FORMATION MECHANISMS AND THE ORIENTATION OF SELF-POLARIZATION IN PZT POLYCRISTALLINE THIN FILMS

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Abstract. The influence of the pressure of the argon-oxygen gas mixture on the composition of $Pb(Zr,Ti)O_3$ (PZT) films deposited by RF magnetron sputtering on the silicon substrate with a platinum layer has been studied. It was demonstrated that the change in the self-polarization vector is unambiguously associated with the variations of the concentration of lead in PZT films in relation to stoichiometric composition. It was found that at the high gas pressure (8 Pa) the entire volume of the thin PZT is crystallized in the perovskite phase, and with decreasing pressure to 2 Pa (and, consequently, with a decrease in lead content) the fraction of the perovskite phase in the film volume significantly decreases. For explanation of the reorientation of the polarization vector we have proposed the model which is based on mechanochemical phenomenon of the diffusion of lead atoms under the mechanical stresses caused by a distinction in the thermal expansion coefficients of the film and the substrate.

1. Introduction

The interest for applications of thin ferroelectric films for the development of micro-electro-mechanical (MEMS) devices is steadily growing up to now [1-6]. The contemporary advancement of technologies of oxide microelectronics allows one to find out the ways of combining the technology of the ferroelectric films formation with the silicon microelectronics. It results in the qualitative leap in the miniaturization and energy consumption of the devices. In order to reduce labor costs in the manufacture of MEMS devices, it is necessary to exclude the formation of the macroscopically stable polarized state. The latter is achieved by applying to a thin film ferroelectric capacitor of an external electric field. This is the time-consuming and therefore quite expensive process. In a number of studies of lead zirconate titanate $Pb(Zr,Ti)O_3$ and barium titanate $BaTiO_3$ thin films, it was shown that the stable polar state could be achieved even without using of an external electric film [7-33]. This polar state, which is commensurable with the value of the spontaneous polarization, is commonly referred to as the self-polarization

or the natural unipolarity. One has to acquire the deep understanding of the nature and mechanisms of the self-polarization phenomenon for the targeted control of this process, and especially the developing on its base various devices.

The existing experimental data show that the main reasons responsible for the appearance of the self-polarization could be:
- the tensile (compressive) or bending mechanical stresses affecting the ferroelectric layer from the side of the substrate and buffer sublayers [7-13],
- the structural damage, arising from the epitaxial growth of the ferroelectric layer [14-17],
- the difference in the work functions of the charge carriers from the upper and lower electrodes produced of different materials, that leads to the difference in Schottky barriers on the upper and low interfaces of the thin-film ferroelectric capacitor [18-19],
- the nonuniform distribution of charged vacancies over the thickness of the ferroelectric layer [20-22],
- the asymmetric formation of the space charge and, consequently, the formation of the internal electric field near the upper and (or) the lower interface; the latter can be caused by the crystallization of the perovskite phase in the ferroelectric in the absence of the upper electrode [23-27].

Theoretical studies of this problem have shown that the self-polarization may occur under changes of the composition over the thickness of the ferroelectric layer (graded ferroelectrics). The latter is especially clearly revealed in the multilayer perovskite films, in which the composition could change in each layer [28]. In a number of studies [4, 10-12] it is assumed that the combination of a few factors of the electric and mechanical nature, affecting simultaneously the PZT layer, is responsible for the appearance of the self-polarization and its large value.

Depending on different factors the self-polarization value may vary in wide-ranging limits from zero to the spontaneous polarization value. In particularly, the self-polarization value essentially depends on the degree of perfection of the structure of the thin ferroelectric layer, its composition and thickness. In its turn, these parameters depend on the film precipitation methods, their thermal treatment, the film orientation in the course of the growth and other factors [9, 11, 13, 27, 29-31].

Up to now, the unambiguous comprehension of mechanisms leading to the appearance of the self-polarization in the films is unavailable. The following question remains unresolved: Why in some cases the polarization vector is directed towards the film [8, 16, 19, 20, 32], and in the others towards the substrate [18-19, 22-25, 27, 29-32]? The authors of the majority of the experimental studies even do not discuss the reasons of an appearance of one or another orientation of the self-polarization vector. The analysis of numerous experimental data leads to the following basic conclusion: the reorientation of the self-polarization vector could be performed by two independent methods [13, 33]. According the first method the direction of polarization vector could be changed by preliminary heating the thin film Pt/PZT/Pt capacitor (with "symmetric' electrodes) above the Curie temperature followed by cooling below the Curie temperature. The second way is the creation of conditions at which the change in the curvature sign of the silicon plate occurs under the action of mechanical bending stresses. With this aim in mind one have to choose, by a certain way, the thickness of the ferroelectric film and the composition and the thickness of the buffer layer on the substrate.

In this paper we study the nature of appearance and orientation of the spontaneous polarization in the thin film Pt/PZT/Pt capacitor that is the important fundamental and applied problem. To achieve this goal, we have explored the model according to which the orientation of the spontaneous vector in the thin film Pt/PZT/Pt capacitor is caused by the charge defects in the ferroelectric film. In Pt/PZT/Pt film capacitor the defects of this kind could be whether the oxygen or lead vacancies. Existence of the oxygen vacancies lead to the electron conduction

of the film, and *visa versa,* the lead vacancies are acceptors and in their presence the film acquires the hole (p-type) conductivity. The sign of the charge carriers determines the sign of the space charge, which is formed on the interface (interfaces) of the studied structure, and consequently, the orientation of the self-polarization vector (see Fig 1).

