Development of physico-technological basics of formation of structural organized ferroelectric films by the method of magnetron sputtering followed by laser processing

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Abstract. The current research considers physico-technological aspects of obtaining structural organized ferroelectric films on the basis of the oxide system of lead zirconate titanate with use of the HF methods of magnetron sputtering with the subsequent laser processing. The approach allows to obtain three types of structural organized films by local laser annealing on the basis of one oxide system: a ferroelectric-semiconductor composite, structure with periodically changing index of refraction and a ferroelectric material with periodically changing residual polarization.

1. Introduction
The development of laser technology is increasingly attracting researchers due to possibilities of creation of metamaterials and structurally-organized environments for various applications [1]. Thus, at present, world scientific groups are providing research on the use of laser technologies in the production of plasmon and acoustic metamaterials consisting of artificial micro- or nanostructures with unique optical and acoustic properties, such as negative refraction, inverse Doppler effect, etc. [2, 3]. One of the most promising and rapidly developing technologies is LDW (laser direct writing) and as its version – LIFT (Laser-induced forward transfer) [4], with which metal structures [5], carbon nanotubes [6], chalcogenide glasses [7], various metamaterials [8, 9] and plasmon devices were produced. Recent works in this area [1, 10] shows perspective of femtosecond laser technologies in the creation of new nanomaterials and structures.

Among the existing variety of materials, perovskites, "active" materials are of high interest due to possibilities to create "smart" composite systems based on these materials. Laser processing of materials that require crystallization in the perovskite structure has its own specifics. Laser technologies have been used in [11–15] for structuring and crystallization of perovskite ferroelectric systems.

In the majority of these researches, laser annealing is used to locally crystallize amorphous films into the ferroelectric phase in order to minimize the heating of the elements surrounding the functional region. When annealing with excimer lasers from photon energies substantially exceeding the width of the forbidden band, in this case absorption, and consequently annealing, takes place in a thin near-surface layer [12]. In addition, the mode structure of the spot of excimer lasers does not allow localization of annealing in the submicrometer region.
It was proposed in [13] to use a single-mode femtosecond laser with a wavelength that falls in the transparency region of the film and at the same time into the absorption region of platinum for annealing a ferroelectric film on a platinized substrate. This method allows to simultaneously solve three problems. First, to approximate the annealing conditions to thermal annealing in the furnace, since the film is heated from the side of platinum. Secondly, heating is performed locally with a Gaussian temperature distribution along the radius of the laser spot. Thirdly, the use of a femtosecond laser makes it possible to diagnose the formation of the ferroelectric phase during annealing. This diagnostic is based on the method of generation of the second optical harmonic, which is an effective method for studying phase transitions, including crystallization into the perovskite phase.

The methods of local crystallization of perovskite microstructures in an amorphous film by a femtosecond laser greatly increase the controllability of the laser annealing process and can be used not only for ferroelectrics but also for a wide range of materials that crystallize into a noncentrosymmetric phase.

2. Methods and approaches

The research is aimed the development of physical basics and technological method of obtaining new functional materials using the interaction of femtosecond laser radiation with multicomponent oxide systems of certain compositions, leading to local phase transformations of the matrix and providing the necessary structural organization. In this work a lead zirconate titanate oxide system is planned to use as a matrix material due to its phase diversity and unique electrophysical and mechanical properties that are of interest in the development of various converters [16] and memory devices [17].

The use of femtosecond laser technology allows solving two problems at once:

1) expansion of the functionality of the perovskite-like oxide system by its spatial and phase structuring; 2) solving the problem of high crystallization temperature by local annealing, which is critical for integrating with other layers and structures. The development of this method requires a deep understanding of the mechanisms of local phase transformations and structural modification of the matrix under the action of laser radiation. It requires fundamental theoretical and experimental studies. In the long term, developed methods and approaches can be used for a wide range of materials in the selection of appropriate modes of laser microprocessing.

The approach consists in a special methodology, which includes:

– the choice of a unique oxide system of lead zirconate titanate, which allows to obtain various phase states of the substance (dielectric and semiconductor phases, pyrochlore and perovskite phases, ferroelectric and paraelectric phases), including possibilities of initiating necessary phase transformations and structural changes under the action of laser radiation;
– special preparation of samples allowing one to obtain, on the basis of one oxide system, three types of structurally-organized media by means of local laser annealing: a ferroelectric-semiconductor composite, a structure with periodically varying refractive index and a ferroelectric film with periodically changing residual polarization.

The methods of obtaining samples in this work consisted of the following stages:

1) Deposition of a structure-forming platinum electrode on a silicon or sapphire substrate with an underlayer of a titanium by method of ion-plasma sputtering.
2) Deposition of an amorphous film of PZT with various excess of lead by the HF method of magnetron sputtering.
3) A heat treatment of a film of PZT to obtain required structure and phase of a matrix.
4) Local laser processing of PZT system to form the structural organized ferroelectric film.

