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Study of the Effect of Ion-Stimulated Deposition Assisted by a Pulsed Laser on the Properties of Zinc Oxide Nanocrystalline Films

O. A. Ageev[a], A. P. Dostanko[b], V. N. Dzhuplin[a], E. G. Zamburg[a], D. E. Vakulov[a], Z. E. Vakulov[a], A. M. Alekseev[c], D. A. Golosov[b], and S. M. Zavadski[b]

[a] *Southern Federal University, Institute of Nanotechnology, Electronics and Electronic Equipment Engineering,*
Shevcenko str. 2, Taganrog, 347905 Russia
e-mail: ageev@sfedu.ru
[b] *Belarusian State University of Informatics and Radioelectronics, P. Brovka str. 6, Minsk, 220013 Belarus,*
e-mail: dmgolosov@gmail.com
[c] *University of Glasgow, School of Physics and Astronomy,*
University Str., Glasgow, G128QQ Great Britain

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Abstract—Nanocrystalline thin films of ZnO have been fabricated using the pulsed laser deposition method. The influence of the ion/atom ratio on the structural, morphological, and electrical parameters of these films is considered. It is established that, in the case of ion action on thin films, their crystalline structure and electrophysical properties are significantly changed. It is demonstrated that modes of ion-assisted deposition can help to control the average grain size in the range from 75.4 ± 2.0 nm to 79.1 ± 2.0 nm, the roughness in the range from 2.14 ± 1.11 nm to 7.30 ± 1.25 nm, and the resistivity and mobility in the range from $(22.6 \pm 2) \times 10^{-4}$ Ohm cm to $(33.6 \pm 2) \times 10^{-4}$ Ohm cm and from 28.21 ± 4.60 cm^2/V s to 71.92 ± 2.50 cm^2/V s, respectively.

Keywords: nanotechnology, nanocrystalline films, zinc oxide, pulsed laser deposition, ion-assisted deposition stimulation, ion/atom ratio, atomic force microscopy, electrophysical properties

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INTRODUCTION

The problem of producing energy-efficient gas-sensing elements that operate at room temperature, do not need heating, and are sensitive to a low level of gas is an issue of the day. These sensors are necessary to manufacture fire safety devices, to monitor environmental conditions, to find CO in parking areas, to disclose gas leakage at factories and on offshore and above-water oil platforms, etc. [1]. However, the existing methods to produce gas-sensing layers ensure manufacturing sensors with a minimum working temperature of 300–400°C and a maximum restoration time [2].

ZnO nanocrystalline films are advanced materials for production of gas-sensing elements that help to solve these problems.

Different methods are used to produce ZnO nanocrystalline films: molecular-beam epitaxy [3], sol-gel technology [4], chemical vapor deposition [5], magnetron sputtering [6], and pulsed laser deposition. Pulsed laser deposition (PLD) is one of the most advanced techniques [7–10]. With PLD, there takes place some ablation of the target material by laser pulses and deposition of it on a substrate. The high adhesion and crystalline perfection of the films that are applied at relatively low temperatures, the possibilities to deposit films with complex stoichiometry due to the simultaneous evaporation of particles from the target surface (congruent ablation), and the possibilities to produce multilayer structures can be considered as advantages of the method.

The ion assisted deposition used at the stage of formation makes it possible to produce a nanocrystalline film with controlled electrophysical properties and stoichiometry by means of governing the energy of the ionizable particles [11].

The purpose of this work is to study the influence of the modes of ion-assisted deposition by a pulsed laser on the morphological and electrophysical parameters of ZnO nanocrystalline films.

EXPERIMENTAL

The diagram of an experimental setup to apply zinc oxide films by ion-assisted PLD is shown in Fig. 1. The films were deposited in a pulsed laser deposition