2. Methods of the preparation and the study of the samples.
Thin layers of the PZT solid solutions were formed using the two-step method. The platinized silicon wafers with the buffer sublayer of 700-nm-thick silicon dioxide, and the adhesive 20-30-nm-thick sublayer of titanium dioxide (Pt/TiO$_2$ /SiO$_2$/Si were used as substrate. At the first stage of film synthesis, using RF magnetron sputtering of the ceramic target, the amorphous layers of Pb (Zr, Ti) O$_3$ solid solutions have been obtained. The deposition process was carried out at ~ 150 °C, at which the film is still in the amorphous state. Then the layers formed in this manner were subjected to the high temperature annealing, which is necessary for the formation of the PZT perovskite (ferroelectric) structure. The annealing temperature was varied in the range of 580 – 650 °C. Note that the thickness of a lower platinum electrode was 60-80 nm, and of the PZT layer 800-1000 nm. On the surface of the produced films a grating was formed from the upper Pt electrodes of area of about 200 x 200 μm. The composition of the thin films corresponded to the region of the morphotropic phase boundary (the atomic ratio Zr/Ti = 54/46), where the majority of physical, including the electromechanical, parameters attained the maximum values [35]. That to compensate the losses of lead during annealing in air, the excess of lead was added as 10 mol % of the lead oxide.

The microstructure and composition of the PZT layers were investigated using the X-rays diffractometer DRON-7, the Carl Zeiss EVO-40 scanning electron microscope equipped with an Oxford INCA energy-dispersive X-ray spectrometer for the measurements of the element composition of thin films, and also the optical microscopy Nikon Eclipse LV150. The self-polarization state of the films was studied by an atomic-force microscope MFP-3D SA, Asylum Research. The measurements have been carried out in the contact regime applying on the conducting probe the alternative voltage of amplitude 5 V and frequency 50 kHz. The scanning field area did not exceed 60×60 μm. The presence of macroscopic polarization was determined from the asymmetry of the dielectric hysteresis loops (*P-V*), which were obtained using the modified Sawyer-Tower circuit, and also by measuring the capacitance-voltage characteristics (*C-V*) with E7-20 immittance meter. The measurements of the pyroelectric response with the magnitude proportional to the degree of unipolarity of the ferroelectric layer were performed in the dynamic mode [33] in the frequency range from 10 to 10^3 Hz.

3. The dependence of the magnitude and direction of the spontaneous polarization of PZT thin films on the concentration of lead oxide
In a number of studies it was shown that the PZT solid solutions, containing an excessive lead oxide concentration relative to the stoichiometric value, exhibit the electron-type conductivity [see for example 36]. This is a clear indication of the presence of the donor oxygen vacancies in the film. It is assumed that the electrons in the PZT films of a given composition can be captured by deep traps located in the vicinity of the lower Pt/PZT interface. The capture of electrons leads to the formation on it negative space charge and to the formation of the internal electric field *E*. This field leads to the alignment of the ferroelectric dipoles parallel to its own direction, i.e., the polarization vector orients toward the bottom electrode (Fig. 1a). Depending on the thickness of the PZT layer the orienting action of the electric field can capture whether the entire thickness of the film layer, or only a part of it. Under the influence of the field on the entire film thickness, the self-polarization can attain the value of the spontaneous polarization for the PZT solid solutions [11, 23, 29].

It is believed that by reducing the excess of lead oxide in the PZT layer the concentration of oxygen vacancies therein will decrease. If the concentration of lead oxide, for one reason or

other, will be less than the concentration of lead oxide corresponding to the stoichiometric composition, but still be sufficient for the perovskite phase formation [37], one can expect the formation of acceptor vacancies of the lead in the film. These vacancies provide the formation of p-type conductivity and positive space charge on a lower Pt / PZT interface, and consequently, the internal electric field directed towards the film surface. This leads to self-polarization oriented parallel to the field, i.e., towards the free surface of the layer (Fig. 1b).
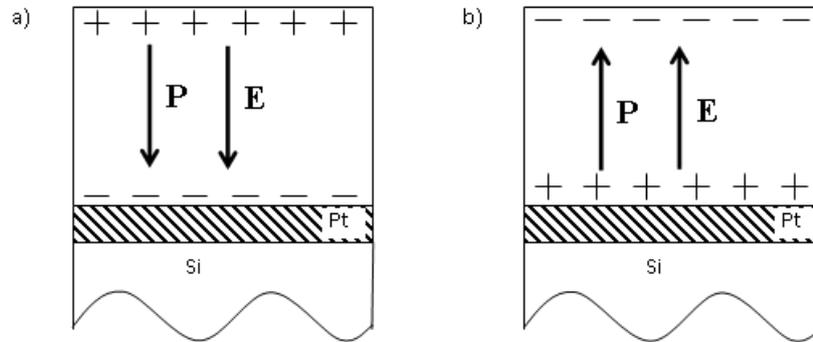
Fig. 1. The change of the orientation of the unipolar state caused by the action of the electric field of the space charge in the bottom interface area, depending on the electron (a), or the hole (b) type of conductivity of the PZT thin layer.

The following techniques can be used to change the content of lead in PZT layer:
- Increasing the heat treatment temperature (annealing) of the layer;
- The use of ceramic PZT targets with different content of excessive lead;
- The use of metal targets in the reactive sputtering vacuum apparatus,
- If the layer is deposited by chemical means using a sol-gel process, it is necessary to reduce the content of lead alcoholates in the gel solution.

