The study of the properties of lead zirconate-titanate films on silicon substrate after halogen lamps rapid thermal annealing

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Abstract. Ferroelectric thin films of lead zirconate titanate (PZT) are important in the creation of ferroelectric MEMS, memory devices, sensors of physical quantities, and energy converters. Thermal annealing is used to obtain satisfactory electro-physical parameters and an optimal crystal structure PZT films. The rapid thermal annealing (RTA) in comparison with isothermal annealing has the possibility of selective annealing of individual layers of the multilayer PZT composition by selecting appropriate temperature and duration of the RTA. The purpose of this work is to study the phase-structural state of PZT films formed by high-frequency reactive plasma sputtering and subjected to rapid thermal annealing by halogen lamps. The PZT thin films with a thickness of 1.0 ± 0.1 µm were deposited by oxygen atmosphere high-frequency reactive plasma sputtering on silicon (100) substrates and silicon substrates with SiO₂ on surface. After applying, PZT film underwent RTA at temperatures of 600-800 °C and with speed 60 degrees/s. With X-ray phase analysis, the structure-phase composition of the PZT film is revealed. Besides that, the effect of RTA was investigated using electron microscopy. It is established that temperature change at RTA leads to a qualitative change in the phase-structural state of the PZT films as compared to their initial state. This gives a chance to use RTA in the formation of the PZT films with given parameters.

1. Introduction
The use of materials in microelectronics in the form of nanostructured thin polycrystalline and epitaxial films (ferroelectrics, ferromagnets, multiferroics, etc.) is largely determined by the state of the art of creating these films. First of all, this is due to the size effects, the density of structural defects and the nature of interaction with the substrate. Thin ferroelectric films of lead zirconate titanate (PZT) are among the most important in the creation of ferroelectric memory devices and ferroelectric microelectromechanical systems (MEMS), as well as sensors of physical quantities and energy converters [1-4]. The use of nanoscale ferroelectric films requires solving a number of technological problems. First of all, these are the tasks of choosing materials, optimizing the composition and thickness of the film, the homogeneity of the film structure, etc. [5, 6]. Herewith, an important problem in the formation of PZT films is their thermal annealing in order to achieve the optimum crystalline structure and electrophysical parameters films at the minimum heat treatment temperature. The advantage of rapid thermal annealing (RTA) in comparison with isothermal treatment, is the possibility of selective annealing of the PZT layer by selecting the appropriate temperature, duration and speed of the RTA [7]. The positive effect of RTA on the structure and electrical properties of PZT thin
films was noted, for example, in [8–10]. The authors showed that the use of RTA of PZT films is an effective tool for changing the crystal structure and improving the electrophysical properties of PZT films. However, in these methods, the PZT structure cannot be formed without thermal annealing. At the same time, the formation of a perovskite crystal structure by high-frequency reactive plasma sputtering already occurs in the process of film growth. Long-term heat treatment for the formation in this method is not used. RTA, in this case, can be used to improve the structure of PZT films.

Therefore, the aim of this work is to study the phase-structural state of PZT films formed by high-frequency reactive plasma sputtering and subjected to rapid thermal annealing by halogen lamps in the temperature range 600–800 °C.

2. Experimental
Ferroelectric PZT thin films of composition Pb(Zr0.3,Ti0.7)O3 were deposited by oxygen atmosphere high-frequency reactive plasma sputtering on p-type silicon (100) substrates and on the similar silicon substrates with SiO2 on surface. High-frequency reactive plasma sputtering was performed on the installation “Plasma 80 SE”. PZT films were formed at a power of 400 W, a substrate temperature of 400 °C and an oxygen pressure in the chamber of 0.45 Torr for 30 minutes. The thickness of formed PZT film was 1.0±0.1 μm. After deposition the film, PZT was subjected to RTA by halogens lamps in air at temperatures of 600–800 °C and speed 60 degrees/s. Rapid thermal annealing was carried out on the installation ITO-18M [11]. The surface of the initial samples and the samples after the RTA were examined using an electron microscope Nova NanoLab 600 - figure 1. The film thickness was measured using an MII-4 optical microscope. X-ray diffraction (XRD) analysis was performed on a DRON-3 unit at the CuKα wavelength - figure 2. The results of the study of the structural-phase composition of the PZT films are presented in table 1.

