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Effect of the lead oxide content on the microstructure and properties of PZT films obtained by RF magnetron sputtering

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Abstract. Experimental studies of the influence of lead oxide as well as temperature and time of heat treatment on the microstructure and ferroelectric properties of PZT films obtained by the high-frequency magnetron sputtering method were carried out. It is shown that the change in the ferroelectric properties of polycrystalline PZT films can be explained by their heterophase structure with inclusions of lead oxide. It was found that the presence of a sublayer of lead oxide leads to a self-polarization of the film of the PZT. During the formation of the perovskite structure, the diffusion of lead oxide to the surface of the film occurs more intensively than after its formation.

1. Introduction

Thin-film ferroelectrics are widely used in microelectronics. Ferroelectric films are used in microelectromechanics, various sensor devices based on piezoelectric and pyroelectric effects in the ferroelectric memory devices, microwave devices, sensors, photovoltaics, etc. [1–6]. The solid solutions of lead zirconate titanate (PZT) are among the most widespread materials for these applications and characterized by a broad spectrum of values of the physical parameters depending on the composition [2, 7].

Studying processes of the PZT thin films, managing their structure and properties are widely discussed in the scientific literature [7–9]. It is caused by the complexity of physico-chemical processes that occur during the formation of the perovskite PZT phase and their dependence on a number of factors. A specific interest in this case is the behavior of lead, vapor volatility and migration ability that in the process of application and crystallization of PZT may lead to changes in structure, composition as well as in the nature of electrically active defects and can cause an influence on the electrical properties of the films [7, 10].

Due to that, a study of the effect of the lead oxide content on the kinetics formation and electrophysical properties of the polycrystalline PZT films as well as development of model representations of the lead diffusion processes in polycrystalline PZT films for predicting their properties are an urgent task both from scientific and practical point of view.

According to modern concepts in [11], a high-temperature annealing in an oxygen containing environment of thin polycrystalline PZT films leads to diffusion of lead on the grain periphery. Similar phenomena were studied in other lead-containing materials where the lead diffusion leads to the formation of the lead oxide phase at the grain boundaries of the polycrystalline films [12]. The impact of forming conditions and defectiveness of PZT films on their ferroelectric polarization were studied in [13].

The aim of this work is study of the effect of lead oxide content and time-temperature regimes of heat treatment on the microstructure and properties of polycrystalline $Pb(Zr, Ti)O_3$ (PZT) films obtained by RF magnetron sputtering.

2. Experimental

PZT films with thickness of 0.3 to 1.5 μm of composition near the morphotropic phase boundary were obtained by reactive magnetron RF sputtering method with subsequent heat treatment in an oxygen containing environment to crystallize the films into the perovskite structure.

Films of lead zirconate titanate were obtained by a two-stage technology (ex-situ). In the first stage, PZT films were deposited by reactive magnetron RF sputtering of a ceramic target with a composition of $Pb(Zr_{0.58}Ti_{0.42})O_3$ on the “cold” (≈130 °C) platinized substrates. At the second stage, PZT films heat treatment in a muffle furnace at air (from 530 to 630 °C within 30...180 min) was performed at various time-temperature conditions. Films rate of heating in a furnace was 10 °C/min, and their cooling was carried out with the furnace. The upper platinum electrodes with an area of 0.18 mm^2 were precipitated by ion-plasma sputtering method through a free mask.

For investigation of the effect of lead oxide on properties of PZT and thin film structures based on them, an additional series of samples was made where an additional thin (10…20 nm) layer of lead oxide between the ferroelectric film and the lower structure-directing Pt electrode was formed.

Thus, two series of film structures samples were made:

- capacitor structures with polycrystalline films of lead zirconate titanate of stoichiometric composition: $Pt/PZT/Pt/Ti/SiO_2/Si$;
- multilayer structures with PZT films and with thin underlayer of lead oxide between the ferroelectric film and the lower structure-directing electrode: $Pt/PZT/PbO/Pt/Ti/SiO_2/Si$.

The values of the coercive fields and residual polarization of PZT films were determined from the dielectric hysteresis loops that were obtained by the method of Sawyer–Tower [14]. The values of the dielectric constant and dielectric loss tangent were determined using immittance meter E7-12 at a frequency of 1 MHz. The study of layers morphology surface was conducted on the atomic force microscope (AFM) “Integra Thermo” with a resolution of 10 nm in the horizontal plane of the investigated film and better than 1 nm in the vertical plane. Microstructure layers study was conducted by raster electron microscopy (REM) with the help of the technological complex Helios Nanolab D449 FEI Company. Studies of the elemental composition were performed on Auger spectrometer ESO-3. The main technical parameters of the instrument are: vacuum in the measuring chamber is less then10^{-9} Torr, energy of the primary electrons is 3 keV, electron probe diameter is 5 μm, electron probe current is $5 \cdot 10^{-7}$A, resolution is 250. The study of the samples phase composition was carried out by X-ray diffraction on Shimadzu XRD 6000 diffractometer. The phase identification was performed using radiometric file cabinets Powder Diffraction File (PDF-2).