In this work we utilized the technique based on the variation of pressure of the working gas mixture (80 % Ar + 20 % O_2). The pressure was changed in the range from 2 to 8 Pa. This allowed us to change the lead content (in relative atomic units Pb / (Zr + Ti)) in the deposited PZT film in a wide range of concentrations - from 0.93 at 2 Pa to 1.21 at 8 Pa. Curve 1 in Fig. 2 shows the variation of the ratio Pb / (Zr + Ti) in the in the amorphous film versus the working pressure in the chamber.
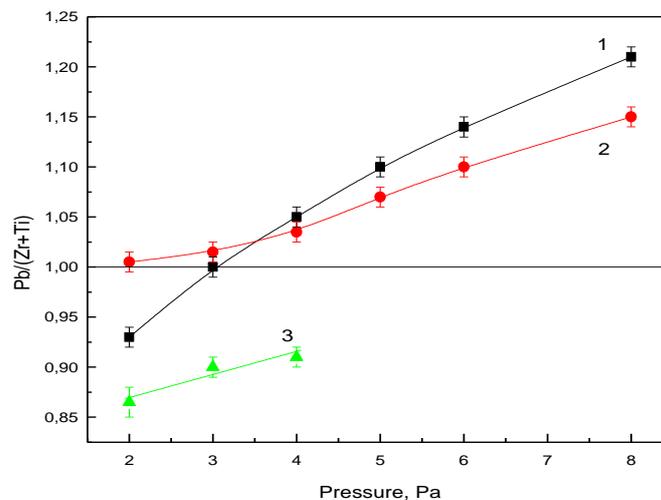

Fig. 2. The ratio of atoms Pb / (Zr + Ti) versus working gas pressure: (1) - in the amorphous film; (2) - in the annealed film in perovskite phase, (3) – in pyrochlore phase.

We think that the reason for such significant variations in the lead content may be the change of the conditions of thermalization of atoms in a gas plasma, when the regime of directional flow of sputtered atoms (Fig. 3a) is replaced by the diffusion mode (Fig. 3b) [38].
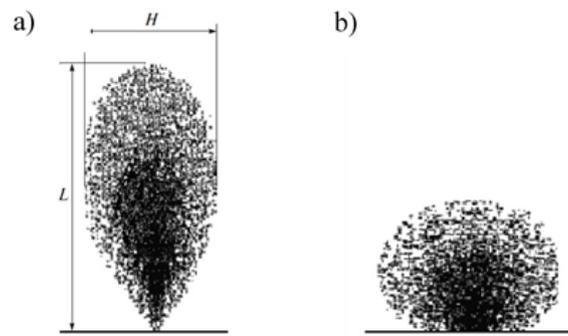

Fig. 3. Diagram of the scattering of metal atoms in the plasma of inert gases in accordance with [38].

Figure 4 shows the optical images of the films formed at different working gas pressures and then annealed in air at 600 °C. It can be seen that if the films were grown at high gas pressures, the perovskite phase and crystallization occur throughout the whole volume of the films (Fig. 4a,b). As pressure decreases, more and more areas remain, which have not transferred into the perovskite phase. In these areas preserved a low-temperature pyrochlore phase (Fig. 4c,d). In the films grown at low gas pressures the perovskite phase was formed only in the form of separate islands (Fig. 4e,f). The volume fraction of this phase was reduced to 20-25 % with the pressure decreasing up to a value equal to 2 Pa (Fig. 5). The reason for this decrease, in our opinion, is a reduction of the lead content in the films with a decrease of the working pressure during the formation of the films. Curve 2 in Fig. 2 shows the average lead content in the perovskite phase (Pe) (at low pressures - in the islands of perovskite phase), and the curve 3 shows the lead content in the pyrochlore phase (Py).
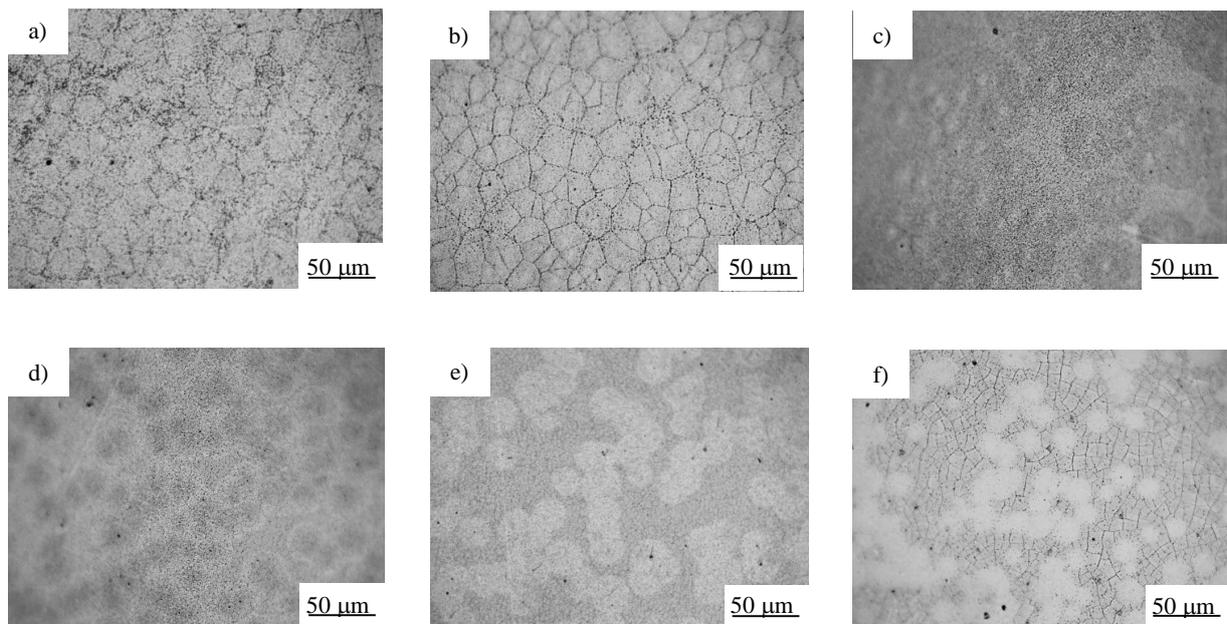

Fig. 4. Optical image of phase contrast (Py / Pe) of PZT thin films, deposited at different gas pressures and annealed in air at 600° C: a) 8 Pa, b) 6 Pa, c) 5 Pa, d) 4 Pa, e) 3 Pa, f) 2 Pa.
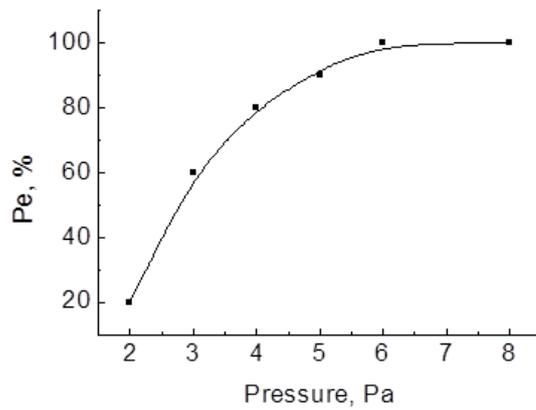
Fig. 5. Content of perovskite phase fraction (Pe) in PZT thin films versus working gas pressure (annealed in air at 600 °C).