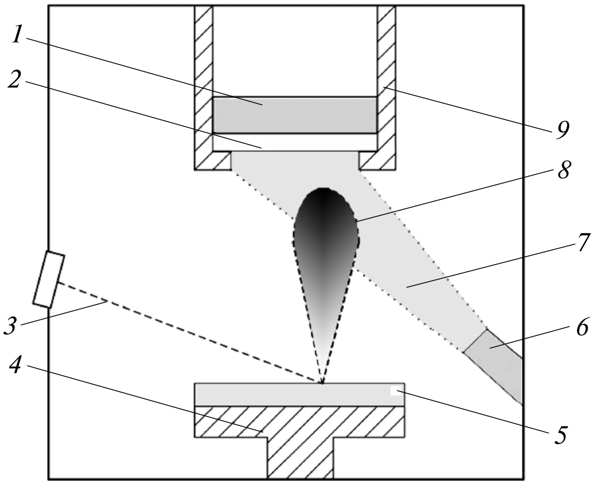

Fig. 1. Schematic diagram of the setup to apply nanocrystalline films by ion-stimulated PLD: (*1*) resistance heater, (*2*) substrate, (*3*) laser beam, (*4*) target holder, (*5*) target, (*6*) ion source, (*7*) ion beam, (*8*) flame, (*9*) substrate holder.

module of a multifunction ultrahigh vacuum-operated nanotechnological facility NANOFAB NTK-9 (SJSC Nanotechnologies MDT, Russia). In the course of PLD, target *5* is sputtered in vacuum by laser pulses *3* and the target material is deposited in the form of flame *8* on substrate *2*, as the figure shows. For spraying complex structures, a planetary system of targets *4* is used, which also ensures their rotation with the aim of uniform sputtering and deposition. For ion stimulation of the formation of ZnO nanocrystalline films, the setup includes broad-beam ion source *6*, which generates beam *7*, which falls on the substrate holder. An excimer laser (with a laser radiation wavelength of 248 nm) was used to evaporate the ZnO target. The laser power density on the ZnO target surface was 2 J/cm^2, and the pulse duration was 20 ns. A KDC 10 DC broad-beam ion source (Kaufman & Robinson Inc., USA) directed at an angle of 45° to the substrate was used for the ion stimulation. The growing film was bombarded by Ar$^+$ ions with an energy of 300 eV at different densities of the ion current. The ion beam current was measured with the help of a probe, which was a metal plate insulated from the setup and substrate holder with ceramic insulators.

The ZnO nanocrystalline films were deposited at a pressure of 10^{-6} Torr. The films were applied on ceramized substrates 15 × 15 mm in size. Five test samples were prepared: no. 1 was produced by the PLD method without any ion stimulation; nos. 2, 3, 4, and 5 were manufactured by the ion-stimulated PLD with an ion/atom ratio of 0.2, 0.4, 0.6, and 0.75, respectively.

An electron gun (k-Space Associates Inc., USA) was used to investigate the film structure by the method of the reflected high-energy electron diffraction (RHEED). The lattice parameter was determined by a kSA-400 specific program in the course of diffraction. The surface morphology of the ZnO films was studied using a NTEGRA nanolaboratory probe (SJSC Nanotechnologies MDT, Russia). AFM images of the surfaces of the applied films were obtained using a NTEGRA Vita nanolaboratory device (SJSC Nanotechnologies MDT, Russia). The surface roughness and the grain size were determined by processing the AFM images with the help of an image analysis program. The electrical parameters were estimated on the basis of the Hall effect measurement system HMS-300 (Ecopia Corp., Korea).

With ion-assisted deposition of a thin film, the relation between the number of ions bombarding the growing film and the number of atoms remaining on the surface of the sample is the key parameter.

The degree of impact of the ion component on the deposition process may be estimated through measuring the ion beam current [12]. By determining the ion beam area, it is possible to find the value of the ion current density, which is necessary to calculate the ion/atom ratio [13]:

$$\frac{I}{A} = \frac{\theta_i}{\theta_a}, \qquad (1)$$

where I/A is the relation of the number of ions participating in the stimulation process to the number of ions of the deposited film, θ_i is the number of ions per unit of the sample area, and θ_a is the number of atoms of the deposited material per unit of the sample area. The number of ions per area unit can be estimated as follows:

$$\theta_i = \frac{i_i}{q}, \qquad (2)$$

where i_i is the density of the ion current (A/cm^2), and q is the electron charge (C). The number of deposited material atoms per unit of the sample area can be estimated by the following formula [13]:

$$\theta_a = 10^{-8} v_A \frac{\rho N}{1.66 \times 10^{-24} \omega}, \qquad (3)$$

where v_A is the rate of the film growth (Å/s); ρ is the density of the deposited substance (g/cm^3); N is the number of atoms in a molecule of the deposed substance; and ω is the molar mass of the deposited substance (g/mole), 1.66×10^{-24} a.m.u.

