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Piezoelectric properties of spherulite thin films of lead zirconate titanate

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Abstract. We studied thin films of lead zirconate titanate, characterized by a spherulitic radial-radiant microstructure, the composition of which corresponds to the region of the morphotropic phase boundary, using the piezoelectric response force microscopy method. Features of the vertical and lateral piezoresponses and the surface potential (Kelvin mode) were revealed. We also compared the piezoelectric response with the radial microstructure features and mechanical stresses formed in the films as a result of crystallization of the perovskite phase from the amorphous phase.

Keywords: piezoelectric force microscopy, lead zirconate titanate thin films, radial-radiant spherulitic microstructure, mechanical stresses, surface potential

Introduction

It is well known that the synthesis of various kinds of thin films, both organic and inorganic materials, can result in the formation of polycrystalline spherulitic structures. Crystallization of spherulites can occur both from solutions and from a solid amorphous phase or during recrystallization of one or another phase (Kooi et al. 2004; Shtukenberg et al. 2012; 2014).

The formation of thin-film spherulitic structures occurs through the nucleation and growth of islands close in shape to ideal disks. The growth of spherulites is accompanied by the formation (branching) of low-angle fibrils (Shtukenberg et al. 2012). The forms in which spherulite structures occur are very diverse, to the point that in one compound, the microstructure of the spherulites can change radically when the synthesis temperature changes.

Among the most common and still the least studied spherulitic forms is the radial microstructure. Such formations, in particular, have been discovered and studied in semiconductors and various thin-film oxides — from metal oxides and quartzites to perovskite oxides (Alkoy et al. 2007; Kolosov, Thölén 2000; Kolosov et al. 2005; Pronin et al. 2018; 2023; Spierings et al. 1993; Staritsyn et al. 2023b; Zhigalina et al. 2018). Studies over the last two decades have shown that the growth of such spherulites is accompanied by a rotation of the growth axis. In quartz (SiO2, GeO2) and perovskite (Pb(Zr,Ti)O3) structures, the tilting gradient ranges from fractions to several degrees per micron (Lutjes et al. 2021; Musterman et al. 2022; Staritsyn et al. 2023b) while in some metal oxides, PLZT and semiconductors it is two orders of magnitude higher (Kolosov, Thölén 2000; Kolosov et al. 2005; Zhigalina et al. 2018). In the latter case, such structures are called transrotation crystals. According to (Lutjes et al. 2021; Musterman et al. 2022; Staritsyn et al. 2023b), the reason for the rotation of the growth axis during the solid-state crystallization of films lies in the mechanical stresses acting in the plane of the substrate caused by changes in the density of the initial and final phases.

Interest in studying the properties of spherulitic ferroelectric films of lead zirconate tatanate ($Pb(Zr,Ti)O_3$ or PZT) is due to the practical lack of data on this topic as well as the fact that PZT solid solutions of compositions corresponding to the region of the morphotropic phase boundary are currently the main materials for microelectromechanical devices (Izyumskaya et al. 2007; Song et al. 2021). The purpose of this work was to study the piezoelectric properties of spherulitic thin films of PZT formed on a platinized silicon substrate.

Sample preparation and research methods

Samples of PZT thin films were prepared by radio-frequency magnetron sputtering of a ceramic target onto a platinized silicon ($Pt/TiO_2/SiO_2/Si$) substrate. The composition of the stoichiometric target $PbZr_{0.54}Ti_{0.46}O_3$ corresponded to the region of the morphotropic phase boundary separating the tetragonal and rhombohedral (monoclinic) modifications of the ferroelectric phase (Cox et al. 2005; Staritsyn et al. 2023a). Deposition occurred at a low temperature and was determined by the heating temperature of the gas argon–oxygen plasma. The substrate temperature could be changed in the range of 90–160 °C by varying the target–substrate distance in the range from 70 to 30 mm (Pronin et al. 2023; Staritsyn et al. 2023a). This led to a change in the concentration of nucleation centers of the perovskite phase by approximately three times, and the average sizes of spherulite blocks, which are polygons, changed from approximately 10–15 to 40–50 μm. High-temperature annealing of the resulting amorphous films was carried out in the air in a SUOL 0.3.2/12 type tube furnace. The accuracy of temperature maintenance did not exceed 0.5 degrees. To obtain island perovskite films, the annealing temperature was 530–550 °C, at which the diameter of the spherulite islands reached 20–30 μm. To obtain continuous films, the temperature was increased to 580 °C. The thickness of the films under study was 500 nm.

