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DEVELOPMENT OF MANUFACTURING TECHNOLOGY OF PHOTO-DIELECTRIC SENSITIVE ELEMENT OF ULTRAVIOLET RANGE ON THE BASIS OF THIN FILMS OF ZINC OXIDE

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Abstract

The development of ultraviolet radiation is essential for solving scientific and practical problems. A large number of application areas related to the registration of ultraviolet radiation requires the expansion of the list of materials used and the creation of new technologies for the production of ultraviolet radiation detectors. Zink oxide thin films are widely used in recording and measuring devices for the ultraviolet range, due to its wide bandgap (3.37 eV) and unique optical characteristics. The purpose of the work is to create a technology for the manufacture of photodielectric sensing element of the ultraviolet range based on zink oxide thin films. To achieve the goal, the following tasks were set and solved: to obtain an experimental sample of the photodielectric-sensing element of the ultraviolet range, investigate the photoelectric effect in zinc oxide films obtained by reactive magnetron sputtering, determine the optimal voltage and frequency of the measuring signal for the operation of the photodielectric sensing element of the ultraviolet range. The article describes the equipment and the sequence of technological operations for the production of thin films of zinc oxide and conducting electrodes by magnetron sputtering. The optimal voltage and frequency of the measuring signal for the sensing element are investigated. The spectral sensitivity of the element in the ultraviolet range was determined

Keywords

Photodielectric effect, ultraviolet radiation, thin films, zinc oxide, magnetron sputtering

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Introduction. Mastering the radiation of the ultraviolet region of the spectrum is essential for solving scientific and practical problems. A large number of application areas associated with the registration of ultraviolet radiation requires the expansion of the list of materials used and the creation of new technologies for the production of ultraviolet detectors. Zinc oxide thin films are widely used in ultraviolet recording and measuring devices because of its wide bandgap (3.37 eV) and unique optical characteristics.

Sensitive elements for detecting ultraviolet radiation based on thin films of zinc oxide have been studied by many domestic and foreign research teams [1–12]. For photosensitive elements, films obtained by ion-plasma methods were used. On a polycrystalline film of zinc oxide obtained by the method of deposition from the gas phase (CVD), designed detectors of the ultraviolet range with a high degree of sensitivity [1]. In the paper [9], the technology of manufacturing a photodetector with gold electrodes and a thin film of zinc oxide, made by high-frequency magnetron sputtering on a K-8 glass substrate, is presented. The photodetector showed a sensitivity of 0.054 A/W under the action of monochromatic radiation with a wavelength of λ = 370 nm. In papers [2–10], photoresistive and photoelectric effects were used as methods for registering the acting radiation, the main disadvantages of using these effects are the strong dependence of the output signal on temperature and high inertia

A significant improvement in the characteristics of the detection of ultraviolet radiation was achieved through the use of hybrid and composite materials. The use of aluminum-doped zinc oxide films has a positive effect on photosensitivity [5]. Many papers on the preparation of near-ultraviolet detectors based on single-crystal films of zinc oxide have been published [6, 7]. Frequent problems in the development of technology for creating photosensitive elements based on zinc oxide are the difficulty of making contact with films or nanorods, high dark currents, and low sensitivity of the created samples [8–10].

An analysis of the published work suggests that ultraviolet radiation affects the optical properties of zinc oxide. This makes it possible to use films and zinc oxide nanorods as sensitive elements for photodetectors, which is reflected in a large number of publications. It is known that the optical properties of zinc oxide thin films depend on the type and technological parameters of production, as well as on the type, duration, and annealing temperature. However, the existing manufacturing techniques of photosensitive elements are hampered by the complexity of producing thin films of zinc oxide with given optical characteristics, as well as the complexity of the formation of contacts to films.

The purpose of this paper is to create a technology for manufacturing a photodielectric ultraviolet sensitive element based on thin films of zinc oxide. To achieve the goal, the following tasks were set:

– obtaining an experimental sample of a photovoltaic ultraviolet sensitive element;

– investigation of the photodielectric effect in zinc oxide films obtained by the method of reactive magnetron sputtering;

– determination of the optimal voltage and frequency of the measuring signal for the operation of the photodielectric sensitive element of the ultraviolet range.

