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Influence of bending deformation in spherulitic films of lead zirconate titanate on the formation of the internal field and self-polarization

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ABSTRACT

Experimental studies of the internal field and self-polarization in thin lead zirconate titanate films formed on platinized silicon substrates using a two-stage radio-frequency magnetron sputtering of a ceramic target were conducted. In the first stage, amorphous films were deposited on a cold substrate, and in the second stage, high-temperature annealing was performed, accompanied by crystallization of the perovskite phase and the formation of a spherulitic microstructure. The aging characteristics of these films, associated with the formation of non-uniform mechanical stresses leading to the upward diffusion of oxygen vacancies (the Gorsky effect), were studied. Estimates were made of the diffusion rate of oxygen vacancies, as well as their concentration, necessary for the formation of an internal field in thin films. It was shown that a change in the crystallization (synthesis) temperature of the perovskite phase can lead to a change in the direction of the gradient vector of non-uniform mechanical stresses and the direction of diffusion of oxygen vacancies towards the substrate.

KEYWORDS

lead zirconate titanate • thin films • spherulitic microstructure • rotational crystals • self-polarization internal field • bending mechanical deformation • Gorsky effect

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Introduction

Thin ferroelectric films are finding increasing use in applied fields [1–6]. One of the main areas of their application is microelectromechanics (MEMS), where lead zirconate titanate (PZT) films occupy a niche of approximately 95 % [7,8]. The most effective is the use of naturally unipolar or self-polarized films, in which the macroscopic polar state is formed during their crystallization. Such films eliminate the need for labor-intensive polarization procedures. Furthermore, as practice has shown, an additional advantage is the increased stability of their polar state to external influences [9–11].

Although the mechanisms of self-polarized state formation have been studied for decades, there is still no consensus on their nature. Several physical causes of its formation are considered. These mechanisms can be roughly divided into electrical and mechanical ones. Electrical mechanisms are associated with:

1. the polarizing effect of the space charge localized at the lower interface of the ferroelectric film [9,10], the electrochemical potential on the thin film surface (Mott potential) [12], and ordered charged defects, in particular, oxygen vacancies [13];
2. differences in the work functions of the lower and upper film interfaces when using different materials as electrodes [14].

Depending on the nature of their action, mechanical mechanisms are divided into (a) tensile or compressive deformation of a thin film in the plane of the substrate, and (b) bending deformation. In the first case, the action of tensile or compressive forces on a thin film can be caused by a difference in the temperature coefficients of linear expansion of the polycrystalline film and the substrate [15,16], and in the case of epitaxial growth of a thin film, by a difference in the parameters of their crystal lattices (misfit) [17]. However, since polycrystalline films are used in the vast majority of practical applications, we will not consider misfit further. The difference in the temperature coefficients of linear expansion of the film and the substrate also leads to bending deformation of this structure, and thus to a deformation gradient.

By its nature, linear deformation (under the action of compression/expansion forces) leads to a reorientation of the ferroelectric polarization vector in directions either as close as possible to the normal to the substrate plane, or to its plane [16,18]. Thus, in thin PZT films deposited on a silicon substrate, the composition of which corresponds to the region of the morphotropic phase boundary (MPB), where the maximum values of electromechanical/piezoelectric coefficients are achieved, the magnitude of tensile mechanical stresses can reach 100–150 MPa, which leads to a partial reorientation of the polarization vector and, accordingly, a decrease in the degree of unipolarity [15,16]. In this case, the deformation itself, being a scalar quantity, cannot be the cause of macroscopic polarization, unlike bending deformation, characterized by a deformation gradient, which is a vector quantity. According to [19,20], such deformation leads to an asymmetric shift of atoms within a unit cell in a multicomponent crystal lattice, the appearance of an internal field and, as a consequence, a macroscopic polar state – an effect subsequently called flexoelectrical one. A similar effect in thin PZT films was observed under strong bending, close to the plastic limit of the silicon substrate (with a curvature radius of about 30 cm) and a lattice deformation of ~ 1 % [21], which is usually not realized in real structures.

Studies conducted in recent years have shown that strong non-uniform deformation is observed in thin films characterized by a spherulitic microstructure. The crystalline phase of these films is formed by the growth and subsequent fusion of individual spherulitic islands from the amorphous phase during high-temperature annealing. In such polycrystalline formations, which are often referred to as rotational crystals, a rotation of the crystal lattice (or growth axis) in radial directions is observed, accompanied by bending deformation [22–28]. In this case, the integral angle of rotation can reach tens and hundreds of degrees, and the rotation rate is hundreds of degrees per micron and more [22–24]. Similar spherulitic formations with a radial-

radiant microstructure are often observed in PZT thin films, and recently attempts have been made to study the relationship between their microstructure and physical properties [28–30]. In particular, it was shown that tensile mechanical stresses can lead to a reorientation of the ferroelectric polarization in directions as close as possible to the plane of the substrate, and in individual spherulitic islands the effect of radially oriented lateral self-polarization was detected [28,29].

It is assumed that in such rotational structures, due to non-uniform deformation, a mechanism for the formation of thickness self-polarization associated with the directional diffusion of charged defects (the Gorsky effect) can be realized [31,32]. Positively charged oxygen vacancies can act as such point defects in PZT films; their directional diffusion can lead to the formation of an internal field and a stable macroscopic polar state. The aim of this work was to identify the role of oxygen vacancies and their diffusion capacity in the formation of an internal field under conditions of non-uniform deformation and to evaluate their contribution to the stability internal field and of self-polarization in thin spherulitic PZT films.

