Original articles

Crystallization features and physical properties of the thin-film heterostructure of lead zirconate titanate – lead oxide

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Abstract

Various diagnostic techniques aimed at studying the structure and physical properties (synchronous thermal analysis, atomic force microscopy operating in the current measurement mode, electron-probe X-ray spectral microanalysis, dynamic method for determining the pyroelectric response) were used to study the crystallization features and physical properties of the thin-film heterostructure PZT – PbO_{1+x} formed by a two-stage technique of RF magnetron sputtering of a ceramic target.

During the first stage, amorphous films were deposited on a "cold" platinized silicon substrate, while the second stage involved high-temperature annealing in air. It was shown that annealing of amorphous films and crystallization of the intermediate pyrochlore phase are accompanied by additional oxidation of the structure resulting in the formation of lead orthoplumbate and lead dioxide and additional oxidation of organic inclusions. The presence of a liquid phase of lead oxide contributes to the formation of the pyrochlore phase.

It was found that lead oxide layers have significantly higher through conductivity than perovskite blocks. It was assumed that the increased conductivity of lead oxide layers is associated with lead dioxide, which has high conductive properties. Self-polarized thin films were detected to have an abnormal electrical response to the strobing thermal exposure, including the typical pyroelectric response, local photoconductivity shunted by layers of the perovskite phase, and through photoconductivity. The presence of photoconductivity is also associated with the conductive properties of lead dioxide.

Keywords: Thin film heterostructure of lead zirconate titanate and lead oxide, Crystallization of pyrochlore and perovskite phases, Differential scanning calorimetry, Thermal analysis, Atomic force microscopy, Pyroelectricity

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1. Introduction

Thin films of lead zirconate titanate ((Pb(Zr,Ti)O$_3$ or PZT), the composition of which corresponds to the morphotropic phase boundary region, are characterized by abnormally high electromechanical and piezoelectric coefficients and are currently the most common materials used in microelectronics [1–3], electro-optics [4], and microelectromechanics (MEMS) [5–7]. Optimization of the film structure and properties is largely associated with the control of their composition. Their formation is characterized by lead loss due to the high volatility of lead oxide vapors at high temperatures [8–9] especially during phase transformations and crystallization and recrystallization of the perovskite phase [10–11]. Experiments have shown that when the lead content is below the stoichiometric content the perovskite phase does not form [11]. To compensate for lead loss, during physical (vacuum) film deposition techniques, excess lead oxide (PbO) is added to the sputtered target. When using chemical methods, excess lead is added to the chemical solution. As a rule, as a result of the formation of the perovskite structure of the films, traces of excess lead oxide remain in the form of separate microinclusions or microlayers depending on its amount. The presence of excess lead in large quantities (over 5–10 mol. %) leads to the appearance of properties different from the single-phase perovskite structure [12–16], and, in particular, to the effect of spontaneous (macroscopic) polarization (self-polarization), the presence of which increases the efficiency and competitiveness of thin PZT films when used in microelectromechanical devices [17–19]. In most studies, lead oxide is identified by its divalent modification, PbO.

The presence of excess lead in thin PZT films indicated the heterostructure (or composite) PZT – PbO$_{1+x}$, where $x = 1 \div 2$, which differs in the arrangement of the lead oxide inclusions PbO$_{1+x}$ in the volume of the thin film, Fig. 1. Despite the increased use of such thin-film composites in practical applications, the configuration of the location of lead oxide inclusions along the thickness has been poorly studied. Another problem is related to understanding which of the three oxides, lead oxide (PbO), lead dioxide (PbO$_2$), or lead orthoplumbate (Pb$_3$O$_4$), is actually present as a component of the heterostructure, since their chemical parameters and electronic properties differ significantly. This makes it impossible to purposefully optimize the production technology and the physical properties of such structures. In this regard, the purpose of this work was to obtain additional data on the peculiarities of the formation process and physical properties of the heterostructure PZT – PbO$_{1+x}$, and to analyze the data obtained both during this and previous research.

