The change in the phase state of thin PZT layers in the region of the morphotropic phase boundary obtained by the RF magnetron sputtering with varying target-substrate distance

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Abstract. The relationship between the microstructure, composition, phase state, and dielectric properties with a change in the distance from the target to the substrate (in the range 30–70 mm) was studied for high-frequency magnetron deposition of thin layers of lead zirconate-titanate (PZT). The composition of the sputtered target of the solid solution of PZT (PbZr0.54Ti0.46O3) corresponded to the region of the morphotropic phase boundary. After depositing the film, the perovskite structure was formed at 580 °C. It is shown that the variation of the distance leads to a change in the composition (elemental ratio of Zr/Ti atoms) within 2%, the character of the spherulite radiant microstructure of the layers, the volumes of monoclinic and tetragonal modifications of the ferroelectric phase coexisting in this concentration region, and also the dielectric properties.

1. Introduction
The solid solutions of lead zirconate-titanate (PZT), corresponding to a morphotropic phase boundary (MPB) between rhombohedral and tetragonal modification of the ferroelectric phase, is characterized by anomalously high electromechanical and piezoelectric moduli [1]. Ceramic materials, corresponding to these compositions, are currently the basic materials of modern piezo-technic. In a number of recent studies, these anomalies have been attributed to the existence of an intermediate monoclinic phase in the MPB region [2–3]. In ceramic solid solutions of PZT, the MPB region, as a rule, occupies an interval of concentrations not exceeding 1–2 percent. However, segregation of zirconium (or titanium) atoms in perovskite microregions can occur due to the use of insufficiently finely dispersed initial metal oxide powders, and also due to the difference in the crystallization temperatures of the perovskite phase in lead titanate (PbTiO3) and lead zirconate (PbZrO3). This leads to elemental microinhomogeneity and, as a result, to the expansion of the region of the MPB and to the decrease of the abnormally high physical characteristics, both in bulk solid solutions and in thin layers of the PZT [4–5]. The aim of the present work was to study the phase state and dielectric properties of thin PZT layers in the MPB region, obtained by high-frequency sputtering of a ceramic target with a variation of the distance from the target to the substrate.

2. Sample preparation and research
A ceramic target of a solid solution (1-x) PbTiO3-x PbZrO3 of composition equal to x = 0.54 was
chosen for the studies. Thin PZT layers with a thickness of ≈500 nm were formed by a two-step procedure [6]. In the first stage, amorphous thin PZT layers were deposited by the RF magnetron sputtering of a ceramic target in an argon-oxygen atmosphere at ~150 °C on silicon substrates, and also on silicon substrates with silicon dioxide sublayers (500 nm thick), titanium dioxide (20–30 nm) and platinum (80 nm) (Si/SiO$_2$/TiO$_2$/Pt). In the second stage, the structures were annealed in air at 580 °C for 1 hour to obtain single-phase perovskite PZT layers deposited on the Si/SiO$_2$/TiO$_2$/Pt substrate. The composition, microstructure, and dielectric properties of thin PZT layers were studied by varying the distance from the target to the substrate (d) in the interval 30-70 mm in steps of 10 mm.

The microstructure of the films was determined using a scanning electron microscope Carl Zeiss EVO-40. To determine the elemental composition, we used an electron-dispersive attachment INCA, the energy of the probing electrons was 12 keV. The phase state was determined using X-ray diffraction analysis (DRON-7), as well as the method of electron backscatter diffraction (EBSD). To determine the dielectric constant, the immittance meter E7-20 was used. The measurement frequency was 10 kHz, the measuring voltage was 40 mV. C-V characteristics were measured by applying a constant bias voltage in the range ±0–8 V.

3. Results and discussion

The results of the change in the composition of the deposited films are shown in figure 1. To obtain them, amorphous thin films of PZT deposited on a silicon substrate (in the absence of a platinum sublayer) were used to avoid distortion in the composition due to the proximity of the L$_{o}$-line of zirconium (2.042 keV) and M$_{o}$ the platinum line (2.048 keV) [7] The change in the distance (d) between the target and the substrate, as seen in figure 1, a, led to a change in the composition of the solid solution of thin amorphous films.

![Figure 1](attachment:image.png)

**Figure 1.** Changes in the content of Ti (a) and the ratio of Pb / (Ti + Zr) atoms (b) in PZT films with varying target-substrate distance.

