Radial non-uniform piezoelectric response of perovskite islands in thin PZT films

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Abstract. A comparative study of the morphology and piezoelectric response of island and continuous perovskite thin PZT films deposited on a platinized silicon substrate Si/SiO2/TiO2/Pt was carried out. It was shown that the self-polarization value of micron-size island films was about 1.4 times higher than that of continuous films. It is assumed that the difference is due to the relaxation of tensile mechanical stresses caused by silicon substrate at the island periphery.

1. Introduction
Thin Pb(Zr,Ti)O3 (PZT) films are used in various silicon microelectronic devices – memory elements (FRAM), microelectromechanical systems (MEMS), and other devices [1-4]. The silicon substrates lead to certain difficulties in their manufacturing due to the difference in the temperature coefficients of linear expansion of silicon and PZT compositions (Zr/(Zr+Ti) = 0.52-0.54) corresponding to the region of the morphotropic phase boundary (MPB). This leads to the appearance of tensile mechanical stresses acting on the thin PZT layer from the substrate, reorientation of the significant part of the spontaneous polarization in directions close to the substrate plane, and decrease in the normally oriented macroscopic polarization, the value of the switched polarization, and the electromechanical coefficients, etc. [5-7].

One way to avoid the deterioration of the above characteristics is to reduce the local (transverse) dimensions of the perovskite regions. Previous studies revealed an increase in switched polarization for micron (submicron) sizes of perovskite regions, demonstrating decrease in the negative role of tensile mechanical stresses [8]. In this regard, the aim of this work was to study the microstructure and physical properties of perovskite islands arising during high-temperature annealing of amorphous thin PZT films.

2. Experimental
Thin films were prepared by ex-situ method of RF magnetron deposition by varying the working gas pressure [9]. The deposited amorphous layers of the composition corresponded to MPB with a thickness of 500-1000 nm were annealed in air at temperatures Tann = 550-600°C. The substrate was platinized silicon wafers with buffer (SiO2) and adhesive (TiO2) layers [Si/SiO2/TiO2/Pt]. Morphology and piezoelectric response were measured using Nterga Prima nanolaboratory (NT-MDT). The contact mode was used for studying the piezoelectric response with the application of AC voltage of 5 V
amplitude at a frequency about 50 kHz. The scanning area did not exceed 60×60 µm². The microstructure of thin films was also studied by the second harmonic generation (SHG) [10].

3. Results

The crystallization of the perovskite phase during high-temperature annealing occurred by nucleation and growth of perovskite islands in the low-temperature (intermediate) pyrochlore matrix. The volume of the perovskite phase depended on the temperature and duration of annealing, as well as pressure of the working gas during film deposition. A study of the piezoelectric response showed that both individual islands and films completely formed in the perovskite phase were characterized by the presence of macroscopic polarization (self-polarization effect). It was shown earlier that the reasons for its appearance were associated with formation of a space charge of oxygen defects near the lower interface of the film, which produced the bulk field leading to orientation of the ferroelectric dipoles [11-12]. A comparison of the properties of individual islands, merging islands, and continuous films allowed revealing several features.

1. The histograms of the distribution of the continuous films were well-formed peaks, the shift of which along the abscissa axis reflected the magnitude of self-polarization (Fig. 1a). In contrast, the histograms of the perovskite islands were characterized by a wide range of values with two maxima, i.e., were strongly inhomogeneous (Fig. 1b). In this case, the displacement of the right-hand side of the distribution significantly exceeded the self-polarization values characteristic of a continuous film.

2. Figure 2 shows an unusual signal of SHG distribution of two perovskite islands touching each other. By the magnitude of the SHG signal, one can quantitatively judge the distribution of polarization in the plane of a thin film. It can be seen from the figure that the signal intensity is radially inhomogeneous and reaches maximum values at the periphery (“crusts”) of the islands. The width of the “crust” with a strong SHG signal region was ~ 3.5-4 µm. Another feature in the distribution was the absence of a strong signal at the boundary between two islands.

Figure 1. Histograms of the piezoelectric response distribution of (a) self-poled continuous and (b) island PZT films.