Sample preparation and research methods

The PZT films were deposited on platinized silicon substrates ($Pt/TiO_2/SiO_2/Si$) using a two-stage high-frequency magnetron sputtering method. The composition of the sputtered ceramic target corresponded to the region of the morphotropic phase boundary and corresponded to the elemental ratio of zirconium and titanium atoms Zr/Ti = 54/46 [28]. To obtain a two-phase structure in the form of perovskite islands with transverse dimensions in the range of 30–40 μm surrounded by a matrix of the low-temperature pyrochlore phase, or a single-phase block structure, the amorphous films deposited at a low substrate temperature were annealed at a temperature of 535–570 °C. The thickness of the PZT films was ~ 500 nm. To carry out electrophysical measurements, platinum electrons with dimensions of 200 × 200 μm^2 were formed on the surface of the films.

The crystal structure and phase state of the films were monitored using X-ray diffraction analysis (Rigaku Ultima IV). Microimages of spherulitic islands were obtained using a scanning electron microscope (Tescan Lyra 3) equipped with an electron backscatter diffraction (EBSD) detector. Processing of the diffraction patterns allowed for the point-by-point generation of orientation maps of the spherulitic islands, along with crystallographic orientation data, and the determination of lattice rotation rates.

To assess the self-polarized state, piezoelectric response force microscopy (PFM) was used on an MFP-3D SA atomic force microscope (Asylum Research). Measurements of the normal component of the piezoresponse were performed in contact mode by applying an alternating voltage of 5 V at 50 kHz to the cantilever. The scanned surface area was 40 × 40 μm^2. The dielectric properties of thin films were studied using an E7-30 immittance meter. Dielectric hysteresis loops and internal field were measured using a modified Sawyer-Tower scheme. Measurements were performed at a frequency of 1 kHz.

Experimental results

Figure 1 shows electron micrographs of the spherulitic microstructure observed in thin PZT films. Crystallization of the perovskite phase in such films occurs through the nucleation and growth of individual perovskite islands, which are nearly circular in shape, in a matrix of the low-temperature non-polar pyrochlore phase (Fig. 1(a)). Further island growth leads to the formation of a polyhedral block structure (Fig. 1(b)). Typically, the spherulitic microstructure consists of distinct regions separated by radial rays, in which new growth centers emerge as growth proceeds. In the studied PZT films, the diameter of individual spherulitic islands (or the linear size of the blocks) reached several tens of micrometers. This pattern of spherulitic growth indicates so-called low-angle non-crystalline (growth) branching.