3. Results and discussion
The surface morphology of PZT films before and after RTA at 700 °C is shown in figure 1.

![Figure 1](image-url)

**Figure 1.** SEM images of the surface of the PZT films on silicon before annealing (a) and after RTA at 700 °C (b).

XRD analysis was performed by comparing the form of diffractograms with the card 01-070-4055 from the PDF-2 database. To highlight the diffractogram peaks in the background of noise, a Savitzky–Golay smoothing filter with an interval width of 7 was used. The initial phase structure of the PZT film formed on both oxidized silicon and silicon plain substrates was identical and is shown in figure 2, diffractogram a.
Studies have shown that the influence of all RTA temperatures on the structure of PZT films formed on oxidized silicon substrates was catastrophic. The perovskite structure of PZT in all cases was transformed into a pyrochlore structure. Further investigation of such films became impractical.

At the same time, it was seen for the PZT films that the polycrystalline perovskite structure of the PZT is formed in the direction of crystal growth (110) and (001) with pronounced preferential directions (110) - figure 2, diffractograms b, c, d. The measured ratio of the intensities of the peaks $I_{100}/I_{110}$ was 0.49-0.52 for the PZT samples that did not were exposed RTA and was expose the RTA at 500 °C and 600 °C. The ratio of peak intensities decreased to 0.43 for a sample annealed at an RTA temperature of 700 °C - figure 2. It can be seen that, at a temperature of RTA of 700 °C, a more pronounced formation of a crystalline perovskite (110) structure occurs. This trend is also noticeable in the growth of the size of the areas of coherent scattering of X-rays from PZT crystallites. The growth of the crystallinity of the structure with increasing temperature RTA affects the increase in the sizes of the PZT blocks. The measurements were carried out on the basis of SEM images of the surface of the PZT films before and after the RTA – figure 1. From table 1 and figures 1

![Figure 2. XRD patterns of PZT films before (a) and after RTA in the mode of 500 °C (b), 600 °C (c) and 700 °C (d).](image-url)

The size of the coherent scattering regions was estimated using the Scherrer’s equation [12]. The size of the coherent scattering regions of the perovskite (110) structure increased more than twice: from 13.0±0.3 nm for the PZT film without annealing to 30.0±4.9 nm for the sample annealed by RTA at temperature of 700°C – table 1. At the same time, the size of the regions of coherent scattering of crystallites of the perovskite (100) structure decreases from 51 to 18 nm. A similar behavior of the perovskite structure for isothermal annealing was observed in [13, 14].

**Table 1. Dimensional factors PZT film**

| Sample | PZT block size (nm) (SEM image) | Size of coherent scattering regions from (001) crystallite (nm) (XRD analysis) | Size of coherent scattering regions from (110) crystallite (nm) (XRD analysis) | Film thickness (µm) | $I_{100}/I_{110}$ |
|--------|--------------------------------|--------------------------------|--------------------------------|-------------------|------------------|
| Without RTA | 117 | 51 | 13 | 1,2 | 0,52 |
| RTA 500 | 132 | 47 | 20 | 1,2 | 0,49 |
| RTA 600 | 155 | 47 | 26 | 0,9 | 0,51 |
| RTA 700 | 285 | 18 | 30 | 0,8 | 0,43 |
it can be seen that as the RTA temperature increases, the block size on the surface of the PZT film increases: from 117±3 nm, for the PZT film without annealing to 285±5 nm for the sample annealed by RTA temperature of 700°C. The latter suggests that as the temperature of the RTA increases, a PZT film is compacted, which is also confirmed by a decrease in the PZT film thickness with an increase RTA temperature.

Studies shown that RTA leads to a qualitative change in the phase-structural state of the PZT film compared to its initial state. RTA of PZT films on oxidized silicon substrates, the perovskite structure of PZT films is transformed into the pyrochlore structure. RTA of PZT films on non-oxidized silicon substrates, reverse processes occur, namely, their crystallinity improves. On one hand, a more pronounced formation of the crystalline perovskite (110) structure occurs. This is expressed in an increase size of the regions of coherent scattering of crystallites and a decrease in the intensity ratio of the 110/110 peaks. On the other hand, a seal of the PZT film is observed, which is expressed in an increase in the size of the PZT blocks and a decrease in the film thickness at higher RTA temperatures. Data analysis showed that PZT films annealed at 500 °C – 600 °C have the best uniformity. The structure of studied films is represented by nanoscale grains with an average size of 20–47 nm, some of which form volumetric clusters that form in the direction of film growth, and is characterized by different grain sizes. The average grain size, the degree of granularity, and the number of columnar clusters in PZT films in range 500 °C – 600 °C RTA less than in other films studied.

4. Conclusions

The results obtained indicate that the observed differences in the structure and phase composition films of the initial state and after the RTA are mainly due to the existence and difference temperature gradient arising in the RTA process. Also, it should be noted that RTA leads to an increase in the crystallinity of PZT film and to the compaction of PZT film. Thus, the results of experimental studies have shown the possibility of using RTA to improve the structure of PZT films.

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