RESULTS AND DISCUSSION

The AFM images of the surface of the zinc oxide film samples applied at different ion/atom ratios are shown in Fig. 2. The value of the film grain diameter was calculated using the Image Analysis program. The results show that the roughness of the nanocrystalline film produced without any ion stimulation of the n-ZnO

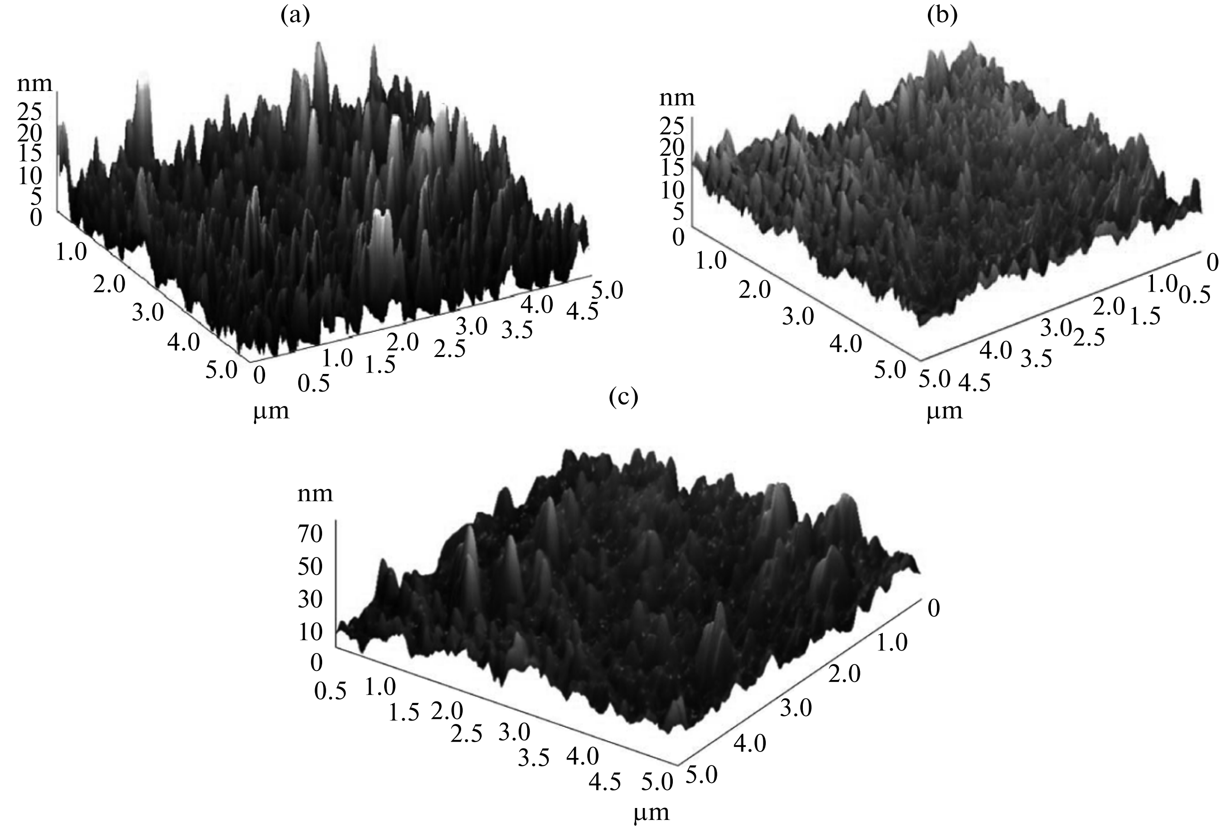

Fig. 2. AFM images of the surface of the ZnO nanocrystalline films produced without ion stimulation (a) and with ion stimulation at the ion/atom ratio of 0.6 (b) and 0.75 (c).