The images of the piezoelectric response (piezo-response) of the films (signal *Mag×Cos*), obtained at different pressures of the gas mixture, are shown in Fig. 6.
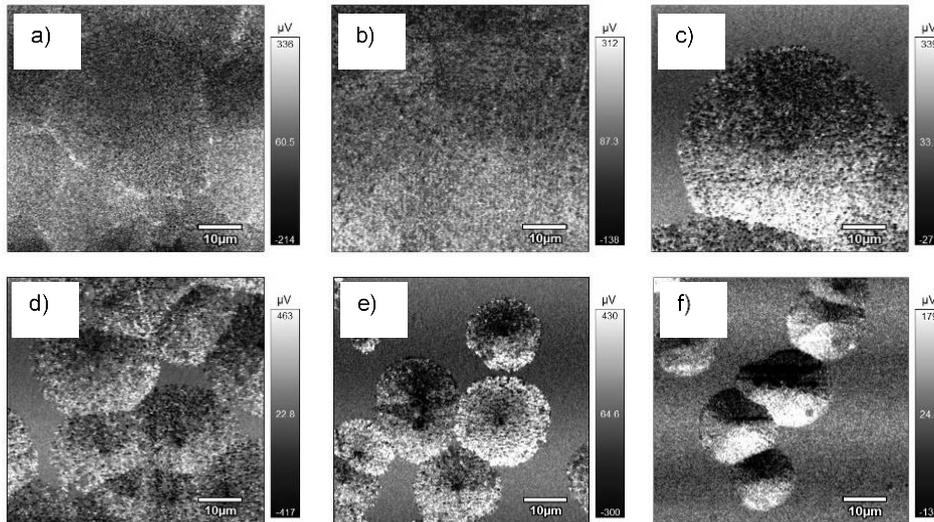

Fig. 6. Piezoresponse force microscopy (PFM) images of piezoelectric response in PZT films at different gas pressure: a) 8 Pa, b) 6 Pa, c) 5 Pa, d) 4 Pa, e) 3 Pa, f) 2 Pa.

Figure 7 shows the histograms plotted on the basis of above data, reflecting the distribution of the self-polarization state of the films over the area within the perovskite phase.
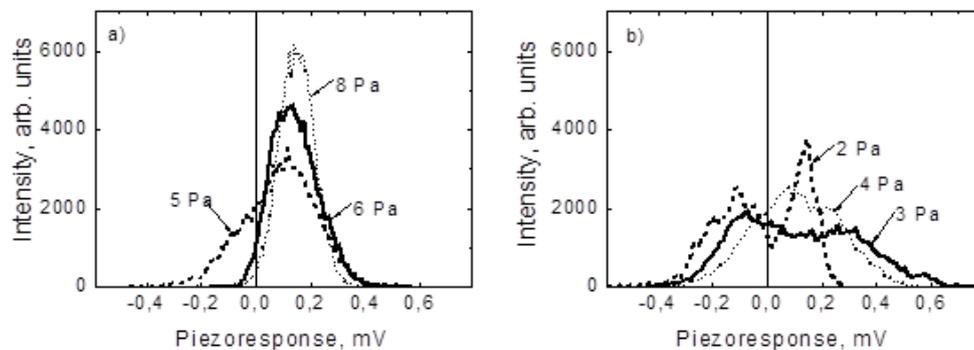

Fig. 7. Histograms showing the distribution of the self-polarization state over the film area at different gas pressure; a) 8, 6 and 5 Pa; b) 4, 3 and 2 Pa.

The piezoelectric response for the films synthesized at high pressures of the gas mixture (8-6 Pa), i.e. for the films that have a high content of lead, is distributed uniformly over the area of the samples (see Fig. 6a,b) and Fig. 7a), the curves corresponding to the pressure 8 and 6 Pa). A shift of the histograms on the abscissa-axis in the positive direction means that the self-polarization vector was oriented towards the bottom interface of the film. A decrease in pressure of the gas mixture leads to a decrease of the shift magnitude. Along with that, a decrease in the value of self-polarization and an increase of heterogeneity of the signal of piezoelectric response occur (Fig. 7a, the curve corresponding to the pressure of 5 Pa). Further pressure reduction leads to a further blurring of the signal and appearing a self-polarization signal with the values significantly higher than for pressure equal to 8 and 6 Pa (Fig. 7a, the curves corresponding to the pressure of 4 and 3 Pa). As well the splitting of the histogram occurred with forming two peaks dependences. This means that in the film are formed micro regions in which self-polarization vectors were directed towards each other (Fig. 7b). For the films, which were grown at a gas mixture pressure of 2 Pa, a clear bimodal distribution with two well-defined peaks has been observed. In this case the blurring of the histograms was reduced.

