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### **Microstructure and ferroelectric properties of submicron polycrystalline lead zirconate titanate films with a gradient composition distribution over the thickness**

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**Abstract.** The paper presents the results of two-layer thin ferroelectric PZT films studies with a change in the lead content over the thickness of the films, obtained by RF magnetron deposition at various pressures of the working gas mixture. The microstructure and elemental composition were investigated by scanning electron microscopy and electron probe X-ray spectral microanalysis. It is shown that the elemental composition and dielectric properties depend on the sequence of layers deposition. The results obtained make it possible to characterize the physical mechanism of self-polarization formation in thin PZT films.

**Keywords:** thin ferroelectric films, lead zirconate titanate, RF magnetron sputtering, non uniform distribution of lead over the thickness

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Материалы конференции

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### **Микроструктура и сегнетоэлектрические свойства субмикронных поликристаллических пленок цирконата титаната свинца с градиентным распределением состава по толщине**

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**Аннотация.** В работе представлены результаты исследований двухслойных тонких сегнетоэлектрических пленок ЦТС с изменением содержания свинца по толщине пленок, полученных ВЧ-магнетронным напылением при различных давлениях рабочей газовой смеси. Микроструктуру и элементный состав исследовали методами сканирующей электронной микроскопии и электронно-зондового рентгеновского микроанализа.

Показано, что элементный состав диэлектрических свойств зависит от последовательности нанесения слоев. Полученные результаты позволяют охарактеризовать физический механизм формирования самополяризации в тонких пленках ЦТС.

**Ключевые слова:** тонкие сегнетоэлектрические пленки, цирконат титаната свинца, высокочастотное магнетронное распыление, неоднородное распределение свинца по толщине

**Ссылка при цитировании:** Валеева А.Р., Пронин И.П., Каптелов Е.Ю., Сенкевич С.В., Немов С.А., Старицын М.В., Микроструктура и сегнетоэлектрические свойства субмикронных поликристаллических пленок цирконата титаната свинца с градиентным распределением состава по толщине // Научно-технические ведомости СПбГПУ: Физико-математические науки. 2023. Т. 16. № 1.1. С. 74–78. DOI: <https://doi.org/10.18721/JPM.161.112>

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## Introduction

Thin ferroelectric films with a perovskite structure are increasingly used in dynamic and static memory elements, microelectromechanical (MEMS) devices, infrared devices, energy harvesters, magnetoelectric converters, and other devices [1–5]. Of greatest interest are polycrystalline thin films of  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  solid solutions (PZT), whose composition corresponds to the region of a morphotropic phase boundary (MPB), where extremely high values of dielectric, electromechanical, pyroelectric, and a number of other physical characteristics are observed [6].

A serious obstacle to achieving the maximum parameters, which leads to smearing of the MPB, is the elemental inhomogeneity of the PZT films over the thickness, associated with both the inhomogeneous distribution of Zr/Ti atoms and of superstoichiometric lead presented in the form of its oxide [7–9]. The reasons for the elemental inhomogeneity may be caused by a number of reasons, related to the methods of forming thin films, the mechanisms of perovskite phase crystallization, as well as a number of parameters, such as the material of the lower electrode, deposition and synthesis temperatures, film thickness, and so on [8, 10, 11]. In [8], in order to reduce the inhomogeneity in the distribution of Zr(Ti) atoms in sol-gel PZT films, each of the precursor sublayers (about 250 nm thick) was formed with a given change (gradient) in the Zr/Ti elemental ratio over the thickness. This approach made it possible to reduce the Zr/Ti gradient by a factor of three (from ~ 15% to ~ 5%) within each layer and significantly increase the dielectric permittivity. In [12, 13] two-layer PZT structures with different compositions were formed by ion-plasma deposition and characterized. It was shown that the phase state, dielectric properties, and such an important characteristic for MEMS as the magnitude of self-polarization (or internal field) [14, 15] depend on the order of the layers in thickness. In contrast to the previous study, bi-layer structures are characterized by the equality of the thicknesses of each of the layers, the reduced total thickness of the two-layer structure, slight variation in the composition (elemental ratio of Zr/Ti) and increased sintering temperatures of the layers.

## Materials and Methods

Two-layer structures were fabricated by RF magnetron sputtering of ceramic PZT target with composition, corresponding to MPB, at two pressures (4 and 8 Pa) of the working gas [16]. Thus, the bi-layer PZT structures consisted of two layers, each 300 nm thick, deposited sequentially at 8 and 4 Pa (sample I) or 4 and 8 Pa (sample II). To form perovskite phase, the samples were then annealed at conventional furnace at 600 °C in air. The platinumized silicon substrate with an adhesive sublayer of titanium dioxide ( $\text{Pt}/\text{TiO}_2/\text{SiO}_2/\text{Si}$ ) used as a substrate. Upper platinum  $120 \times 120 \mu\text{m}$  contact pads were applied to study dielectric properties.