Measurements of the piezoelectric response of PZT thin films were carried out using piezoresponse force microscopy (PFM) and Kelvin probe force microscopy (KPFM). To determine the vertical and lateral piezoresponses, an atomic force microscope (Ntegra Prima, NT-MDT SI, Russia) equipped with platinum-coated cantilevers (NSG01, NT-MDT SI, Russia) with a spring stiffness of ~5 N/m was used. The piezoresponse signal and its phase were measured in the contact mode by applying an alternating voltage of 5 V to the cantilever at a frequency of 50 kHz. The area of the scanned surface was 40×40 μm.

Experiments to determine the surface potential (Kelvin modes) were carried out using the same atomic force microscope. For KPFM measurements, the surface topography was first scanned in semi-contact mode, and then the probe was raised to a height of 50 nm, with a voltage of 1 V applied to it. All KPFM mappings were performed at room temperature, each mapping taking about 30 minutes.

Experimental results and their discussion

In island spherulitic films, the most significant results were obtained when studying the lateral piezoresponse and surface potential. Fig. 1 shows images of the lateral response (a–c) and the Kelvin mode signal (g–i) as well as the diametric distributions of the corresponding signals (d–f) and (j–l) respectively, for islands differing in size and the stage of crystallization of the perovskite phase. The diametral section of the lateral polarization indicates a radial distribution of polarization, from a signal close to zero to a maximum signal recorded near the interface of the spherulitic island with the nonpolar low-temperature pyrochlore phase surrounding the island. The polarization vector is directed from the center of the island towards the periphery. That is why, in the diametrical distribution, the signal of the lateral piezoresponse in the center of the island passes through the zero mark.