Thus, a decrease of gas pressure results in a decrease in content of lead, which, in its turn, leads to the gradual reorientation of polar ferroelectric dipoles from orientation towards the substrate to reorientation towards the free surface of the film. This dynamic is clearly seen in the histogram representing the dependence of the thin film areas oriented both towards the substrate and towards the free surface versus the pressure of the gas mixture (see Fig. 8). We believe that the self-polarization is a consequence of the formation of the space charge on the lower interface of the film-substrate. As we showed above, the space charge is formed by the oxygen vacancies. This means that the reduction in the value of self-polarization is uniquely associated with a reduction of excess lead oxide concentration in the films, and thus the decrease in concentration of oxygen vacancies.
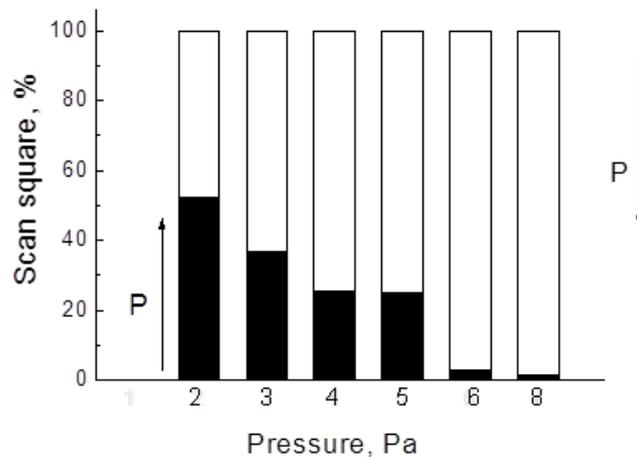

Fig. 8. Histogram showing the ratio of the scanned areas in the PZT films with the opposite orientation of the self-polarization vector.

The formation of micro regions with the self-polarization oriented towards the free film surface can be explained by occurrence of lead vacancies (at the integral ratio of Pb/(Zr+ Ti) close to the stoichiometric). The occurrence of lead vacancies may be associated with mechanisms of nucleation and growth of islands of the perovskite phase in the pyrochlore phase matrix, which can lead to the nonuniform distribution of lead over the thickness of the ferroelectric layer. Similar nonuniformity may be caused also by nonuniform mechanical stresses that develop in a thin layer of a ferroelectric as a result of mechanical interaction with the silicon substrate. The discussion of these mechanisms is provided at the finale section of the article.

From the point of view of electrical neutrality, the occurrence of micro regions in the ferroelectric layer, in which the self-polarization vector in reference to a normal to the surface can be directed in one or another side, appears quite reasonable and can be considered as a partition on a 180-degree or 90-degree quasi-domains, lowering the free energy of the system.

Returning to the vacancy model of the self-polarization formation, we note that in order to obtain in a thin PZT film, a significant concentration of lead vacancies, which would exceed the concentration of oxygen vacancies, one have to use additional technological methods. This will be the subject of a separate report.

4. Influence of the high-temperature annealing on the properties and microstructure of Pt / PZT / Pt layers

The second series of PZT thin films was synthesized at a pressure of the working gas mixture equal to 6 Pa. Then all the films in this series were annealed at temperatures 580-650 °C. After annealing, the upper Pt electrodes were deposited on the surface of the films and their structural and electrical characterization was studied. Thereafter, the films were heated somewhat higher the Curie temperature of 400 °C. Then the films were cooled to a room temperature and again the characterization of their structure and electrophysical properties was carried out. The measurements of the film composition showed that with increasing annealing temperature (T_{ann}) the excessive lead content in the film linearly decreases. At the annealing temperature $T_{ann} = 580\,^{\circ}\text{C}$ the lead content, on average, in the film was higher of the stoichiometric content by 11 % and at $T_{ann} = 650\,^{\circ}\text{C}$ only by $\approx 3\,\%$.

The initial films exhibit the asymmetry of C-V (and P-V) curves. A small shift of these curves toward the negative voltage values indicates the presence of the internal electric field (about 5 kV/cm at $T_{ann} = 580\,^{\circ}\text{C}$) in the film and its weak unipolarity (Fig. 9a). The vector of this field has been directed towards the lower electrode (Fig. 10a). The typical form of the hysteresis loop (P-V curve), reflecting the presence of the internal field, is shown in Fig. 11a.
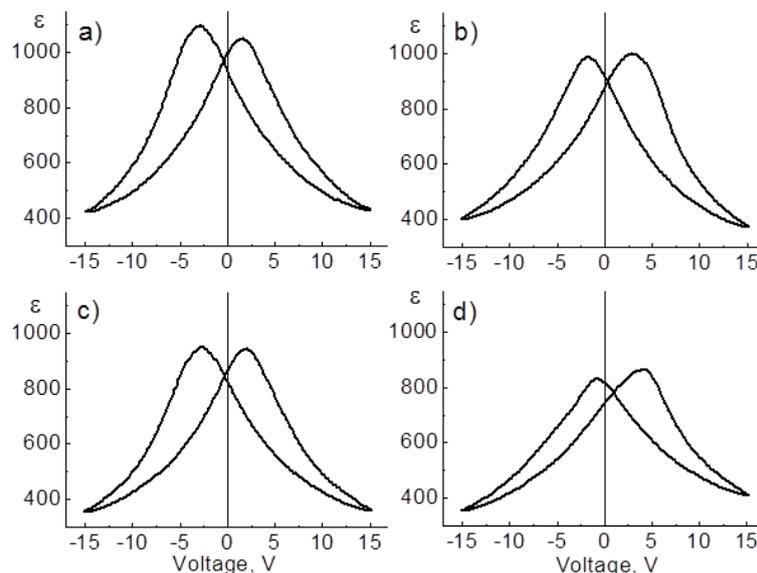

Fig. 9. The reversible ε-V dependences specific to PZT films, the perovskite phase crystallization of which was carried out at: a) $T_{ann} = 580\,^{\circ}\text{C}$ and c), 620 °C; and also immediately after heating above the Curie temperature of the capacitor PZT structures, b) films annealed at $T_{ann} = 580\,^{\circ}\text{C}$ and, d) films annealed at $T_{ann} = 620\,^{\circ}\text{C}$).