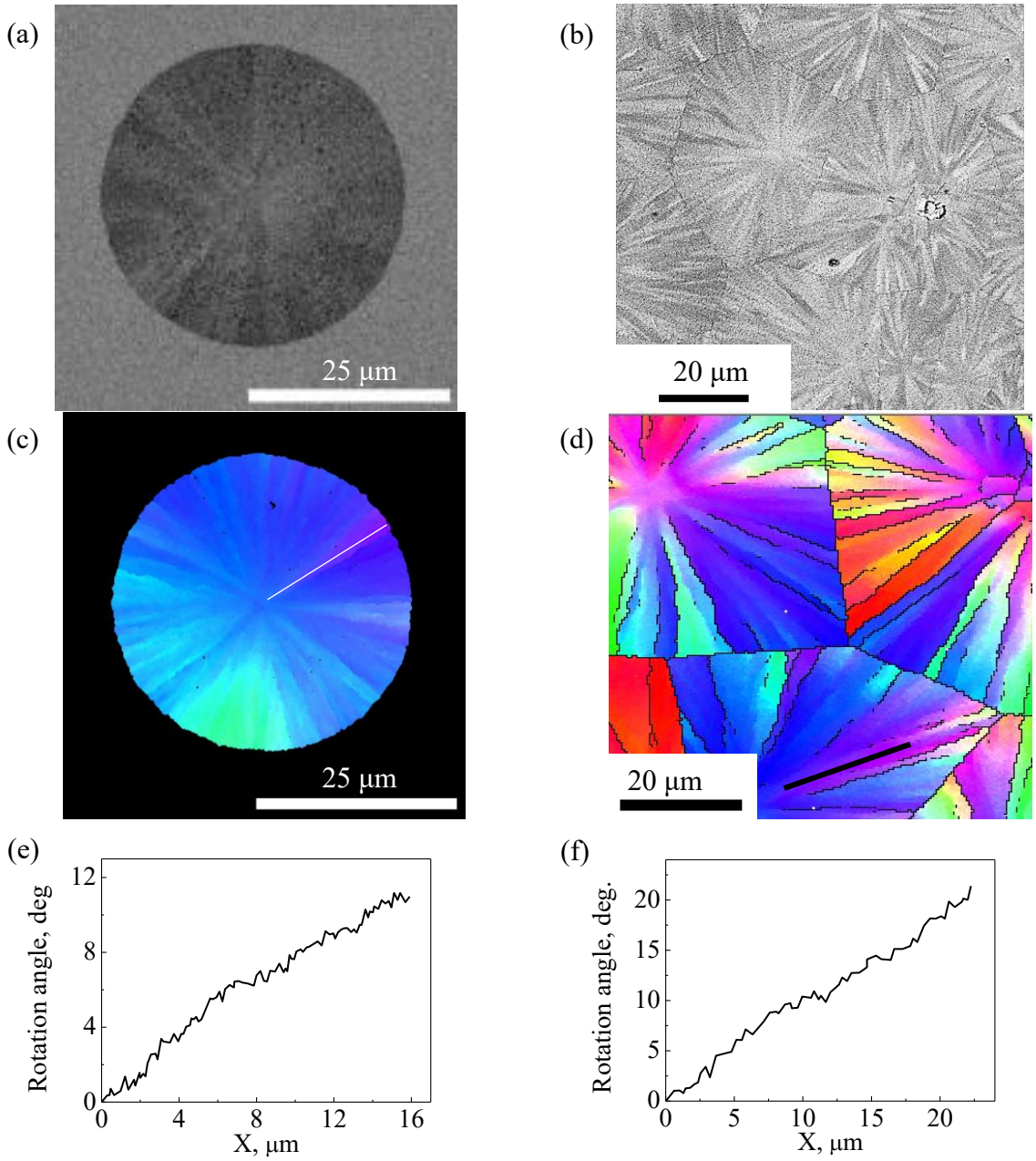

Fig. 1. Electron images of the spherulitic microstructure (a,b), EBSD maps (c,d) and dependence of the rotation angle (φ) of the lattice along the marked radial directions (e,f), the application of strong alternating fields, and long-term aging at room temperature

It is believed that one of the microstructural features of radial-rayed spherulites is the rotation of the growth axis (crystal lattice) around a direction perpendicular to the radial rays. In EBSD images, this manifests itself as a smooth change in color gamut with radial movement from the center of the spherulites to their periphery (Fig. 1(c,d)). Figure 1(e,f) shows near-linear dependences of the lattice rotation angle (φ) along the indicated radial directions. The rotation angle in the studied films reached 20–30°, and the rotation rate (gradient) varied from 0.5 to 1.2 deg/μm.

In the works devoted to the study of the properties of rotational crystals, it was noted that such non-uniform deformation of the crystal lattice is a consequence of the action of mechanical stresses arising during the formation of the crystalline phase from the amorphous phase during high-temperature annealing, which is accompanied by a change in the density of the thin film [22–28]. The results of the study of dielectric hysteresis loops and piezoelectric response presented below revealed changes in the polar characteristics of self-polarized PZT thin films during the influence of temperature (high-temperature annealing above the Curie).

