in thin PZT films whose composition corresponds to the morphotropic phase boundary, and also within several percent smoothly change the ratio of zirconium and titanium atoms. This makes it possible to search for optimal PZT compositions, and also to form thin films with a given composition gradient along their thickness.

Acknowledgments

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References

- [1] Jaffe B, Cook W R and Jaffe H 1971 *Piezoelectric Ceramics* (London: Academic Press)

- [2] Noheda B, Cox D E, Shirane G, Guo R, Jones B and Cross L E 2001 *Phys. Rev. B* **63** 014103
- [3] Sviridov E, Sem I, Alyoshin V, Biryukov S and Dudkevich V 1995 *Mater. Res. Soc. Symp. Proc.* **361** 141–6
- [4] Kholkin A L, Brooks K G, Taylor D V, Hiboux S and Setter N 1998 *Integrated Ferroelectrics* **22** 525–33
- [5] Afanasjev V P, Petrov A A, Pronin I P, Tarakanov E A, Pankrashkin A V, Kaptelov E Yu and Graul J 2001 *J. Phys.: Condensed Matter* **13** 8755–63
- [6] Suchaneck G, Sandner T, Deineka A, Gerlach G and Jastrabik L 2004 *Ferroelectrics* **289** 309–16
- [7] Pronin I P, Kaptelov E Ju, Senkevich S V, Klimov V A, Zajceva N V, Shaplygina T A, Pronin V P and Kukushkin S A 2010 *Physics of Solid State* **52** 124–8
- [8] Volpyas V A and Kozyrev A B 2011 *J. Exp. Theor. Phys.* **113**(1) 172–9
- [9] Volpyas V A, Tumarkin A V, Michaylov A K, Kozyrev A B and Platonov R A 2016 *Technical Physics Letters* **42**(14) 87–93