The value of the internal electric field in the films, synthesized at a working gas mixture pressure of 6 Pa, was not great. With increasing annealing temperature T_{ann} the electric field becomes even smaller. A decrease of the field takes place in such a way that the C-V

characteristic in the film, which was initially formed at a temperature of 650° C, became almost symmetrical (Fig. 9c). A sign of pyroelectric response, defined by us, confirms the data on the direction of the self-polarization vector. A heating of the samples above the Curie temperature led to a change in the direction of the shift of the dependencies C-V (and P-V). As a rule, they were shifted in a positive direction on the X-axis. This means that there is formed the inner field in the films, which is oriented towards the free surface of the film (Fig. 9d, 10c, and 11c).
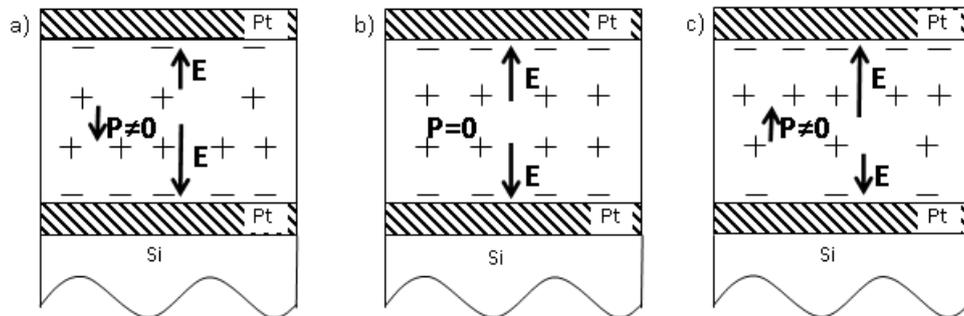

Fig. 10. The change of the unipolar state orientation due to the electric field of the space charge in the region of bottom interface, depending on the electron (a) or the hole (c) conductivity type of the thin PZT layer.

Figure 11 presents three characteristic dielectric hysteresis loops of the capacitor. The data were obtained by studying the polarization process in the capacitors that were kept for one year. In the process of aging of the samples the asymmetric shape of the hysteresis loops (Fig. 11a and 11c), reflecting the orientation of the self-polarization vector, has undergone significant changes. Statistically, in about 50 % of cases, instead of the asymmetric loops, prevailed the symmetric, so called, "double" loops or loops with a "waist" (Fig. 11b). A similar shape of the loops indicates that in the fine ferroelectric layer there were formed the oppositely directed (facing each other) the internal electric fields (Fig. 10b). Besides the double loops in the films formed at $T_{ann} = 580°C$ and $T_{ann} = 600°C$, there were observed the loops shifted, in most cases, towards negative voltages (Fig. 11a). In the film formed at higher annealing temperatures ($T_{ann} = 620 °C$ and $T_{ann} = 650 °C$) the shifts of P-V curves, for the most part, were observed in the opposite side (Fig. 11c). The observed changes, in particular, may be associated with features of crystallization of sufficiently thick polycrystalline films, which may contain several large and thick perovskite grains [29]. The changes in the character of the internal fields during aging reflect the rather complex processes occurring in the samples. These processes appear to be related to both the migration of charged defects and the relaxation of mechanical stresses [39].
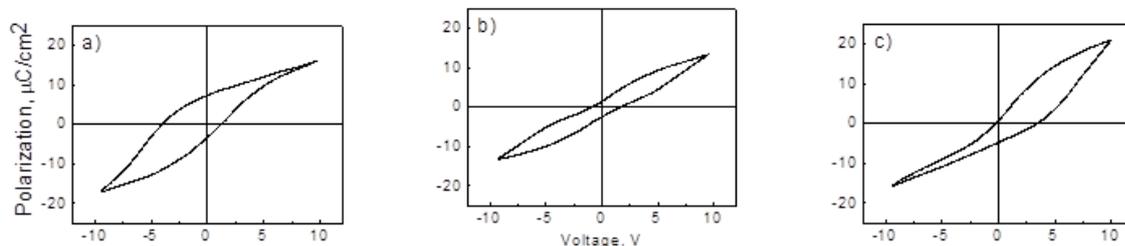

Fig. 11. The dielectric hysteresis loops for the PZT capacitor structures, corresponding to different versions of the unipolar state shown in Fig. 10. Measurement frequency is 1 kHz.

Note, that in the films with the perovskite structure formed at the annealing temperature of 580 °C, the direction of self-polarization vector usually remained unchanged. These data were obtained as a result of measurements of film pyroelectric response. The reliability of this conclusion is confirmed by a large number (about 20) of the measurements.
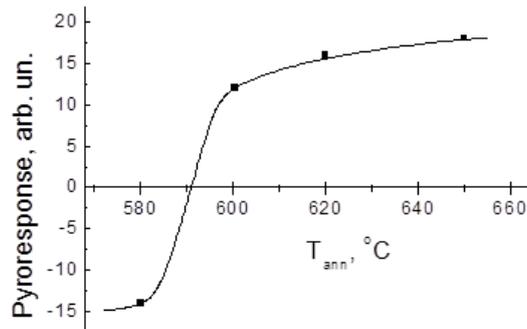
Fig. 12. The change of the sign of the pyroelectric response and direction of the self-polarization vector as a result of high heating of the capacitance structure of Pt / PZT / Pt above the Curie temperature in thin films formed at temperatures of 580-650 °C.

Thus, the heating of the capacitance structure Pt/PZT /Pt, in most cases, have led to the reorientation of the self-polarization vector towards the free surface, i.e. towards the top electrode, and the probability of the reorientation increasing with increasing the annealing temperature. The experimental data on the reorientation of the self-polarization vector due to heating of the thin-film Pt/PZT/Pt capacitor above the Curie temperature and subsequent cooling to room temperature, allow us to deduce a few conclusions. 1. The change in the direction of self-polarization vector may be associated with the change of the growth mechanism of perovskite phase. This leads to a redistribution of the mobile charges between the upper and lower interfaces of the ferroelectric film and to their subsequent capture at the upper or at the lower interface. 2. The sign of the space charges formed on the upper and lower interfaces of the ferroelectric layer may be also changed. But in any case, the observed phenomena are uniquely associated with the presence of intrinsic point defects which are the oxygen or lead vacancies.