2. Sample preparation and research methods

The heterostructure was formed using a two-stage technique. During the first stage, RF magnetron sputtering of a ceramic target was used to deposit amorphous films at the temperature of the substrate determined by the heating temperature of the argon-oxygen plasma which
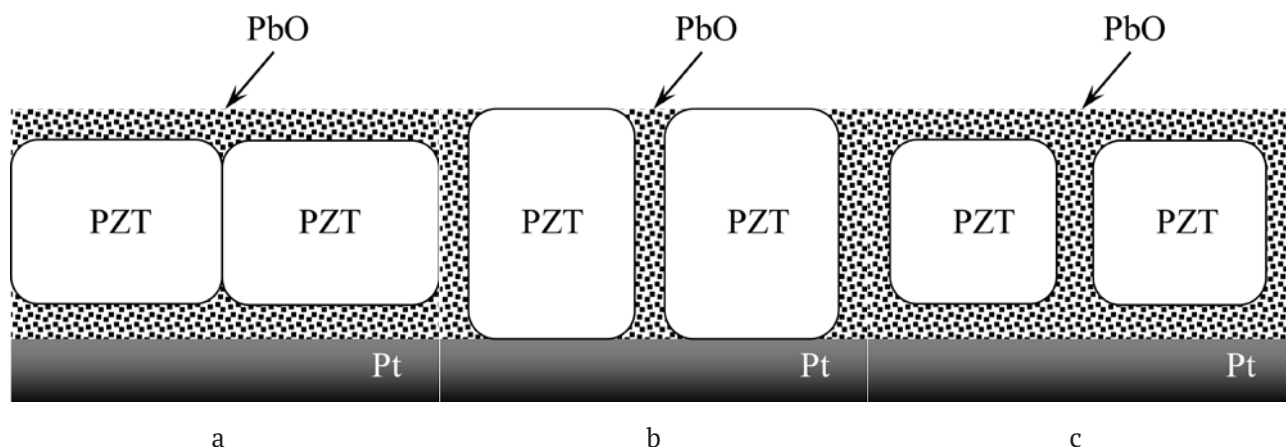

Fig. 1. Different arrangement of lead oxide layers (a-c) in the PZT–PbO$_{1+x}$ heterostructure

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was 130–140 °C at a gas mixture pressure of 8 Pa. Platinized silicon wafers were used as a substrate. The composition of the sputtering target corresponded to the region of the morphotropic phase boundary ($PbZr_{0.54}Ti_{0.46}O_3$). To compensate for lead loss, 10 mol % of PbO was added to the target. The thickness of the formed films was 200–500 nm. To take electrophysical measurements, a 200×200 μm platinum electrode array was formed on the surface of the samples.

The phase state of the films was studied by X-ray diffraction phase analysis (DRON-7) and optical microscopy. Phase transformations were monitored by synchronous thermal analysis using a STA 429 CD unit. Heating was carried out in the temperature range from 20 to 560 °C at a rate of 10 °C/min in an air and in an argon atmosphere. When taking the measurements, the mass of the sample and the change in enthalpy were evaluated.

The perovskite structure was formed by annealing amorphous films in air at 550–600 °C for 1 hour. The state of the microstructure was monitored by scanning electron microscopy (EVO-40) and atomic force microscopy in the contact mode of current measurement (Solver P47, NT-MDT). The composition of the thin films was determined by electron probe X-ray microanalysis using an INCA analyzer. Dielectric properties were studied using an E7-20 immitance meter. The pyroelectric properties of the films were studied by the dynamic technique using a strobing heat flow of laser radiation at a wavelength of 632.8 nm [14].