3. Results and discussion

Conducted researches have shown a significant influence of temperature – time regimes of heat treatment on the structure and properties of PZT films. The films that are annealed at 550 °C have small values of dielectric permittivity (ε), residual polarization and management factor. This can be explained by heterophase structure of the films i.e. inclusions of pyrochlore phase together with crystallites of perovskite phase are stored at interfaces. With increasing temperature, the proportion of pyrochlore phase is reduced, which leads to an increase of permittivity and residual polarization at 580 °C. With further increase of the annealing temperature, the observed decrease in dielectric constant values can be associated with the formation of thin layers of lead oxide, which occurs in the intergrain space and at the interface with platinum electrodes.

The presence of heterophase PZT film structure is confirmed by research results that were carried out by X-ray diffraction the beam moving method. After the heat treatment, PZT films have a polycrystalline structure with a preferential orientation in the direction of (110). With the rise of annealing temperature to 580 °C, the degree of texturing films increases. With further increase in temperature or time of heat treatment, the appearance of lead oxide phase occurs, which is accompanied by a decrease of intensities of all reflections from the perovskite phase. Presumably, a formation of lead oxide occurs near interfaces and in the periphery of PZT crystallites. It is also reasonable to assume that the structural changes associated with a reduction in the degree of ordering caused by the advent of lead oxide, should lead to a modification of the film surface.

The study results of surface morphology of PZT films showed that the film that has passed heat treatment at 530 °C has a lower surface roughness in comparison with films formed at higher temperatures. Moreover, PZT films formed at a temperature of 530 °C are characterized by low values of dielectric constant. This indicates that the films are in the pyrochlore phase, which begins its formation at temperatures above 450 °C.

With the increase of annealing temperature, the surface of films becomes more developed due to the crystallization process of the perovskite phase and the formation of the columnar structure. The surface of formed PZT films is characterized by developed morphology at temperature of 580 °C during 70 min, due to the presence of formations from an individual crystallites with sizes up to 1 μm. The crystallites have a diameter of about 150…250 nm. With increasing temperature, the formations become smaller and larger crystallites become more clearly with an approximate diameter of 200…300 nm. A longer duration of heat treatment at temperature of 580 °C leads to reduction in sizes of formations and decrease of the surface roughness. A heat treatment at 600 °C leads to the disintegration of formations into individual crystallites with a diameter of 250…350 nm.

The maximum value of the dielectric constant was 770 among investigated series of samples had films that were annealed at 580 °C. Obviously, such low values of dielectric constant can be explained by violation of films stoichiometry, i.e. the formation of PZT layers occurred without compensation of the lead oxide loss.

Reduction of ε while increasing temperature or time of heat treatment higher than 580 °C is connected with a pinning process of polarization charges located in the formed interlayers of lead oxide. It is assumed that the formation of lead oxide interlayers occurs by lead atoms located in a perovskite crystal lattice. Their move to the intergrain and interface boundaries of section leads to decrease of switching ferroelectric volume and reduce ε. Apparently, during longer heat treatment, the thickness of interlayers of PbO and quantity of pinning charges at the interfaces increase, which lead to the cessation of polarization of the ferroelectric volume. This is confirmed by the increase of the switching fields for films that were annealed at 600 °C. Studies of the effect of lead oxide sublayer on the properties of PZT and thin film structures based on them were performed (figures 1–3). Figure 1 shows that the PZT film that was formed at 600 °C is characterized by an average grain size of 90 nm without a sublayer and has a surface roughness of 50 nm.