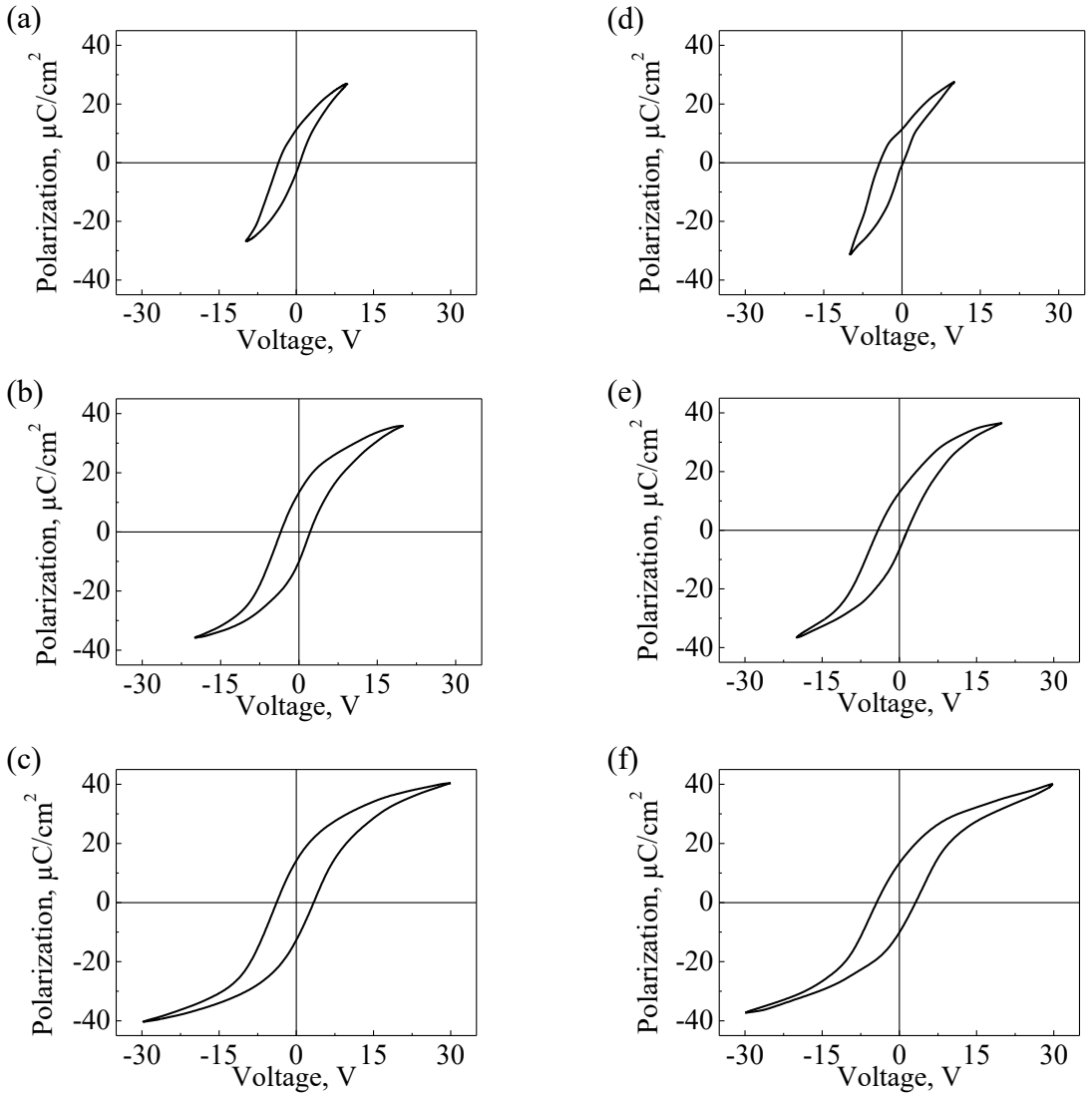

Fig. 2. Dielectric hysteresis loops of perovskite films at voltages of 10, 20 and 30 V, formed at a distance from the target to the substrate of 30 mm, immediately after deposition (a,b,c) and after long-term exposure (d,e,f)

Figure 2 shows the dielectric hysteresis loops (*P-V*) of an as-prepared film (Fig. 2(a–c) and one subjected to long-term aging (more than 4 years) (Fig. 2(d–e)) under the application of an alternating field with an amplitude from 200 to 600 kV/cm. The magnitude of the internal field (E_{int}) in the films was estimated from the shift of the *P-V* loops along the abscissa axis. It is evident that in as-prepared films the value of E_{int} was ~ 14 kV/cm. The application of a strong field (600 kV/cm) resulted in almost complete symmetrization of the hysteresis loop, that is, the disappearance of the internal field (Fig. 2(c)). A similar symmetrization of the P-V loops (even in relatively weak fields) was also observed during annealing of the sample at temperatures close to the Curie temperature (~ 380 °C) or higher [33,34]. Long-term aging of such samples resulted in the appearance of strong asymmetry in the *P-V* loops and an increase in E_{int} to ~ 23 kV/cm when an alternating field of 400 kV/cm was applied. However, no loop symmetrization occurred in a strong field (Fig. 2(e)).

Figure 3 shows the hysteresis loops of self-polarized films after long-term aging (Fig. 3(a)), as well as their changes after high-temperature annealing above the Curie temperature (~400 °C) and subsequent aging. It is evident that in such films, the internal field was maintained even in a strong field (400 kV/cm) after annealing of the samples, although the value of E_{int} decreased significantly, Fig. 3(b). Further aging of the samples (for ~ 10^7 s) at room temperature led to an increase in asymmetry, i.e., an increase in E_{int} by ~ 6 kV/cm (Fig. 3(c)).

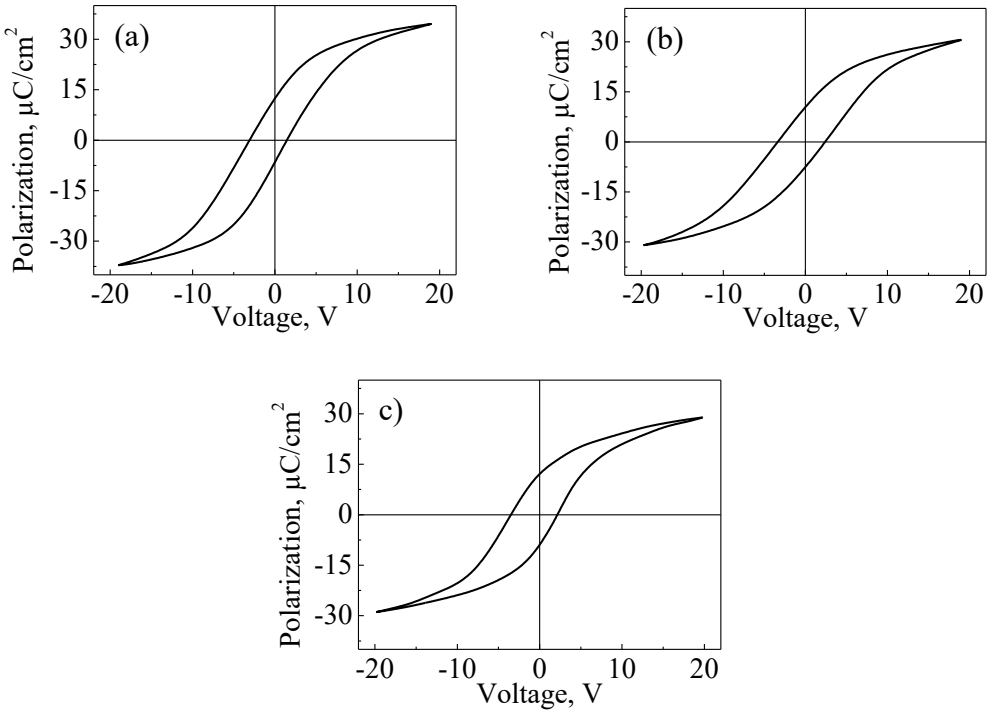

Fig. 3. Dielectric hysteresis loops after long-term aging (a), annealing at 400 °C (b) and subsequent aging for 1600 h (c)

The change in the value of E_{int} (and, consequently, the value of natural unipolarity or self-polarization P_{self}) was caused by a change in the temperature at which the crystallization (synthesis) of the perovskite phase of thin films (T_{sint}) occurred. Figure 4

shows the change in these parameters with T_{sint} varying in the range of 535–550 °C. It is evident that P_{self} and E_{int} reach their maximum values at 540–545 °C (Fig. 4(a,b), respectively) and then decrease sharply. We associate this behavior with the significant role of excess lead in the thin film bulk, presented in the form of its oxide (PbO) or dioxide (PbO_2), and a change in its content with increasing T_{sint} (Fig. 4(c)). It has been previously shown that such a change in the lead oxide content is associated with the competition of two mechanisms of crystallization of the perovskite phase, when the formation and growth of perovskite islands begins either from the free surface of the thin film, which is accompanied by the extrusion of excess lead oxide towards the lower interface, or by nucleation and growth from the lower interface of the film upwards and the extrusion of excess lead towards the surface of the film [35].