LYRA 3 scanning electron microscope (Tescan) with the X-Max 80 energy dispersive attachment (energy of the probe beam was 12 keV) used for microstructure and elemental analyses. To control the phase state, X-ray diffraction and optical microscopy were attracted. E7-20 immittance meter used to diagnose the dielectric properties. Dielectric hysteresis loops were studied at modified Sawyer-Tower circuit at 1 kHz.

### Results and Discussion

Table 1 shows the elemental analysis data for amorphous structures and structures annealed at 600 °C. It can be seen that the lead content in the PZT layer, deposited at 4 Pa, is slightly lower than the stoichiometric ( $Pb/(Zr + Ti) \sim 0.99$ ) and nearly 17% less than in the layer deposited at 8 Pa ( $Pb/(Zr + Ti) \sim 1.16$ ), and Ti/Zr ratio is closed to 45/55. Structure annealing resulted in invariability of Pb content and decrease in Ti of about 1% in the top layer of sample I and in essential decrease of Pb content and increase in Ti of about 1% in the top layer of sample II.

The composition changes (Ti/Zr ratio) on depth in annealed structures are defined by the changes in perovskite phase formation. In sample I perovskite nucleation occurs near the lower interface of the structure, while in sample II it occurs near its upper surface. Since the synthesis temperature of the perovskite phase is lower for lead titanate than for lead zirconate, this leads to the migration of Ti atoms in the direction of the nucleation centers of the perovskite phase and, as a consequence, to partial segregation of titanium and zirconium atoms [8]. Nevertheless, estimates show that in the sintered structures, the total inhomogeneity in the Ti/Zr distribution of atoms over the thickness does not exceed 5%.

Table 1

The data of elemental analysis of the amorphous and high temperature annealed PZT structures and dielectric parameters of perovskite capacitor

Samples I and II	Pb/(Zr + Ti)		Ti/Zr		$\epsilon_{max}$ , 10 kHz	$(P_r^+ + P_r^-)/2$ , $\mu C/cm^2$
	Amorphous phase	Perovskite phase	Amorphous phase	Perovskite phase		
$\frac{4Pa}{8Pa}$	0.99	0.99	44.7/55.3	43.6/56.4	1000	16
$\frac{8Pa}{4Pa}$	1.16	1.05	45.1/54.9	45.9/54.1	880	13

A comparison of the dielectric properties of bi-layer structures showed that in structure I the dielectric permittivity ( $\epsilon_{max}$ ), obtained from the reversible dependences of  $\epsilon(V)$  (Fig. 1 and Table 1), noticeably exceeds the analogous value characteristic of structure II. An even greater difference was observed for the values of the remanent polarization  $P_r$  (Fig. 2, a, b, Table 1).

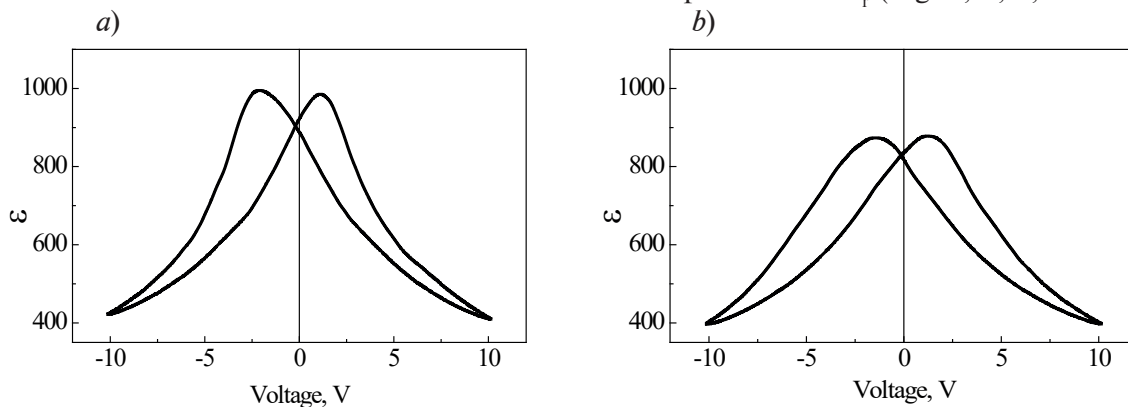


Fig. 1. The reversible dependences of dielectric permittivity ( $\epsilon-V$ ) of samples I (a) and II (b).