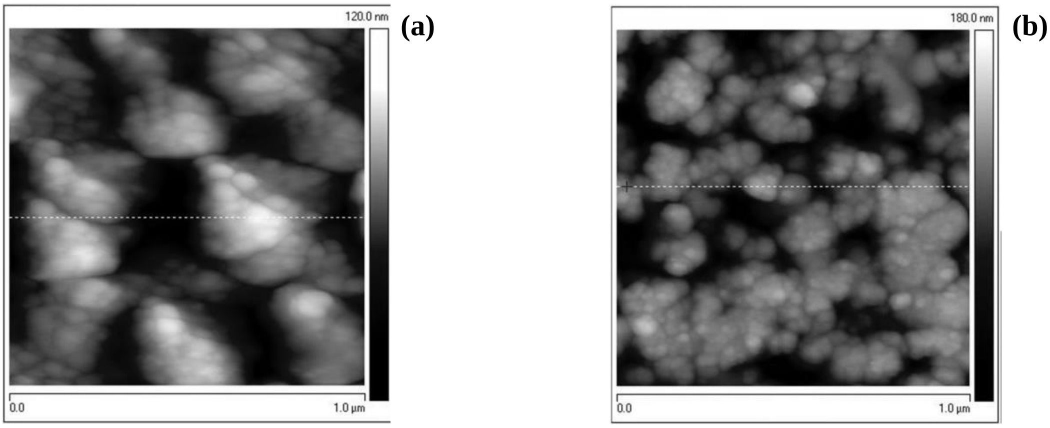

Figure 1. AFM images of the surface of PZT film without a PbO sublayer **(a)** and the surface of PZT film with a 10 nm thick PbO sublayer **(b)**.

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The film formed at 600 °C with a sublayer of 10 nm has a grain size of 70 nm and a surface roughness of 60 nm; with a sublayer of 20 nm has the grain size of 30 nm and the surface roughness of 10 nm. Therefore, the presence of the lead oxide underlayer leads to a more dense formation of crystallization centers of the perovskite phase that results in a decrease of the grain size and increase of their number. This prevents the formation of grain conglomerates that leads to a significant decrease in surface roughness of the PZT film.

Studies of electrical characteristics showed that the permittivity of the sample without a sublayer is significantly higher (ε = 760) than in the sample with the sublayer (ε = 410). PZT films without a sublayer and with PbO are characterized by the residual polarization in the 13 and 11 μC/cm^2, the value of the coercive field is 110 and 185 kV/cm, respectively. It is worth noting that the dielectric hysteresis loop of PZT-PbO sample is shifted to the left that indicates the presence of a built-in electric field of about 15 kV/cm (figure 2).

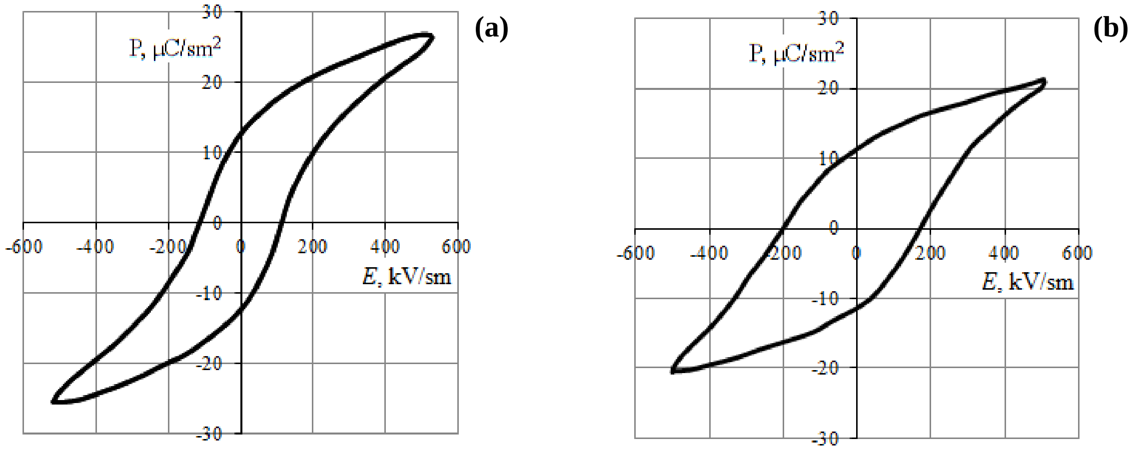

Figure 2. Dielectric hysteresis loops of the capacitor structures based on PZT film without a PbO sublayer **(a)** and with a 10 nm thick PbO sublayer **(b)**.

It is also confirmed by the shift of the current-voltage characteristics of the capacitor structures based on the PZT-PbO film (figure 3).