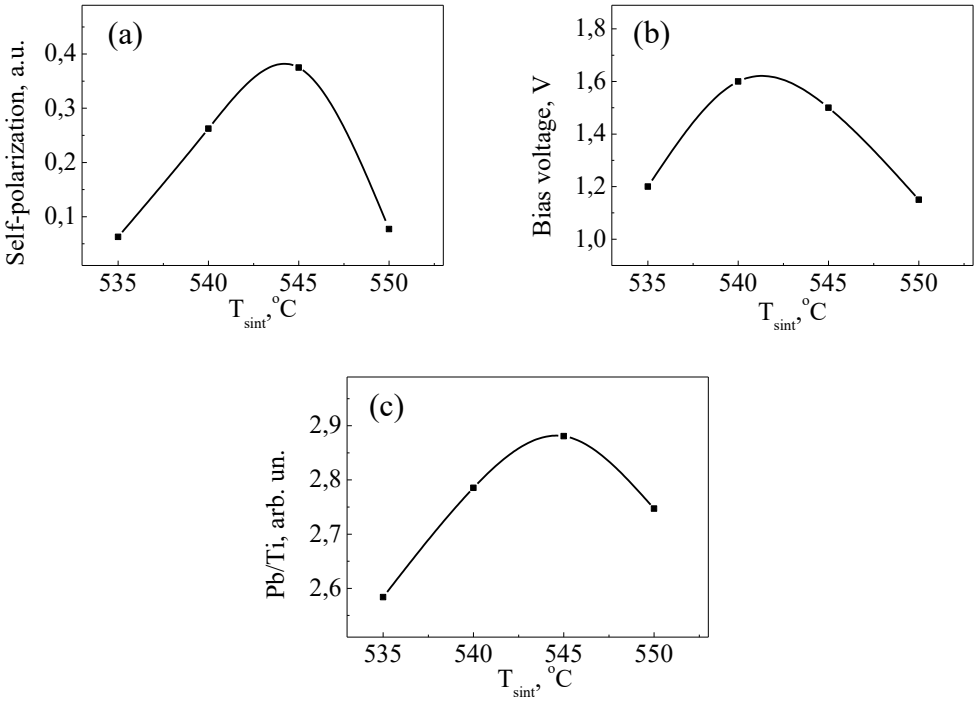

Fig. 4. Change in the values of self-polarization (a), internal field (b) and lead excess (in the form of the elemental ratio of Pb/Ti atoms) (c) depending on the T_{sint}

Discussion

To explain the obtained results, we will use the approach previously developed by the authors, according to which the formation of an internal field in thin PZT films during the crystallization of the perovskite phase is associated with the orienting action of the field of the negative space charge localized at deep traps in the film near the film-lower (platinum) electrode interface in the absence of the upper electrode [10]. Such a charge state of the film is shown schematically in Fig. 5(a), where the negative charges are electrons localized at deep traps and charged oxygen vacancies, in a first approximation, uniformly distributed over the thickness of the ferroelectric film. It is also assumed that the presence of excess lead oxide located at the film interfaces, in the intercrystallite space and at the boundaries of spherulitic blocks creates conditions for the formation of a sufficiently high concentration of oxygen vacancies [35].