3. Results and discussion

Synchronous thermal analysis (DSC curves) of films with a thickness of 500 nm in an air atmosphere showed that in the range of temperatures from 430 to 480 °C there was a change in the system enthalpy due to the chemical transformation and crystallization of the intermediate pyrochlore phase. The results are represented by curve 1 for an empty crucible, curve 2 for a sample placed in the system, and the DDSC differential curve is represented by curve 3 (Fig. 2). There were no other changes in the system enthalpy up to a temperature of 600 °C, however, microstructural studies showed that low concentrations of individual islets of the perovskite phase appeared in the film. The linear size of such islets did not exceed 1–2 μm.
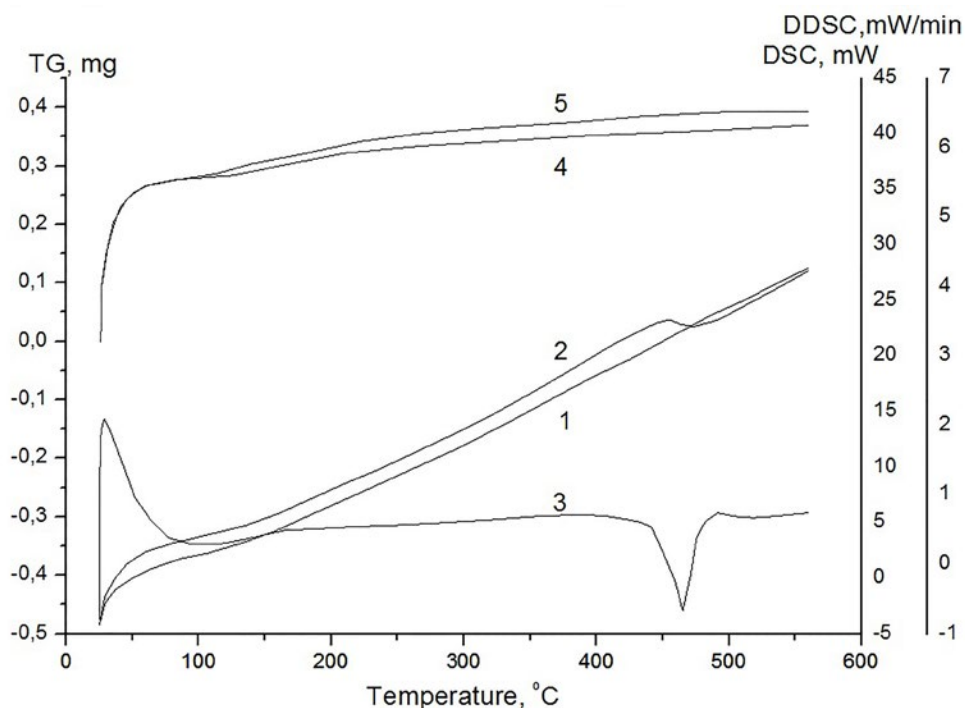

Fig. 2. Results of synchronous thermal analysis. DSC analysis corresponds to curve *1* (for an empty crucible), and *2* (for a crucible with a sample). Curve *3* represents the derivative of the DSC – DDSC curve. Curves *4* and *5* reflect the change in the mass of the empty crucible and the crucible with the sample, respectively

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When similar measurements were taken in an argon atmosphere, there were no changes in the system enthalpy. An analysis of the change in mass (TG curves 4 and 5) showed that in air there was additional oxidation of thin films and the change in the total mass was ~ 3 µg (microgram) with a total film mass of ~ 50 µg. This meant that the amount of oxygen in the film increased by approximately ~ 40% and the mass by ~ 6%.

The additional oxidation of the film observed in the experiment (and the increase in the mass of the sample) against the background of the formation of the pyrochlore phase seem to be illogical. Indeed, according to previously obtained results, during the crystallization of the pyrochlore phase from the amorphous phase in samples similar to the studied, the estimated lead losses were 5–7% [16]. These losses are due to the pushing of excess lead in the form of oxide to the interphase regions (between the amorphous and pyrochlore phases), the diffusion rate in the interphase regions near the surface of the film due to their porosity is significantly higher than in the amorphous or pyrochlore phases. Similar processes occur during the crystallization and recrystallization of the perovskite phase at high annealing temperatures and are also accompanied by the removal of excess lead oxide [16]. No decrease in mass in the studied samples at high temperatures may indicate that under the conditions of a rapidly rising temperature and a low rate of diffusion of lead (oxide) to the surface of the thin film, lead depletion will only occur in its near-surface part. This should have practically no effect on the total mass of the sample.

The data of elemental analysis of samples of amorphous films showed that the relative oxygen content in them was excessive and 1.3 times higher than necessary for the synthesis of the pyrochlore phase with the chemical formula $A_2B_2O_6$ or the perovskite phase with the formula ABO_3, where lead atoms were located in position A, whereas titanium or zirconium atoms were located in position B. What is more, the excess of lead was ~ 25% relative to the stoichiometric composition. In addition, it was found that the films contained carbon, which indicated

the presence of organic matter in the vacuum system, which was largely responsible for the presence of excess oxygen. In this regard, we associate the additional oxidation of samples not only with the chemical reactions of lead oxide (PbO) with oxygen and the formation of either lead orthoplumbate Pb_3O_4 or lead dioxide PbO_2 [20]:

$$2PbO + O_2 = 2PbO_2;\qquad (1)$$

$$6PbO + O_2 = 2Pb_3O_4;\qquad (2)$$

$$Pb_3O_4 + O_2 = 3PbO_2,\qquad (3)$$

but also carbon oxidation. Calculations showed that when lead is additionally oxidized to the tetravalent state, an increase in the film mass due to this will be 75% while 25% of increase will be due to carbon oxidation. However, it is difficult to say now what is the real distribution of lead oxide modifications in the heterostructure. The temperature range for lead dioxide stability can be used as an argument against its presence: at 290 °C it changes into a liquid state, while the melting points of lead orthoplumbate and lead oxide are 830 and 890 °C, respectively. The argument in favor of the possible presence of lead dioxide is that the melting point of lead dioxide in a thin film is likely to be significantly higher than in its bulk analog. In addition, the crystallization of both the intermediate pyrochlore phase and the perovskite phase will be significantly simpler in the presence of mobile layers of the liquid phase. Further experiments made it possible to evaluate qualitatively if certain modifications of lead oxide were present in the studied heterostructure.