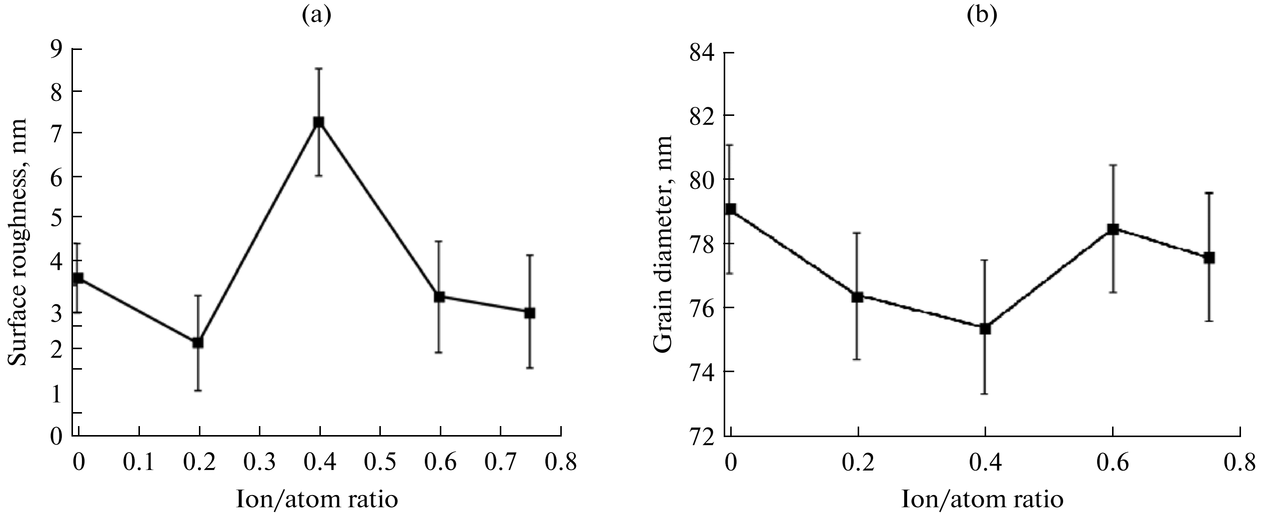

Fig. 3. Dependence of the surface roughness (a) and the grain diameter (b) of the ZnO nanocrystalline films on the ion/atom ratio.

is 4.4 ± 0.4 nm. In the case of ion stimulation with an ion/atom ratio of 0.2, the film surface roughness is decreased to 2.14 ± 1.11 nm. As the ion/atom ratio increases to 0.4, the roughness grows to 7.30 ± 1.25 nm. The grain diameter for the ZnO nanocrystalline film for the sample without any ion stimulation is 79.1 ± 2 nm. When the ion stimulation is used in the modes corresponding to the ion/atom ratio values of 0.4 and 0.75, the grain diameter was 75.4 ± 2.0 and 77.6 ± 2.0 nm, respectively (Fig. 3).

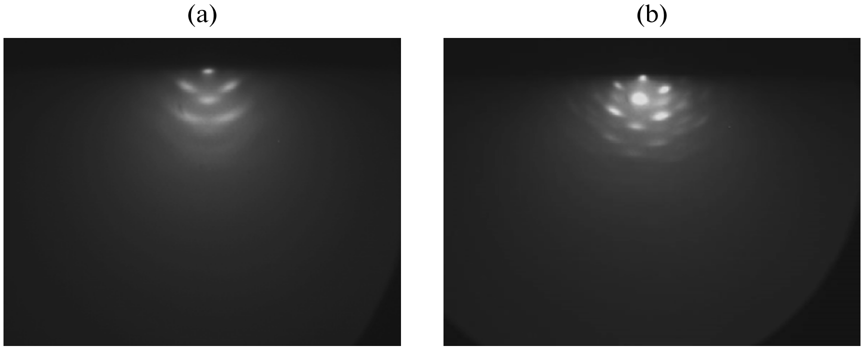

Fig. 4. Diffractograms of the ZnO nanocrystalline films at the *i*/*A* ratios of 0 (a) and of 0.75 (b).