5. The concentration of lead and the nature of the reorientation of the self-polarization vector

The experimental data presented in Fig. 2 show the following:
- High temperature annealing results in a reduction of lead content, which may be due to the fact that lead, at high temperatures, can change its oxidation state in a wide range;
- In a two-phase film occurs the redistribution of lead between the regions occupied by the perovskite and pyrochlore phases. The effect is most pronounced in films deposited at a pressure of a gas mixture of 2 Pa.

These data clearly demonstrate that crystallization of the perovskite phase in thin films with content of lead lower than the stoichiometric composition (i.e., the atomic ratio (Pb / (Zr + Ti) <1)), does not practically occur. Note that in [37] also was demonstrated that the perovskite phase crystallization in the entire volume of the thin film can take place only if the ratio Pb/(Zr+Ti) does not deviate below the stoichiometric amount on (2-3) %.

We may also assume that a change in the oxidation state of lead (for example, from +2 to +4) formally results in his deviation from the stoichiometric concentration. Indeed, with increasing of oxidation state of lead the number of oxygen atoms should also increase in order to preserve the stoichiometry composition. However, if its concentration is constant the oxygen vacancies will appear in oxygen sublattice.

Since the formation of the ferroelectric properties of PZT films is associated with the formation of the perovskite phase, we believe that the most likely the reorientation of the self-polarization vector with the heating of the Pt/PZT/Pt structures is related with the creation of perovskite nuclei and their subsequent overgrowth near the free surface, or with the similar nucleation process near the bottom surface (Fig. 13) [40]. The experiment shows that the

formation of the perovskite phase is possible only if the film has a stoichiometric lead composition, or if it contains a lead excess. This means that during the annealing the intensive redistribution (diffusion) of lead atoms from one edge to the other occur in the film.
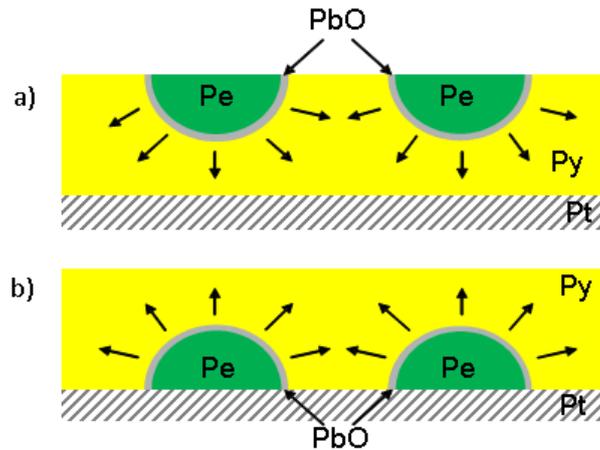

Fig. 13. Schematic representation of the nucleation of the perovskite phase (Pe) in the pyrochlore phase matrix (Py) on the top (a) and bottom (b) interfaces of the thin PZT layer. The arrows indicate the direction of growing of Pe-phase and of displacing of lead-oxide excess either to a lower platinum electrode, or to the free surface.

This raises the reasonable question. Whether this mechanism unique or we can discovery other phenomena responsible for the diffusion of lead atoms? To answer the question, let us turn to the phenomenon, which was discovered in 1935 and is well-known to scientists engaged in research of metal alloys. This phenomenon is called Gorsky effect [40]. A more detailed description of Gorsky effect and its modern interpretation can be found in [41, 42]. The essence of the Gorsky effect is as follows. In a solid, which is under the influence of non-uniform bending elastic stresses, atoms having a larger size will move towards the extended area, whereas vacancies and the atoms, having a smaller size will move in the direction of the compressed area in order to compensate the action of the external compressive force in full compliance with the Le Chatelier's principle. Fig. 14 qualitatively illustrates the physical essence of the Gorsky effect.
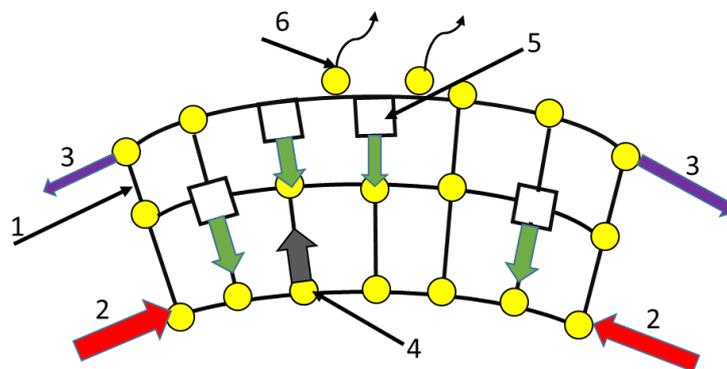

Fig. 14. Schematic representation of the Gorsky effect; 1 - the crystal part curved under the action of elastic stresses; 2 - elastic stresses; 3 - directions of stretching of the crystal; 4 - atoms and their direction of motion under the action of elastic stresses; 5 - vacancies and their direction of motion under the action of elastic stresses; 6 - evaporation of atoms from the surface of the crystal.