The formation of the perovskite structure was accompanied by the removal of organic inclusions, a diffusion to the surface, and subsequent evaporation of a significant part of excess lead. What is more, the oxygen content practically corresponded to the chemical formula of the heterostructure PZT – PbO_{1+x}.

Fig. 3 shows an image of a film with a thickness of 200 nm obtained by atomic force microscopy in the conductivity mode. A constant voltage of 10 V was applied to the conducting probe. It was obvious that the conductivity differed significantly (by several times) in polycrystalline
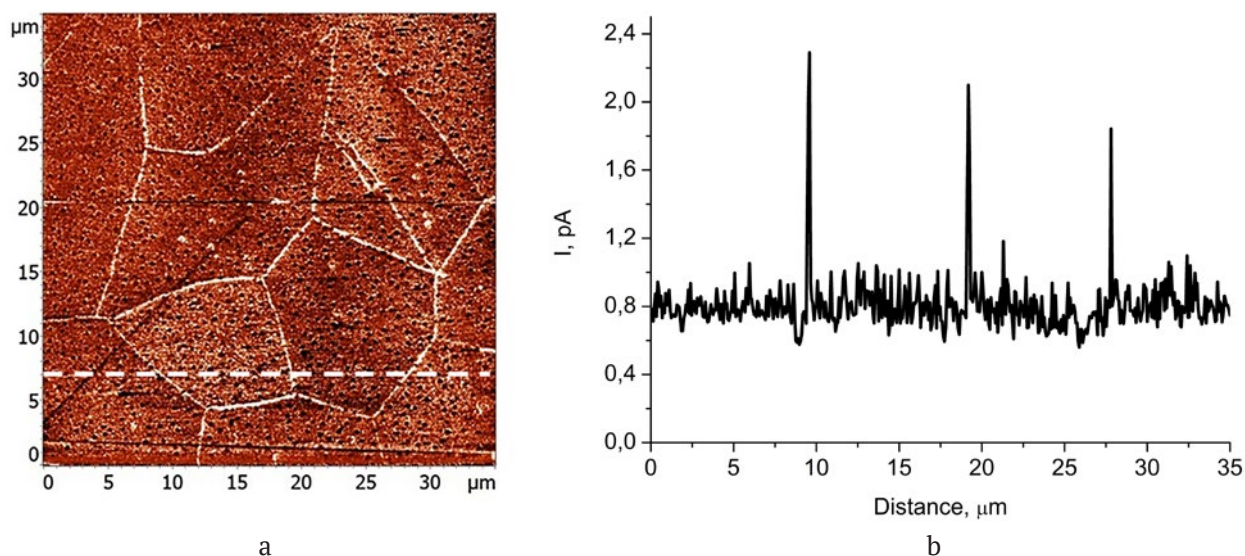
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Fig. 3. AFM map of a thin PZT perovskite film, obtained in conduction mode (a) and current distribution profile through the sample along the horizontal dotted line (b)

(spherulitic) blocks and interblock boundaries. The interblock boundaries are inclusions of excess lead in the form of oxide. A comparative analysis of the conductive layers of lead oxides (PbO, PbO_2, Pb_3O_4) indicated that it was lead dioxide that had the conductive (semiconductor) properties, whose impurity zone was located below the conductivity zone by ~ 0.2 eV [21]. For comparison, the band gap width of PbO was 2.59 eV and at room temperature it exhibited dielectric properties with a dielectric constant of ~ 10. A fairly wide gap width was also characteristic of lead orthoplumbate (2.14 eV).