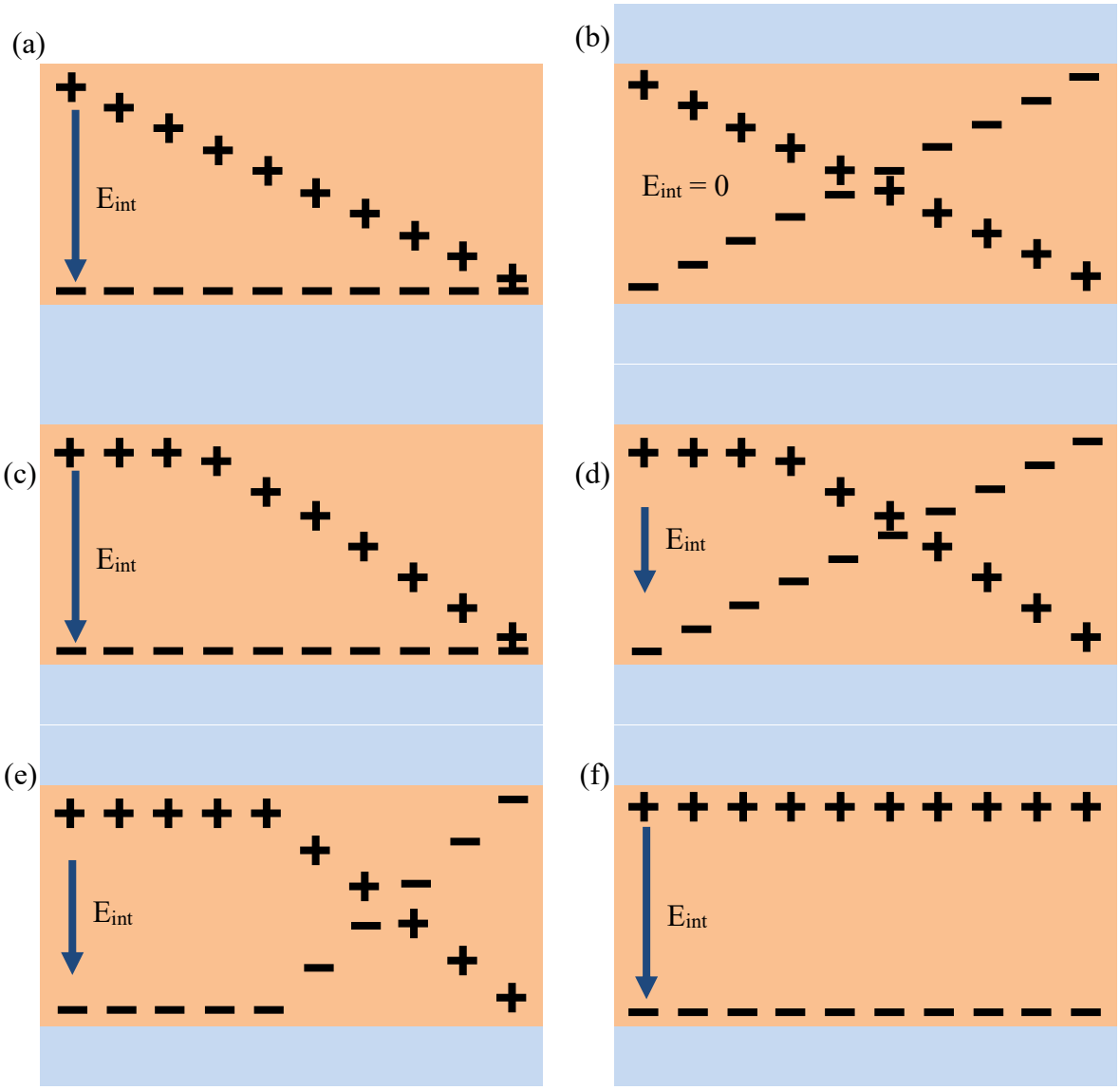

Fig. 5. Schematic representation of the distribution of positive and negative charges during the formation of a self-polarized state in a thin ferroelectric film: (a) in a freshly prepared sample, (b) after high-temperature annealing, (c) after aging of the self-polarized film, (d) after high-temperature annealing of the self-polarized film, (e) after subsequent aging, (f) limiting state as a result of aging. The magnitude and direction of the internal field (E_{int}) are indicated by arrows

Thus, the orientation of the electric field polarizing the ferroelectric is determined by the field of the negative space charge, which is sufficient to reorient some of the ferroelectric dipoles in the film. Figure 5(b) illustrates the process of hysteresis loop symmetrization, which occurs due to sample depolarization following high-temperature annealing, the depletion of deep traps, and the uniform distribution of the electron gas across the film's thickness. A similar state is also achieved by applying a strong alternating field.

It is assumed that the uniform distribution of charged oxygen vacancies in as-prepared samples is associated with their low diffusion rates in the perovskite lattice across the film thickness, and their ordering (or "ascending diffusion") can be caused by a mechanical stress gradient (the Gorsky effect) [32]. According to previous studies, this

gradient is formed during the crystallization and growth of spherulitic islands due to the difference in densities of the amorphous (or low-temperature pyrochlore) and perovskite phases [28,30]. Calculations show that in a non-uniformly deformed lattice at high rotation rates, the bending strain can reach fairly large values (~ 0.5–1 %) [28,30]. Figure 6 demonstrates that the mechanical stress gradient vector can be oriented either toward the lower (Fig. 6(a)) or upper (Fig. 6(b)) film interface, depending on which (upper or lower) film interface is near which nucleation and growth of perovskite islands occurs. In the first case, when the crystal lattice (growth axis) rotates toward the center of the spherulitic island, this leads to the diffusion of oxygen vacancies toward the free surface of the film (toward lattice compression) and will contribute to an increase in the internal field. In the second case, when the growth axis rotates away from the center and toward the periphery of the island, the movement of vacancies will occur in the opposite direction – toward the lower film interface, as a result of which the magnitude of the internal field will decrease. Thus, in a mechanically inhomogeneous crystal lattice, one can expect a noticeable diffusion of charged oxygen vacancies in the direction where lattice compression should be observed, Fig. 7. The results obtained in this work indicate that a variant is realized in the films in which the mechanical stress gradient determined the direction of diffusion of oxygen vacancies toward the free surface of the thin film (Fig. 6(a)).

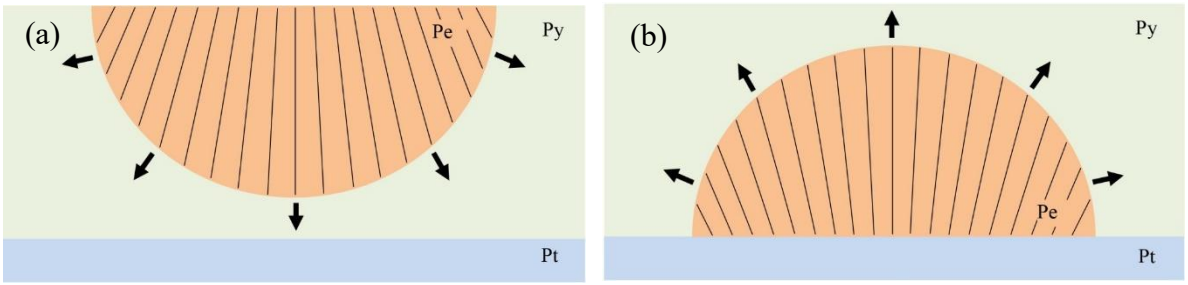

Fig. 6. Model of growth of spherulitic islands from the free surface of the film (a) and from the lower film-substrate interface (b)