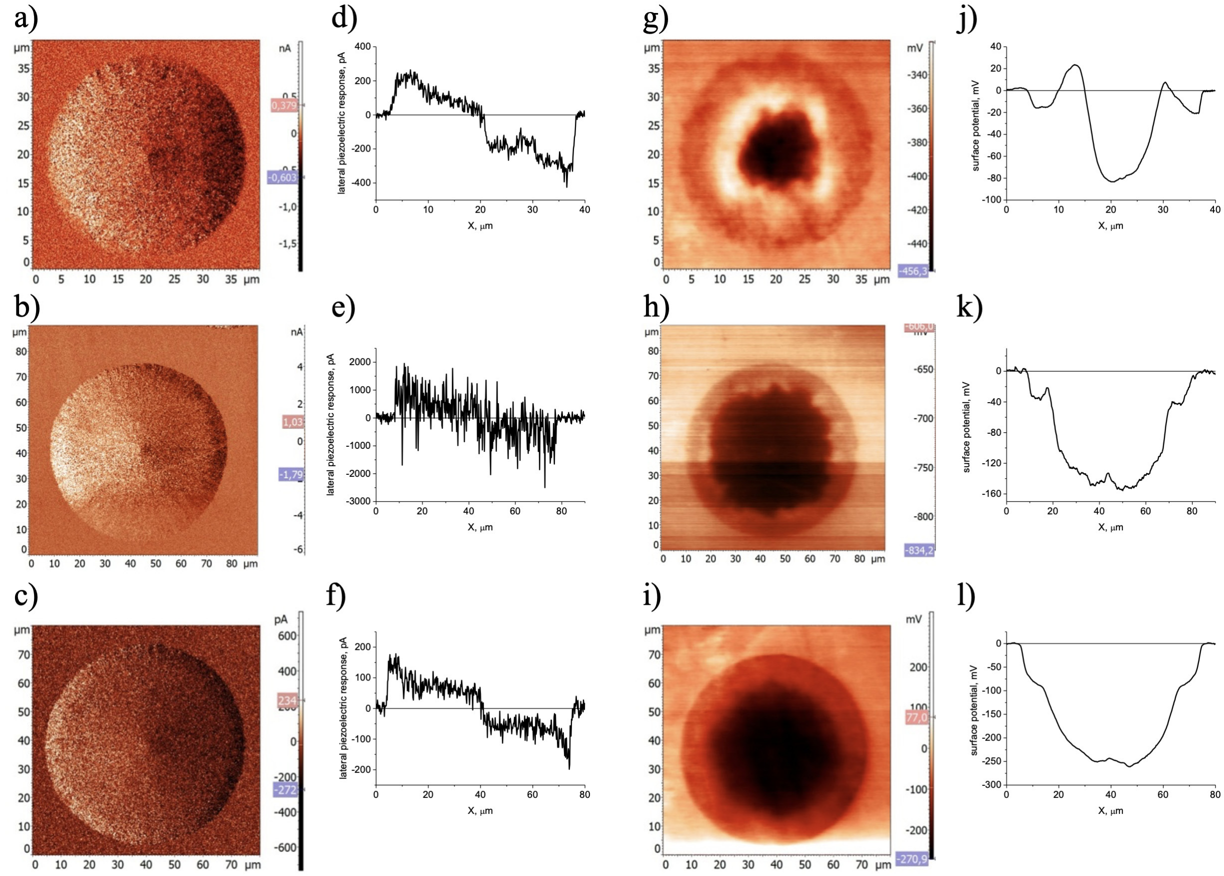

Fig. 1. Images of the lateral piezoelectric response (a, b, c) and surface potential (Kelvin mode) (g, h, i) of perovskite islands at different recrystallization stages of the perovskite phase with the corresponding diametrical horizontal signal distributions, (d, e, f) and (j, k, l)

We previously observed a similar behavior of the lateral piezoresponse (Kiselev et al. 2023), and to date it has been confirmed by the results of studying island spherulitic films of various sizes. However, it turned out that the nature of the polarization distribution can differ significantly in amplitude near the center of the island when reaching the shelf and near the edge, Fig. 1 (g–i). A clearer understanding of the crystallization processes of radial-radiant spherulite islands (and the continuous perovkite phase consisting of spherulitic blocks) is provided by data on the Kelvin mode of the studied islands, Fig. 1(d–e) and (j–l). The results indicate the presence of an intermediate (less dense) perovskite phase, characterized by a less ordered perovskite structure and the presence of numerous pores. The region of the spherulite island, where a change in the sign of the surface potential is observed, is a zone of recrystallization of the perovskite phase, which is most clearly visible in Fig. 1 (d–f) and (j–l). The completion of the recrystallization process of the perovskite phase is accompanied by a more uniform distribution of both the lateral piezoresponse signal and the surface potential, Fig. 1f and 1l.

Noteworthy is the negative potential both in the region of the intermediate perovskite phase and in its denser modification. The reasons for the formation of a negative surface potential are apparently related to the presence of traps at the interface between the thin film and the environment, as well as at the lower interface, occupied by electrons that are more mobile charges, Fig. 2. The reasons for the change in potential during recrystallization of the perovskite phase require additional study.

The mechanism of the appearance of radially oriented lateral polarization is in some respects similar to the mechanism of spontaneous polarization oriented normally to the film/substrate plane. In the case of self-polarization, the driving force is the localization of mobile charges (electrons) at deep traps of the morphologically developed thin film/bottom (platinum) electrode interface (Fig. 2) and the reorientation of ferroelectric dipoles under the influence of the electric field of the formed space charge (Balke et al. 2009; Pronin et al. 2003).