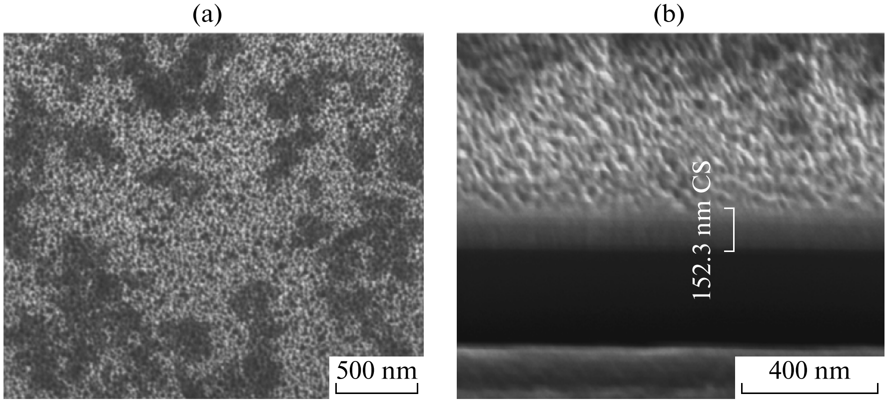

Fig. 5. SEM images of the surface (a) and cross section (b) of the ZnO nanocrystalline film applied by the method of the ion stimulated PLD.

Sample nos. 1 and 5 have been studied by the method of reflected high-energy electron diffraction, and the results are depicted in Fig. 4. In the diffractograms of the samples that were produced by the method of ion assisted pulsed laser deposition, there appears a diffraction pattern typical for nanocrystalline films. For the sample that was manufactured without any ion stimulation, the lattice parameter of the ZnO nanocrystalline films was 0.26 nm. The SEM images of the surface and cross section of sample no. 3 are presented in Fig. 5. The images confirm that a nanocrystalline structure is formed in the case of the ion bombardment.

Figure 6 represents the dependences of the electrophysical parameters of the produced ZnO nanocrystalline films on the ion/atom ratio. The measurements of the electrophysical parameters showed that the ZnO nanocrystalline films are characterized by the *n*-type of conductivity. The charge carrier concentration in the ZnO nanocrystalline film produced without any ion stimulation was $(5.5 \pm 0.5) \times 10^{16}$ cm^{-3}. With the increasing ion/atom ratio, the charge carrier concentration in the ZnO nanocrystalline films initially increased to $(9.771 \pm 0.5) \times 10^{16}$ cm^{-3} at $i/A = 0.6$, and then it decreased to $(3.484 \pm 0.6) \times 10^{16}$ cm^{-3} at $i/A = 0.75$. At the ion/atom ratio of 0.6, the charge carrier mobility in the ZnO nanocrystalline films decreased from 30.92 ± 2.6 (without any ion stimulation) to 28.21 ± 4.6 cm^2/(V s). As the ion/atom ratio increases to 0.75, the growth of the charge carrier mobility to a value of 73 ± 0.7 cm^2/(V s) is observed. When the ion stimulation is used in the course of formation of the ZnO nanocrystalline films in the mode that corresponds to the ion/atom ratio of 0.6, the resistivity drops to $(28.8 \pm 2.5) \times 10^{-4}$ Ohm cm, while the resistivity of the ZnO nanocrystalline film produced without any ion stimulation is $(36.6 \pm 2) \times 10^{-4}$ Ohm cm. With the further increase in the ion/atom ratio (to 0.75), the resistivity grows to 2.5×10^{-3} Ohm cm.

Thus, it has been established that the change in the ion/atom ratio influences the properties of the ZnO nanocrystalline films produced with the ion-stimulated PLD and makes it possible to manufacture films with controlled electrophysical parameters.

With the ion stimulation at the stage of formation, the crystalline film structure is changed. With the ion/atom ratio increasing, the grain diameter decreases; this is supposed to be associated with ion etching of the ZnO film surface. In this case, the surface roughness decreases; this is supposed to be caused