3. Technological points of formation of the structure and discussion

Lead oxide and PZT films were obtained by the method of reactive HF magnetron sputtering on special equipment. In a vacuum chamber there are two magnetrons with a diameter of 100 mm connected to the high-frequency generator working at frequency of 13,56 MHz and allowing to vary power input to a magnetron from 10 W to 1000 W.
Powder PbO₂ and ceramics Pb₀.₈₁Sr₀.₀₄Na₀.₀₄Bi₀.₀₉Zr₀.₅₈Ti₀.₄₂O₃ were used as the targets. This PZT ceramics was chosen because it is characterized by good ferroelectric properties with values of dielectric constant and loss of angle 1630 and 0,021 respectively (passport data). As a rule, when the oxygen-containing materials are sputtered, the deviation from stoichiometry in oxygen is observed in the resulting film. Therefore, to compensate the loss of oxygen in the growing films, target sputtering was carried out in a argon-oxygen gas mixture. The thickness of the PZT films were varied from 250 to 600 nm (Fig. 1). To choose the optimal parameters for the deposition of PbO₂ film, samples were obtained with a power variation. As a result, the optimal working power of 14W was chosen, which provides a reproducible result in thickness. Table 1 shows the deposition regimes of the layers.

| Process parameters                  | PbO₂      | PZT       |
|-------------------------------------|-----------|-----------|
| Power of HF-charge, W               | 14        | 100       |
| Diameter of a target, mm            | 100       | 100       |
| Composition of gas mixture          | 76% Ar+24% O₂ | 76% Ar+24% O₂ |
| Pressure of gas mixture, mmHg       | 10⁻²      | 10⁻²      |
| Substrate temperature, °C           | 130       | 130       |
| Growth rate of films, nm/min        | 0.7       | 5.8       |

The next stage in the formation of the structure was temperature annealing in air in a muffle furnace. Depending on the problem being solved, the annealing temperature was varied over a wide range. The final stage of the treatment was local annealing with femtosecond laser radiation from the near-IR range.

Figure 1. The SEM image of a PZT film.

Figure 2 shows the results of the absorption spectra investigation of PZT films using a Nicolet 6700 FT-IR spectrometer. It can be seen that the absorption maximum lies in the wavelength range from 0.3 μm to 0.4 μm. The laser processing modes were chosen on the basis of the spectra.

Figure 2. PZT absorption spectra in wavelength range from 0.3 to 1.1 μm (a) and from 1 to 8 μm (b).
Table 2 shows three types of structures formed.

**Table 2. Types of structural organized ferroelectric films on the basis of the PZT system.**

| Type of structure | Ferroelectric-semiconductor composite | Structure with periodically varying index of refraction | Ferroelectric with variable residual polarization |
|-------------------|---------------------------------------|--------------------------------------------------------|--------------------------------------------------|
| Phase composition | Heterophase film consisting of ferroelectric PZT grains and lead oxide inclusions | PZT film, locally crystallized in perovskite structure in pyrochlore matrix | Self-Polarized PZT film (perovskite phase) with locally depolarized regions |
| The layers obtained by the high-frequency magnetron sputtering method (at 130 °C) | Multilayer system of PZT and PbOₓ layers | PZT film of stoichiometric composition | PZT film with a nanosized PbOₓ sublayer |
| Heat treatment in furnace | – | 450 °C, 60 min | 600 °C, 15 min |
| Laser processing parameters: power; input; pulse width | 0.3...0.35 J/cm²; 500 ms | 0.3...0.35 J/cm²; 100...500 ms | 0.18...0.25 J/cm²; 100...500 ms |

Composite ferroelectric-semiconductor films, which are of interest due to their unique photoelectric properties, were formed by crystallization of PZT-PbOₓ multilayer structure. The formation mechanism of such heterophase system is associated with the moving of the excess lead oxide on the periphery of growing PZT crystallites from the centers of nucleation at the interfaces of the structure at temperatures of 580...620 °C [18, 19]. By varying the thicknesses and the number of layers of PZT and PbOₓ, as well as the laser processing modes, it is possible to control the ratio and size of the phase inclusions in the system.

Creation of structures with periodically changing index of refraction on the basis of the PZT is possible due to the significant optical contrast of the low-temperature and high-temperature PZT phases. PZT film crystallizes in the perovskite phase at temperatures around 450 °C. When the temperature is raised to 570 °C and higher, a growth of crystallites with a perovskite structure occurs in the pyrochlore matrix.

Obtaining of a ferroelectric film with periodically varying residual polarization is achieved by the formation of a self-polarized film and subsequent local destruction of the self-polarized state by the action of laser radiation. The preparation of self-polarized PZT films in the present work is carried out by forming a two-layer system from a PZT with a nanosized (10 nm) PbOₓ sublayer and its further crystallization in air at a temperature of 600 °C.

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). The study of layers microstructure was carried out by the atomic force microscope (AFM) "Integra Thermo" and by raster electron microscopy (REM) with the help of the technological complex Helios Nanolab D449 FEI Company. The self-polarization and depolarization states of PZT films were determined by the method of volt-faradic characteristics. For this case, the upper platinum electrodes with an area of 0.18 mm² were precipitated by ion-plasma sputtering method through a free mask.

It should be noted that the main problem in the preparation of structures based on the PZT is the high volatility of lead oxide [20], which leads to difficulties in controlling the composition of the films and the formation of pores during laser processing. This requires a serious optimization of technological regimes.
4. Conclusions
The general physico-technological aspects of obtaining structural organized ferroelectric films on the basis of PZT oxide system were studied with use of the method of HF magnetron sputtering with the subsequent laser processing. The approach allows to obtain three types of structural organized films by local laser annealing on the basis of one oxide system: ferroelectric-semiconductor composite, structure with periodically changing index of refraction and ferroelectric material with periodically changing residual polarization. The main problem in the preparation of such structures is the high volatility of lead oxide, which leads to difficulties in controlling the composition of the films and the formation of pores during laser processing.

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