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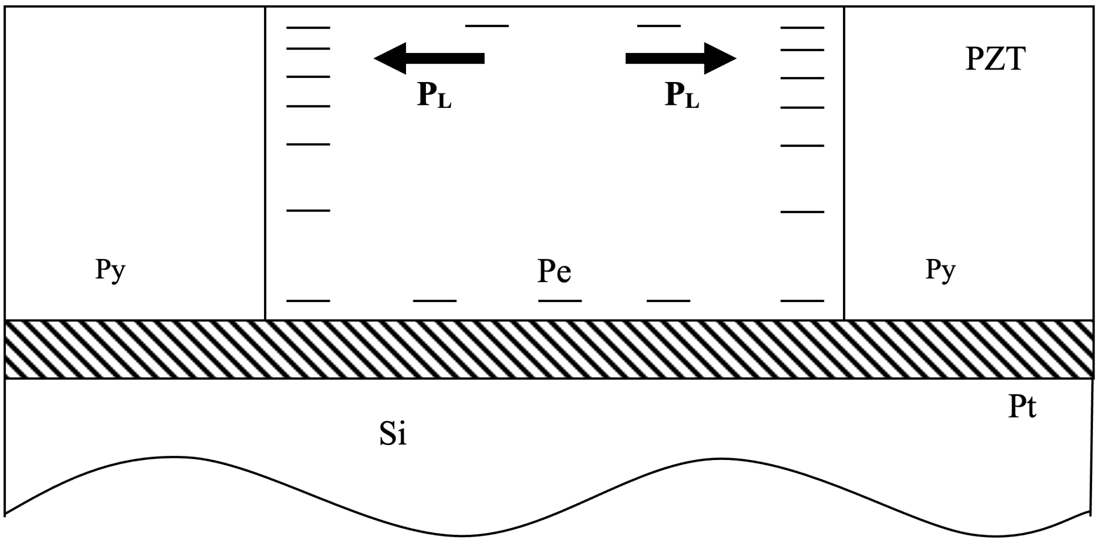

Fig. 2. Model radial section of the emergence of lateral polarization (P_L) in spherulitic perovskite (Pe) island (radial section) surrounded by low-temperature pyrochlore (Py) phase as a result of inhomogeneous space charge distribution

In our case, the difference in the mechanism for the appearance of radial-lateral polarization is, on the one hand, associated with the action of tensile radial stresses that orient ferroelectric dipoles in the plane of the thin film in directions as close as possible to the radial ones; on the other hand, it has to do with the action of the electric field formed by the localization of mobile charge carriers (electrons) on the loose (porous) perovskit–pyrochlore interface, Fig. 2. In this case, the lower interface (PZT/Pt) of the film is an equipotential surface, and the charges concentrated at the interface of the island with the pyrochlore phase are nonuniformly distributed throughout the thickness of the island, with the maximum potential near the free surface.

The results of studying the piezoelectric properties of continuous spherulitic films are presented in Figs. 3 and 4. To date, the data obtained on the vertical piezoresponse of thin films differing in the size of the spherulitic blocks (with varying target–substrate distance) have been systematized. Research on the lateral piezoelectric effect and surface potential and their analysis require significant additional efforts, and their results will be published later.

The first column of Fig. 3 reflects the PFM image (self-polarization) of the vertical signal; the second column is the distribution of the amplitude of the self-polarization signal over the scanning area; the third column is the PFM image of the vertical piezoresponse signal after polarization of the film with a voltage of +40 V and –40 V, respectively; and the fourth column is the distribution of the piezoresponse during repolarization films along horizontal sections.

Fig. 4 accumulates the study results presented in Fig. 3 when varying the target–substrate distance in the range d = 30–70 mm. The upper figure (Fig. 4a) shows the change in the self-polarization averaged over the scanning area. It can be seen that as d increases, the dependence passes through a minimum (at d = 40 mm), reaches a maximum and then decreases again. Similarly, a decrease in the value of residual polarization P_r (Fig. 4b) calculated as the average value under the positive and negative influence of a strong polarizing electric field is observed.