Such differences are likely related to the fact that during the nucleation of the perovskite phase in the lower part of structure I excess lead is squeezed upwards and enriches the upper layer, which leads to almost complete crystallization of the structure into the perovskite phase [10, 16]. In structure II the nucleation of the perovskite phase in the upper layer leads to both extrusion of lead into the lower part of the structure and migration to the surface, where oxidized lead evaporates into the atmosphere. In this case, we assume that when lead is deficient, local microregions of the nonferroelectric pyrochlore phase remain near the lower interface, which are

characterized by a low ( $\sim 30\text{--}40$ ) dielectric permittivity. This leads both to a decrease in the effective dielectric permittivity of the two-layer structure and to a redistribution of the applied external voltage between the regions of the pyrochlore and perovskite phases and to a decrease in the switchable polarization.

Figures 2, *c* and 2, *d* reflect the difference in the behavior of the internal field values, obtained from the hysteresis loops in structures I and II with an increase of applied voltage amplitude. The presence of an internal field ( $E_{\text{int}}$ ), whose vector in both cases is oriented towards the free surface of the structure, reflects the inhomogeneous distribution of charged oxygen vacancies over the thickness of the structure. The observed difference in the behavior of  $E_{\text{int}}$  (V) in structures I and II still remains unclear and requires further research.

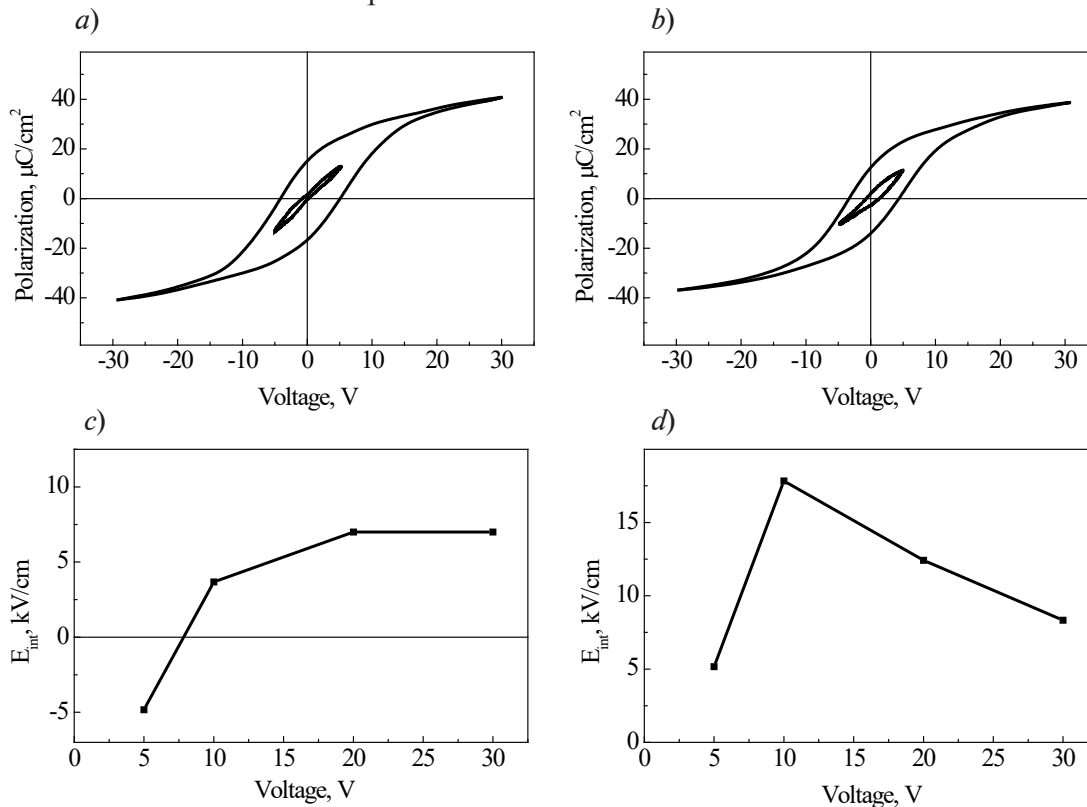


Fig. 2. Variations of hysteresis loops and internal field ( $E_{\text{int}}$ ) depending on the applied voltage of samples I (*a, c*) and II (*b, d*), correspondingly

### Conclusion

Two bi-layer ferroelectric PZT structures with a highly inhomogeneous distribution of lead over the thickness were formed, the difference between which was in the sequence of layer deposition at working gas pressures of 4 and 8 Pa. The thickness of each of the layers was 300 nm. Crystallization of the perovskite phase was carried out at 600 °C. It is shown that a change in the sequence of deposition leads to a difference in the composition and a change in the mechanism of the perovskite phase crystallization, which, in turn, leads to a difference in the values of the dielectric permittivity, remanent polarization and internal field.

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