During annealing, due to the difference in the coefficients of thermal expansion of the film, the buffer layers. and the silicon substrate the elastic stresses arise, which lead to a bending of

the film and substrate, that, in fact, we observed for all samples. If the film is curved convex upwards, the atoms of larger size will be "collected" at the surface of the film. If we are dealing with chemical compounds of stoichiometric composition, it is quite possible that the tensile stresses (see Fig. 14) will lead to the exit of the atoms on the film surface. At the same time, in the vicinity of the boundary there will be formed the vacancies of atoms which were removed, in full accordance with the theory of the formation of pores under load [43]. Now, on the basis of Gorsky effect, we consider what to be happening in our system. In this paper we do not calculate strictly quantitatively the diffusion flows of atoms of different kinds under the action of mechanical stresses. Let us make the simplified and qualitative consideration of the basic processes, which, in our view, correctly explains the physics of the processes leading to the formation of the internal electric field and try to determine its direction depending on the composition of the PZT film. Note that, in general, for accurate calculation of the processes occurring in bending of the PZT layer, it is necessary to investigate Gorsky effect in each of the PZT crystal sublattices and take into account their impact on each other. Moreover, it is necessary to calculate the bending stresses, using, for example, the Stoney formula for the multilayer system, which arise because of the difference in thermal expansion coefficients of the Si substrate, SiO_2 buffer layer, platinum electrode and PZT film. These calculations need to be carried out for different thicknesses of each layer and different annealing temperatures. Thus, here we consider only qualitatively that will occur in films with different stoichiometry.

PZT Stoichiometric films. Let us consider the case where the film is curved convex upwards. The largest of the existing PZT atoms, the atoms of lead (Pb covalent radius is equal to 1.47Å) under compressive stress gradient will move to the top surface of the film. Towards them, in direction to the substrate will move the Pb vacancies. If lead atoms do not evaporate, their concentration near the top surface will be higher than the concentration of oxygen atoms. This results in the fact that near the top film surface the oxygen vacancy concentration will be higher than in the film depth. The oxygen vacancies are donors of electrons and they will be positively charged with the dissociation. Since electron mobility is higher than an oxygen vacancy, a positive charge is formed near the top film surface. The electrons formed as a result of the dissociation of the donor oxygen vacancies, will diffuse to the lower boundary of the interface, where they can be captured at deep traps. As a result, the internal field will be directed from the top towards the bottom interface. With increasing of the annealing temperature the tensile stresses will increase. It can result in the output of a part of lead atoms on the top film surface and even their evaporation. In this case, near the surface of the film are formed the vacancies of lead. They are the electron acceptors. Therefore, near the top interface will be formed the p-type conductivity, which leads to the formation of the positive space charge near the bottom surface of the film and, as a consequence, the internal field is directed from the bottom toward the top interface.

Consider the case where the substrate with the film is convex downwards. Since in this case, the lead atoms could not be removed effectively from the film (in the first case, they could reach the surface of the film and even evaporate), they will accumulate on the film-substrate interface, and the oxygen vacancies will collect near the lower interface.

Near the top surface of the film, on the contrary, it will be lack of lead atoms and, as a consequence, their excess vacancies. The lead vacancies are negatively charged and therefore the field will be directed from the substrate toward the top film surface. Here various options may take place. Charge compensation can occur, or conversely, electrons and holes can create additional internal field (such as p-n junction), which depends on the energy of the traps and as result the internal field will increase.

PZT films with Pb sub-stoichiometric content. Let the film is convex upward. In this case, the Gorsky effect will lead to further decrease in the concentration of Pb (if the Pb evaporate during the annealing) and to an increase of concentration of Pb vacancies. The highest

concentration of vacancies will be near the top surface of the film. The vacancies of lead are acceptors. Therefore, near the upper interface will be formed the p-type conductivity, which leads to the formation of the positive space charge near the surface of the film and, as a consequence, the internal field is directed from the upper to the lower interface.

If the substrate with film is convex downwards, then, as in the case of stoichiometric composition, Pb atoms cannot effectively be removed from the film. Their concentration will increase. This in turn leads to the stoichiometry near the lower interface. The result will be the compensation of the charges, and the intensity of the internal field will either be small or it will be completely absent.

PZT films with Pb over- stoichiometric content. If the film is curved convex upwards, one could observe even greater increase in the concentration of Pb near the top surface (if the lead does not evaporate). In this case the concentration of oxygen vacancies will also increase that resulting in that the internal field will be directed from the upper to the lower interface.

If the film is convex downwards, the oxygen vacancies will accumulate near the bottom. The field will be directed from the top to the bottom interface.

6. Results and conclusions

1**.** The method of RF magnetron sputtering of the ceramic target has been adapted for growing thin polycrystalline PZT films with different concentrations of lead. The proposed technique is based on the variation the pressure of the working gas mixture in the range from 2 to 8 Pa, which allows to obtain PZT films with the lead content from the super stoichiometric (atomic ratio Pb/(Zr+Ti) = 1.21) to the composition with Pb/ (Zr + Ti) = 0.93 that is below the stoichiometric ratio.

2. In the films deposited at low pressure of the gas mixture the perovskite phase is formed only in the part of the film volume, and an increase of the lead content in areas of perovskite phase (with simultaneous reduction of its content in the pyrochlore phase) occurs due to the diffusion of lead in the course of annealing.

3. It is shown that with decreasing of the lead concentration, there occurs the reorientation of the self-polarization vector in some micro-regions of the film. It is expected that these changes are associated with changes in the nature of the charge defects - from the donor oxygen vacancies (with a lead large excess) to the acceptor lead vacancies (at an atomic ratio of Pb/(Zr+Ti) close to the stoichiometric).

4. The peculiarities of the reorientation of the self-polarization vector in the thin-film Pt/PZT/Pt capacitor, when heated above the Curie temperature, have been studied. It has been shown that reorientation depend on the temperature at which the perovskite phase was formed. We have suggested that the competition between the nucleation of perovskite phase near the bottom or top interface of the thin film is responsible for the observed changes.

5. We have proposed the new model of formation of the space charge, based on the mechanochemical effect of redistribution of atoms with different sizes under the action of elastic stresses caused by a difference in the thermal coefficients of the film-substrate expansion.

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