The passage of both dependencies through a minimum at d = 40 mm correlates with the ideas developed in some works (Kiselev et al. 2023; Pronin et al. 2023; Staritsyn et al. 2023a; 2023b), namely that an increase in the size of spherulitic blocks leads to an increase in lateral tensile mechanical stresses and, as a consequence, to an increase in the rotation gradient of the growth axis and the appearance of new open high-angle boundaries. It can be assumed that strong mechanical stresses can induce a phase transition in films associated with the rotation of oxygen octahedra (antiferrodistortion phase transition), which leads both to a decrease in the crystal lattice parameter of the perovskite structure and to the appearance of dielectric anomalies in the films of compositions corresponding to the region of the morphotropic phase boundary (Staritsyn et al. 2023a).

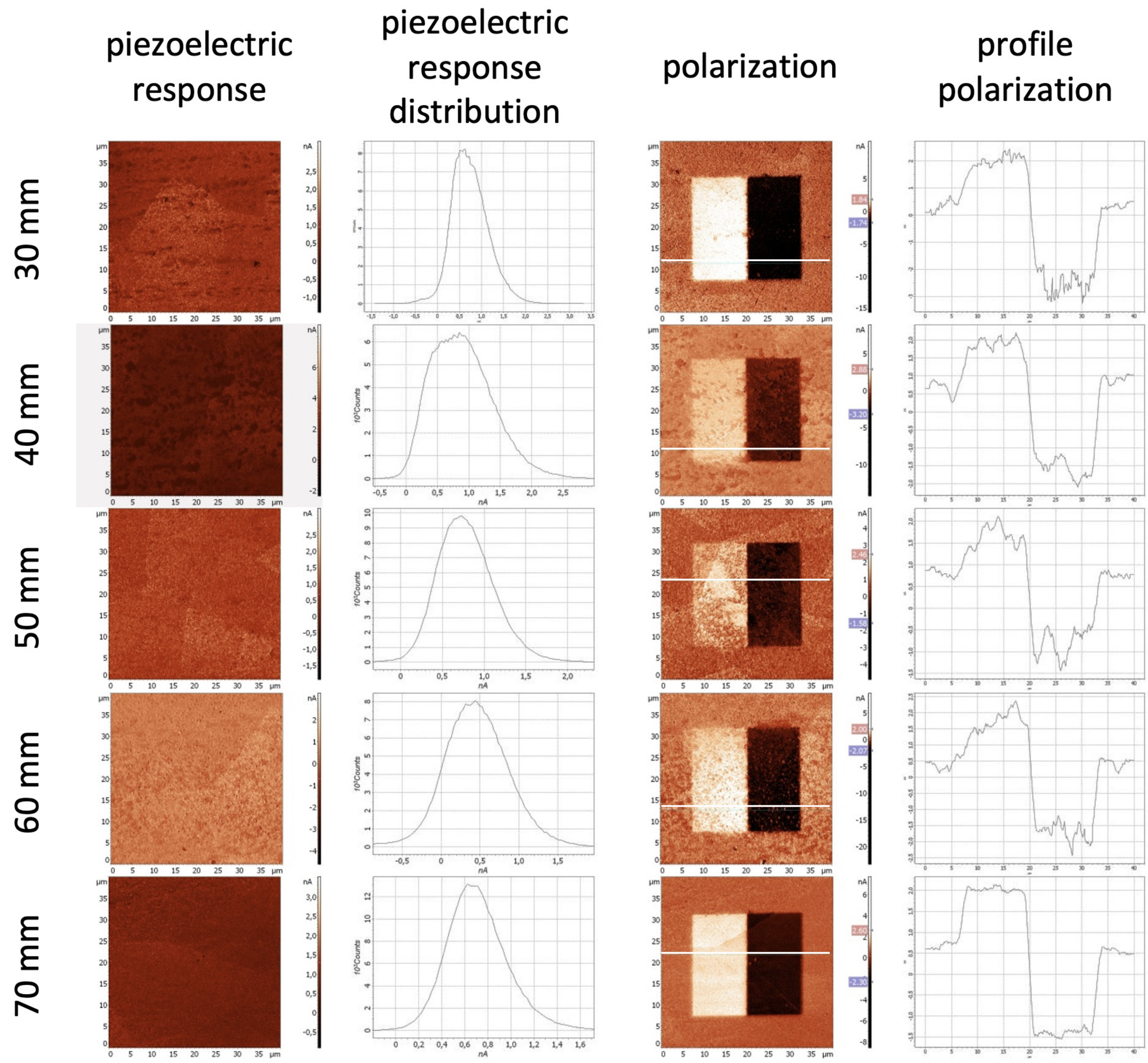

Fig. 3. Images of the piezoelectric response of PZT films (the first column — self-polarized films) with histograms of the distribution of the piezoelectric response over their area (the second column — self-polarization), piezoelectric response after polarization with positive +40 V (light areas) and negative –40 V (dark areas) voltage (the third column) with corresponding cross-section profiles (the fourth column)