The elemental ratio of atoms varied from Ti/Zr ≈ 47/53 in films deposited at d = 30 mm to ≈ 45.3/54.7 in films deposited at d = 70 mm. Thus, the composition change in the region of the MPB was about 1.7% with a change in d from 30 to 70 mm. Somewhat more, about 5%, the content of lead atoms changed as d increases, expressed as the elemental ratio Pb/(Ti + Zr), figure 1(b).

The reasons for such changes are 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 the substrate placed in the center. Analysis of the literature data shows that in the investigated target-substrate distance interval at the working gas pressure of 8 Pa, the lead atoms become thermalized when the directed motion of the atomized atoms is replaced by a diffusion motion characterized by an isotropic form of atom propagation [8].

The SEM images in figures 2(a), (c), (e) reflect the change in the spherulitic microstructure of the perovskite phase in thin PZT layers formed on Si/SiO$_2$/TiO$_2$/Pt substrates with increasing d obtained in the mode of selection of backward reflected electrons. The change in the spherulite microstructure
consisted in a decrease in the average size of the spherulite blocks with increasing d (i.e., with an increase in the concentration of the nucleation centers of the perovskite phase), as well as in the density of radial rays in spherulite blocks.

Figure 2. SEM image in the mode of selection of backward reflected electrons (a), (c), (e) and phase images (b), (d), (f) of PZT films formed at different distances from the target to the substrate: 30 mm (a), (b), 50 mm (c), (d) and 70 mm (e), (f).
It can be seen that in films deposited at \( d = 70 \) mm, the radial character of the structure is close to disappearing (figure 2(d)). It can be assumed that such changes are associated with a change in the microinhomogeneity of the atoms that make up the composition of the film. However, in order to understand the reasons for such changes, separate studies are required.

Figures 2(b), (d), (f) shows the changes in the ratio of monoclinic and tetragonal modifications of the ferroelectric phase determined by the EBSD method [9]. Variations in the distance from the target to the substrate led to a slight change in the stability of the monoclinic and tetragonal modifications of the ferroelectric phase. Averaging over scanning regions equal to 50*50 \( \mu \text{m} \) showed that the ratio of volumes of monoclinic (M) and tetragonal (T) phases increased from M/T \( \approx 52/42 \) in films deposited at \( d = 30 \) mm to \( \approx 55/40 \) in films deposited at \( d = 70 \) mm (part of the volume of the films could not be identified). The reasons for such minor changes in the stability of the M and T phases when the composition of the solid solution is changed by 2 \% may indicate a significant width of the MPB region. However, it should be taken into account that the obtained data give information only about the thin near-surface layer of the PZT (not exceeding several nanometers). Changes in the volume of the film can be more significant, which, however, requires the use of other methods of investigation.

Figure 3 shows the characteristic volt-capacitive C-V curves (or reverse dependences of the dielectric constant, \( \varepsilon \)-V) for the Pt/PZT/Pt capacitor structures at different distances from the target to the substrate (30 mm and 70 mm). It can be seen that in a film made at \( d = 70 \) mm, a large value of the dielectric constant is observed, and the C-V dependence itself takes a more symmetrical form.

Figure 4 shows the dependence of the value of the internal field \( E_{\text{int}} \) (a) and the dielectric permittivity (b) of the PZT films with a change in \( d \), measured at room temperature. The value of \( E_{\text{int}} \) (figure 4(a)) was determined from the shift of the C-V characteristics along the abscissa axis toward negative voltages (see figure 3), which corresponded to the orientation of the field vector directed from the free surface to the lower electrode.

With increasing target-substrate distance, the \( E_{\text{int}} \) fell monotonically. This behavior can be explained by the increase in the amount of lead oxide, but this contradicts its role in the formation of the internal field and the naturally unipolar state in thin PZT films [10]. However, the nature of the dependence can be explained if to assume that the observed changes are associated with a change in the location of excess lead oxide between the lower and upper interfaces.

Figure 4(b) reflects the anomalous behavior of the dielectric constant caused by the change in the composition of the PZT solid solution, the microstructure, and the phase state. It was expected that in the region of the MPB the dielectric constant will pass through a maximum, but the experimental data go against expectations. The reasons for this behavior are not yet clear and require further research.
4. Conclusions
The carried out researches have shown that by changing the distance from the target to the substrate, it is possible to vary (within 2 %) the composition of thin films of PZT in the region of MPB, which provides a tool for searching for optimal electromechanical parameters. It is shown that this leads to a strong change in the character of the spherolitic microstructure of the films, to the values of the internal field and the dielectric permittivity. However, additional research is required to find out the reasons for such changes.

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Figure 4. The experimental dependence of the permittivity (a) and the internal field (b) of thin PZT films with a change in the target-substrate distance.