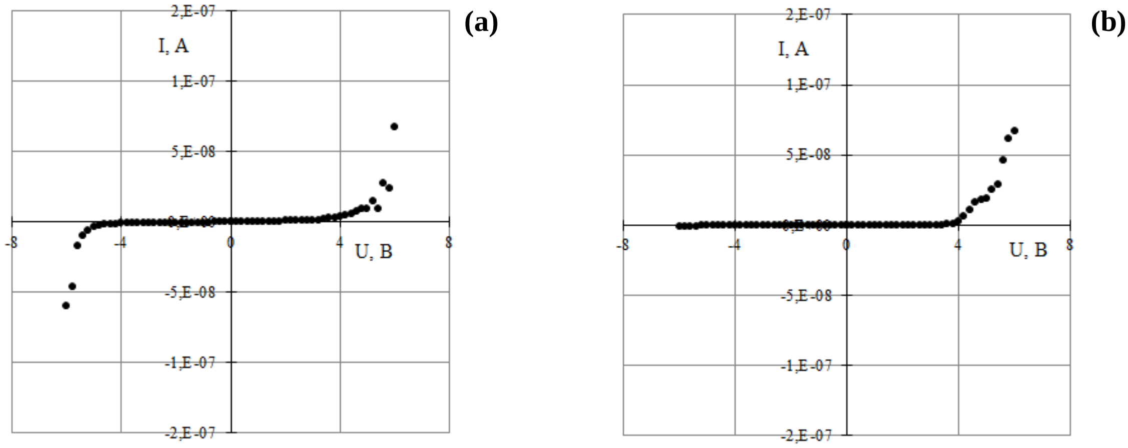

Figure 3. Current-voltage characteristics of the capacitor structures based on PZT film without a PbO sublayer **(a)** and with a 10 nm thick PbO sublayer **(b)**.

Results of researches testify that high-temperature heat treatment of PZT films leads to loss of lead oxide. In this paper, the attempt to experimentally determine such losses was made. The following experiment was carried out to solve the task. Samples of PZT films with 100 nm of thickness and with formed perovskite structure (the formation occurred in air during 30 min at 580 °C) were subjected to further heat treatment for 180 min. Auger spectra samples of PZT films have been identified: immediately after the HF magnetron sputtering, after formation of the perovskite phase and after further annealing (table 1).

Table 1. The intensities of the signals of the components of the PZT films, determined from Auger spectra.

PZT films	Pb	O	Ti	Zr
After deposition on the “cold” substrate	3	9.75	2.25	1
After formation of perovskite phase	2.5	10.5	3	1
After repeated annealing in air	1.5	8	3.25	1
After annealing in vacuum	1.5	7	3	1

According to results in table 1, the amount of lead oxide on the film surface was reduced more intensely than at the additional heat treatment in air or in vacuum during the formation of the perovskite phase. This indicates that during the formation of the perovskite structure, the diffusion of lead oxide to the surface of the film occurs more intensively than after its formation.

4. Conclusions

It is shown that the content of lead oxide has a significant effect on the structure and properties of PZT films obtained by the high-frequency magnetron sputtering. The fixation of polarization processes occurs by charges located in interlayers of lead oxide, which in turn leads to a decrease in the dielectric constant and to the growth of coercive fields. It was shown that the presence of a sublayer of lead oxide leads to a more dense formation of the crystallization centers of the perovskite phase and to the appearance of a charge at the lower interface. The built-in charge at the interface between the PZT film and the lower electrode causes the self-polarized state of the PZT film. During the formation of the perovskite structure, the diffusion of lead oxide to the surface of the film occurs more intensively than after its formation.

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References

[1] Dawber M and Bousquet E 2013 *MRS bulletin* **38**(12) 1048–55
[2] Afanasjev V P, Chigirev D A, Mukhin N V and Petrov A A 2016 *Ferroelectrics* **496**(1) 170–6
[3] Aman A, Majcherek S, Hirsch S and Schmidt B 2015 *Journal of Applied Physics* **118** 164105
[4] Levitskii V S, Redka D N and Terukov E I 2016 *Ferroelectrics* **496**(1) 163–9
[5] Schmidt M-P, Oseev A, Lucklum R, Zubtsov M and Hirsch S 2016 *Microsystem Technologies* **22**(7) 1593–9
[6] Oseev A, Schmidt M-P, Hirsch S, Brose A and Schmidt B 2017 *Sensors and Actuators B: Chemical* **239** 1213–20
[7] Sigov A S, Vorotilov K A and Zhigalina O M 2012 *Ferroelectrics* **433**(1) 146–57
[8] Sanjeev A and Ramesh R 1998 *Annu. Rev. Mater. Res.* **28** 463–99
[9] Pronin V P, Senkevich S V, Kaptelov E Yu and Pronin I P 2013 *Phys. Solid State* **55**(1) 105–8
[10] Mukhin N V 2014 *Glass Phys. Chem.* **40**(2) 238–42
[11] Mukhin N V 2016 *Glass Phys. Chem.* **42**(1) 64–9
[12] Maraeva E V, Moshnikov V A and Tairov Yu M 2013 *Semiconductors* **47**(10) 1422–5
[13] Afanasjev V P, Petrov A A, Pronin I P et al. 2001 *J. Phys.: Condens. Matter* **13**(39) 8755–63