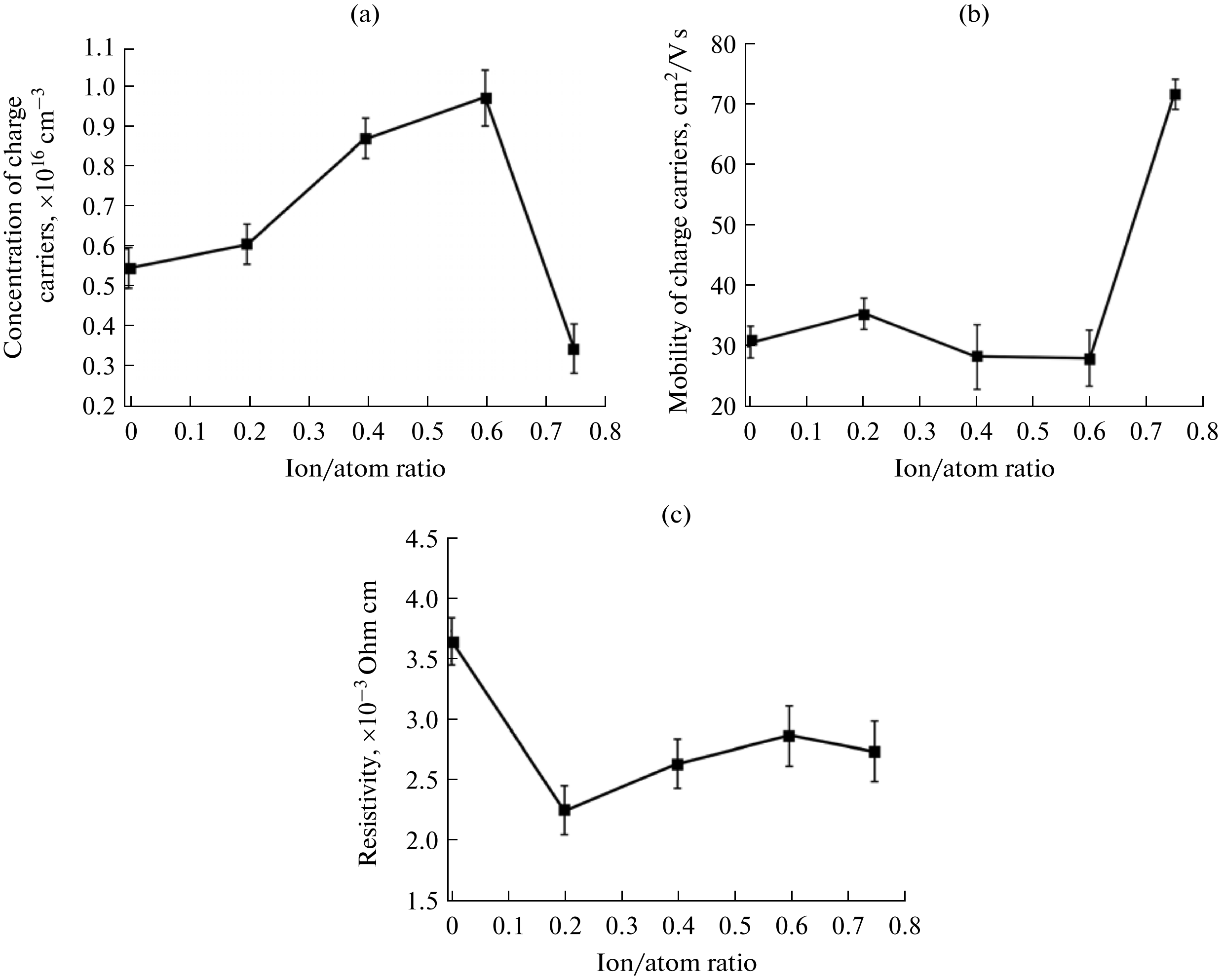

Fig. 6. Dependences of the concentration (a) and mobility (b) of the charge carries and the resistivity of the ZnO films (c) on the ion/atom ratio.

by the effect of the crystal surface polishing under the action of a high power ion flux. This is confirmed by the SEM and AFM images.

The electron mobility in the ZnO films increases with the ion stimulation, which confirms the changes in the structure of the ZnO nanocrystalline films caused by the stimulating ions at the ion/atom ratio of 0.6.

CONCLUSIONS

It is established that, with the ion stimulation in the course of the ZnO film growth by the PLD method, the electrophysical properties of the films and their crystal structure are effected. The changes in the crystal structure and electrophysical properties of the applied films depend on the ion/atom ratio on the condensation surface of the growing film.

It is possible to govern the concentration and mobility of the charge carriers, the grain sizes, and the film surface roughness in a wide range of parameters with varying the modes of the ion action on the growing film. The ion stimulation at the formation of films by the PLD method makes it possible to enlarge the range of the electrophysical properties of the produced ZnO nanocrystalline films.

The results can be used to design devices and technologies of production of sensing elements on the basis of ZnO nanocrystalline films (gas sensors, UV detectors, piezoelectric elements, functional elements of nanosystem equipment).

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