Another confirmation of the highly conductive properties of lead dioxide is the results of the study of the electrical response of self-polarized PZT films under the influence of a strobing heat flow produced by laser radiation at a wavelength of 632.8 nm. Fig. 4a shows the pyroelectric response of the film (narrow peaks on the leading and trailing edges of the thermal pulse), in which the inclusions of lead oxide did not exceed 7–8%, and were mainly located near the lower and upper interface of the structure (Fig. 1a). An increase in the content of lead oxide (up to 10–11%) led to the appearance of a significant amplitude of opposite polarity on the edges of pulses, which indicates a local (non-through) photocurrent (Fig. 4b). A similar effect can be achieved by increasing

the content of lead oxide and the formation of discontinuous (separate) fragments located along the boundaries of perovskite grains or blocks. Finally, a further increase in the content of lead oxide (over 15%) in the heterostructure led to the formation of inclusions of lead oxide which formed conductive channels (Fig. 1b) and to the emergence of through photoconductivity in the form of a shelf on the electrical response signal, Fig. 4c. Such conductive properties, similar to the case of the conductivity of interblock boundaries, are characteristic of lead dioxide.

Dielectric measurements showed that an increase in the content of lead oxide in the composite led to a sharp decrease (three times or more, from 900 to 250) in the effective value of dielectric constant and an increase in dielectric losses. This was due to the formation of thin dielectric layers of PbO_{1+x} located along the thickness consecutive to the perovskite layers.

4. Conclusions

We studied the crystallization features and physical properties of the thin-film heterostructure $PZT – PbO_{1+x}$ formed by the two-stage technique of RF magnetron sputtering. It was shown that the annealing of amorphous films is accompanied by their additional oxidation which is absolutely necessary for the
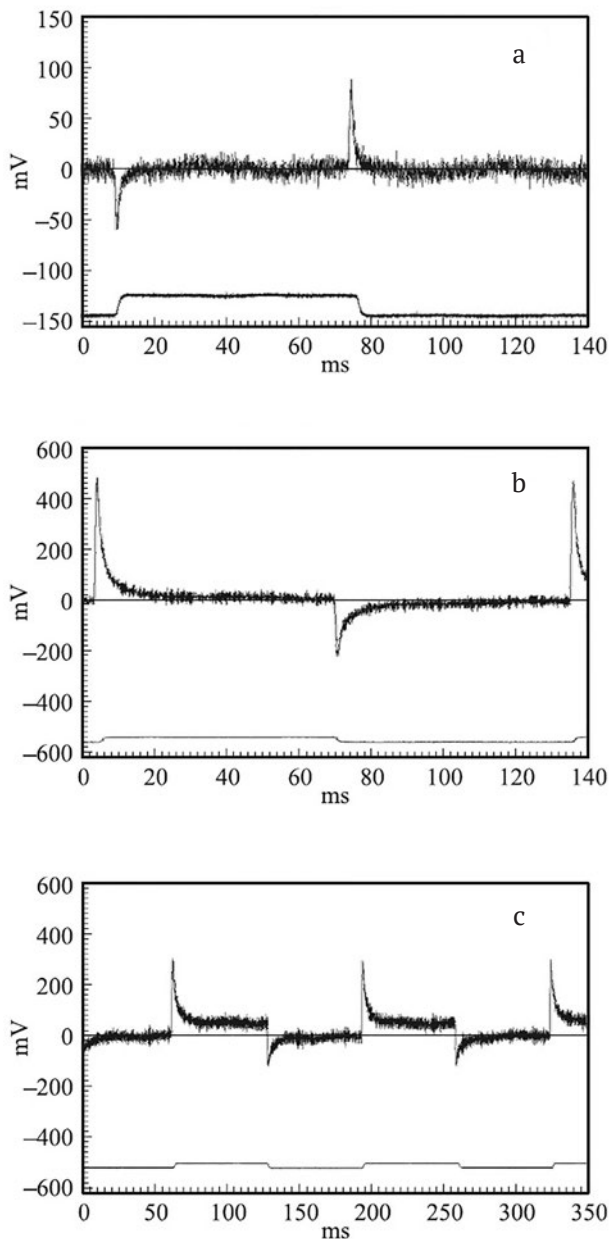
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Fig. 4. Changes in the shape and magnitude of the electrical response under rectangularly modulated thermal radiation in self-polarized PZT films with increasing content of lead oxide inclusions PbO_{1+x}: a) 7-8%, b) 11-12%, c) over 15%

crystallization of the intermediate pyrochlorine phase and the subsequent transformation into the perovskite phase. The obtained results indicate that the second component of the heterostructure in the form of lead oxide should in reality be a mixture of oxides (PbO, PbO_2, Pb_3O_4) with different lead valencies. The difference between the conductive and dielectric properties of

lead oxides leads to the appearance of unusual properties uncharacteristic of a single-phase perovskite structure.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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