Figure 2. Nonlinear optical images (SHG) of two touching perovskite islands.
3. The heterogeneity of surface morphology was the most pronounced on the periphery of the islands (Fig. 3). At the interface between the perovskite and pyrochlore phases, an increase in the film thickness was observed from the side of the pyrochlore phase, which sharply decreased upon transition to the perovskite phase. A sharp drop, as is well known, is associated with a difference in phase densities [13-14]. The reason for the increase in thickness on the side of the pyrochlore phase is not entirely clear. On the one hand, this may be due to the excess lead oxide present in the deposited film, which is displaced to the interface during crystallization of the dense perovskite phase. On the other hand, a feature of the solid-state phase transformation of the film on the substrate surface is the transition through an intermediate state, which is characterized by an increase in the porosity of the film, and, as a result, an increase in its thickness. In particular, excess lead oxide can just lead to an increase in porosity.

4. A study of the piezoelectric response of perovskite islands, reflecting the degree of unipolarity (self-polarization), revealed a radial inhomogeneity: the maximum signal was observed at the edges of the islands, and the signal significantly decreased towards the centre. It turned out that the degree of radial heterogeneity depended on the size of the islands: with a size (diameter) increase, the signal

![Figure 3](image-url)

**Figure 3.** (a) The surface topography of the perovskite island; (b) the profile along the line.

![Figure 4](image-url)

**Figure 4.** (a,b,c) Piezoelectric force microscopy images and (d,e,f) piezoelectric response profiles of perovskite islands of various diameters.
changed more smoothly. It can be seen that the “crust” region was most clearly manifested in small islands (Fig. 4a), and with an increase in the diameter of the islands, the “crust” region was eroded (Fig. 4b,c). Nevertheless, the difference in the piezoelectric response in the centre of the island and at the periphery remained (Fig. 4).

4. Discussion
The analysis of the results obtained (Figs. 1-4) allowed us to make the assumption that the reason for the heterogeneity of the piezoelectric response of the islands, the signal of the second optical harmonic in them, and the difference in the distribution of the piezoelectric response in the continuous film and the island is related to the mechanical stresses acting on the PZT film from the silicon substrate [5-7]. The temperature coefficient of linear expansion of a thin film of the composition corresponding to MPB, as noted earlier, is greater than that of a silicon substrate, which leads to stretching of the film under the two-dimensional mechanical stresses. It is assumed that in the periphery of the perovskite island there is a relaxation of mechanical stresses on the pores, as a result of which the reorientation of the ferroelectric polarization is noticeably facilitated. We cannot exclude the greater likelihood of the formation of a monoclinic modification of the ferroelectric phase [15] in the absence of mechanical stresses [16]. This assumption is also supported by the results of studying the phase state of thin PZT films by the method of reflected electron diffraction, where the content (fraction) of the monoclinic phase increased in island perovskite films in comparison with continuous ones [17].

The results obtained indicate that the width of the “crust” with high piezoresponse values is equal 3.5-4.0 μm, where its value is approximately 1.4-1.6 times higher than in the continuous film. Based on these data, the dependence of the averaged piezoelectric response over the island area depending on its area is plotted in relative units (Fig. 5, solid curve). A constant value on the curve, equal to the unity, corresponds to the maximum signal of the piezoelectric response of the island, the radius of which does not exceed a critical size equal to the width of the "crust" ~ 3.7 μm. The decrease in the average piezoelectric response signal with an increase in the diameter of the island occurs to the level of the signal from the continuous film corresponding to the magnitude of the piezoelectric response signal in the central part of the island. For calculations, the signal magnitude was 1.4 times less than the piezoelectric response signal of the “crust”.

The points in Figure 5 correspond to the experimental data of the averaged values of the piezoelectric response signal over the area of islands normalized with respect to the maximum signal. It can be seen that a comparison of the model curve with the above parameters and experimental data is in good agreement with each other.

5. Conclusion
The results of the study suggest that, in order to obtain thin PZT films with maximum self-polarization, a periodic island structure should be constructed. A similar structure can be obtained, in particular, by femtosecond laser annealing [18-19]. Another chance for obtaining highly effective self-poled films is
the use of substrates with a higher temperature coefficient of linear expansion. In the latter case, the field of practical use of such films is limited by the complexity of integration with silicon microelectronics.

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