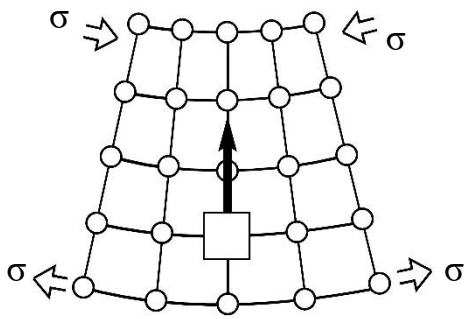

Fig. 7. Schematic model of the motion of an oxygen vacancy in a perovskite lattice under conditions of non-uniform (bending) deformation

The directed diffusion of charged oxygen vacancies during aging results in their gradual accumulation near the upper interface of the film, which is shown in Fig. 5(c). High-temperature annealing of the aged film results in the release of electrons from deep traps, as a result of which the internal field decreases (Fig. 5(d)), which corresponds to

a decrease in the hysteresis loop asymmetry (Fig. 3(b)), but maintaining a significant internal field (~ 9 kV/cm). Subsequent aging (3 months) leads to further accumulation of charged oxygen vacancies near the upper interface (Fig. 5(d)), an increase in the internal field (up to ~ 15 kV/cm), Fig. 3(c). It is assumed that in the presence of a sufficient concentration of charged oxygen vacancies, the initial value of the internal field (~ 23 kV/cm, Fig. 3(a)) is expected to be reached in the limit with the ordering of charged vacancies near the upper interface of the thin film (Fig. 5(e)). It should be noted that the difference between the unipolar state in freshly prepared films and films after their long-term aging lies in the formation of a stable macroscopic polar state caused by the diffusion of oxygen vacancies, which is extremely difficult to destroy under the influence of strong alternating fields and an increase in temperature.

The schematic charge redistribution shown in Fig. 8 reflects the change in excess lead oxide with T_{sint} (Fig. 4), which affects the mechanism of perovskite phase formation (Fig. 6). An increase in excess lead oxide leads to an increase in the concentration of oxygen vacancies, an increase in the space charge the internal field (Figs. 8(a,b)). A subsequent decrease in lead oxide leads to a redistribution of deep traps across the film thickness, a change in the position of the space charge, and a change in the concentration of oxygen vacancies, which affects the magnitude of the internal field (Fig. 8(c)).

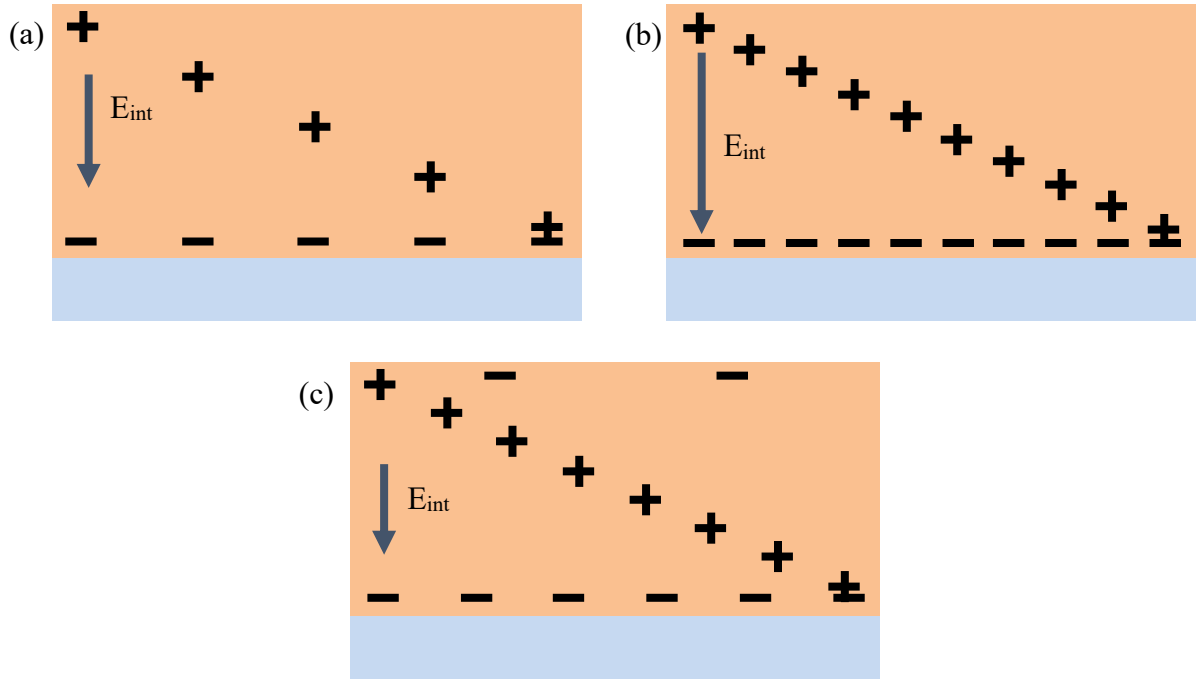

Fig. 8. Schematic distribution of charges in a thin film during the implementation of the mechanism of perovskite island growth from the free surface of the film: (a) with a small excess of lead oxide and a low concentration of separated charges, (b) with an increase in excess lead oxide and charge concentration, and (c) during the implementation of the mechanism of island growth from the lower interface of the film. The magnitude and direction of the internal field (E_{int}) are indicated by arrows