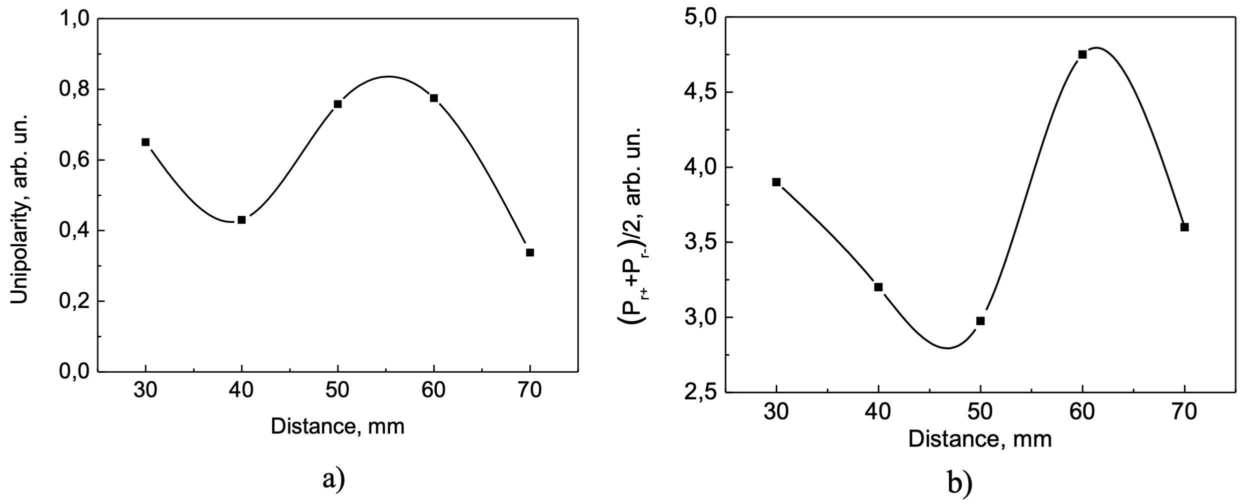

Fig. 4. Changes in self-polarization (a) and residual polarization (b) measured from the piezoelectric response of PZT versus target–substrate distance

Conclusions

A study of the piezoelectric properties of island and continuous spherulitшc PZT films showed that:

— phase recrystallization leads to anomalous changes in the lateral polarization and surface potential of perovskite islands;

— a mechanism for the formation of radial-radiant polarization is proposed, associated with the polarizing effect of a negative bulk charge accumulated at the interface of the island with the pyrochlore phase;

— in continuous spherulitic films, a nonlinear change in self-polarization and residual polarization was revealed with an increasing size of spherulitic blocks;

— it is assumed that anomalous changes in the structure and physical properties of spherulitic films are associated with the induction of octahedra tilting of the perovskite lattice, caused by the action of strong lateral tensile stresses.

Conflict of Interest

The authors delare that there is no conflict of interest, either existing or potential.

Author Contributions

The authors have made an equal contribution to the preparation of this paper.

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