Estimates of the diffusion rate of oxygen vacancies and the internal field

To estimate the upward diffusion flux (I_V) of oxygen vacancies under the action of a mechanical stress gradient, we use the equation describing the Gorsky effect [31,32]:

$$I_V = - N_V \times D_V/(k_B T) \times \partial\sigma/\partial x \times \omega_V, \quad (1)$$

where N_V is the density of oxygen vacancies, D_V is their diffusion coefficient at room temperature, k_B is the Boltzmann constant, $\partial\sigma/\partial x$ is the mechanical stress gradient (σ) across the film thickness (x), and ω_V is the volume occupied by a vacancy in the perovskite lattice. To estimate the flux, reasonable values of oxygen vacancy concentration were used: ~ 0.01 % of the number of oxygen atoms in the octahedral sublattice of the perovskite structure, i.e. $N_V \sim 10^{24}$ m^{-3}, $D_V \sim 5\times10^{20}$ m^{-2} s^{-1} [36], $T \sim 295$ K, $\sigma \sim 300$ MPa at a growth axis rotation rate of ~ 0.6 deg/μm, $x \sim 0.5\times10^{-6}$ m [10], $\omega_V \sim 8\times10^{-30}$ m^{-3}. Then the value of I_V will be ~ 6×10^{10} m^{-2} s^{-1}.

As is well known, the flow of atoms (or vacancies) can be represented as the product of the density of atoms (vacancies) (N_V) and the velocity of their movement (υ), i.e. $I_V = N_V \times \upsilon$. Then the velocity of vacancies will be $\upsilon = I_V/N_V \sim 6\times10^{-12}$ m/s. This means that during the aging period (e.g., 3 months or ~ 10^7 s), the distance that oxygen vacancies will move will be 0.6×10^{-6} m or ~ 0.6 μm. Thus, virtually all of the available charged oxygen vacancies should move to the upper interface of the film.

However, judging by the experimental results, the internal field does not reach the value measured in as-prepared films. The most likely reason for this is the lack of charged oxygen vacancies in the thin film, caused by the fact that not all oxygen vacancies are charged at room temperature. This is due to the relatively high activation energies of electrons and charged vacancies (E_a). At room temperature, E_a is estimated to be ~ 0.22 eV [10]. This means that only 1.3 % of the oxygen vacancies in the thin film will be charged – $N_V^{2+} = 1.3\times10^{22}$ m^{-3}.

To estimate the concentration of charged oxygen vacancies that create a stable internal field, we use the relationship between the charge density ($\Delta\sigma$) and the internal field strength (ΔE_{int}):

$$\Delta\sigma \sim \varepsilon\varepsilon_0\Delta E_{int}, \quad (2)$$

where ε is the relative permittivity, which is ~ 700 at room temperature, and ε_0 is the permittivity. Thus, an increase in E_{int} = 10 kV/cm requires ~2×10^{16} m^{-2} of charged oxygen vacancies localized near the upper interface of the thin film. This means that the number of charged oxygen vacancies located throughout the thin film (~ 0.7×10^{16}), normalized per square meter of surface area, is several times lower than the required density.

In this regard, under conditions of a deficiency of charged oxygen vacancies, the formation of a field of ordered vacancies can occur in two stages. In the first stage, charged vacancies present in the film bulk accumulate relatively rapidly (over a period of ~10^6–10^7 s) near the upper film interface due to upward diffusion. In the second stage, the rate of increase in volume charge, which is significantly slower, will be determined by the activation energy of electrons/charged oxygen vacancies.

Conclusions

Experimental studies were conducted to examine changes in the internal field and self-polarization associated with the influence of the crystallization (synthesis) temperature of submicron spherulitic PZT films and their aging under the action of non-uniform mechanical stresses that form in the films as a result of crystallization of the perovskite phase from the amorphous (or intermediate pyrochlore phase) during high-temperature annealing. It was shown that the film aging process is accompanied by the directed

diffusion of oxygen vacancies, leading to the emergence of a stable internal field. Estimates were made of the diffusion rate of oxygen vacancies, as well as their concentration, necessary for the formation of an internal field in thin films. It was shown that a change in the crystallization (synthesis) temperature of the perovskite phase can lead to a change in the direction of the gradient vector of non-uniform mechanical stresses and the direction of diffusion of oxygen vacancies towards the substrate. The obtained results allow us to specify the physical mechanisms of both electrical and mechanical nature that lead to the formation of a internal field and self-polarized state and its stability in thin PZT films.

CRediT authorship contribution statement

Alsu R. Valeeva: investigation, data curation; **Michail V. Staritsyn**: investigation, data curation, writing – original draft; **Stanislav V. Senkevich**: data curation, writing – review & editing; **Eugenii Yu. Kaptelov**: investigation, data curation, writing – original draft; **Igor P. Pronin**: conceptualization, writing – review & editing, supervision; **Dmitrii A. Kiselev**: investigation, data curation, writing – original draft; **Sergey A. Nemov**: conceptualization, writing – review & editing.

Conflict of interest

The authors declare that they have no conflict of interest.

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