Description of technological equipment. The vacuum deposition unit UVN-71PZ (УВН-71П3) serves for the deposition of polycrystalline films of various materials by the method of magnetron sputtering. The main structural component of the installation is a vacuum deposition chamber.

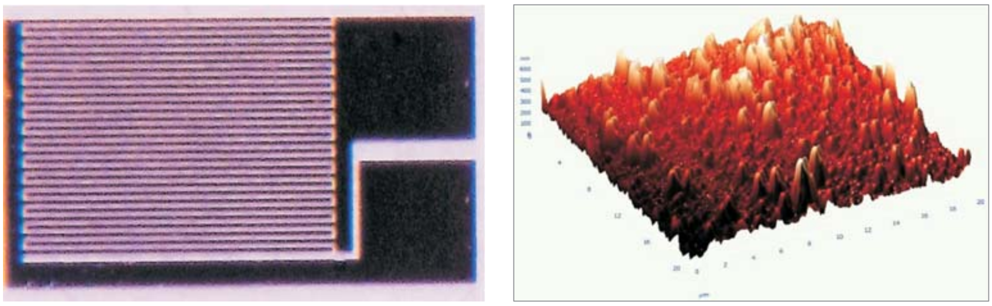
Three magnetrons and a resistive heater are mounted in the chamber; the radius of the magnetron target is 50 mm. Zinc oxide films are deposited onto substrates installed in a holder, which is driven by a variable frequency asynchronous motor, the distance between the substrate and the magnetron is (100 ± 2) mm.

The pumping system UVN-71PZ is built on the diffusion pump N-250 (Н-250) and rotary vane pump Alcatel. The evacuation system allows to obtain a vacuum of up to $2\cdot10^{-3}$ Pa, which is sufficient for magnetron sputtering. Magnetron power supplies function in a pulsed mode and have a mechanism for extinguishing microarcs.

Processing technique primary sensitive element. According to [11], the photodielectric effect is a change in the dielectric constant of a material due to the absorption of radiation from the optical region of the spectrum. To study the photodielectric effect in thin films of zinc oxide, a test version of the sensitive element was manufactured.

Test variants of sensitive elements on the photodielectric effect are obtained using the following technology. A film of aluminum with a chromium underlayer was sprayed onto a substrate made of KV (КВ) glass with a thickness of 1.5 mm using magnetron sputtering on a modernized UVN-71PZ installation. Spraying was performed in a single technological cycle, after cleaning the substrate in a soap solution, in distilled water and acetone vapors for 15 minutes. Targets of aluminum and chromium were sprayed with a working pressure of argon of 1 Pa, a magnetron power of 0.8 kW, and a substrate heating of (130 ± 3) °C. The total thickness of metal films was 500–550 nm. After cooling, the sample was covered with a thin layer of photoresist, rotating in a centrifuge, to obtain a thin uniform layer. Then the substrate with a layer of photoresist was dried for 10 minutes in a laboratory oven of infrared heating at a temperature of 100 °C. Then the photoresist was exposed to the DRSh-250 (ДРШ-250) mercury-quartz ultraviolet lamp through a photomask, which had opaque areas from the emulsion corresponding to the a metallization areas of the product. The location and shape of the electrodes was chosen in the form of the structure used in the interdigital transducers, in this case the two parts of the interdigital transducer can be considered as plates of a planar capacitor. The distance between the pins of the interdigital transducer is 20 μm, the number of pins is 29. The photoresist was developed in 0.4 % potassium hydrochloride solution. After that, the substrate with the developed photoresist underwent tanning for 10 minutes at a temperature of 100 °C. Then the developed photoresist was etched with a mixture of distilled water (40 g) and orthophosphoric (10 g), nitric (40 g) and acetic (10 g) acids. After washing and drying in a laboratory centrifuge, the surface of the interdigital transducer was monitored with an Integra Prima scanning probe microscope for breakage and closure of the electrodes. After that, the procedure was repeated for the chromium underlayer, where a solution of hydrochloric acid (62 g) and distilled water (50 g) was used as an etchant. The misalignment of the interdigital transducer relative to the substrate edge was allowed within ± 30 μm.

After interoperational cleaning in a soapy solution, distilled water, and acetone, for 15 min from above, the interdigital electrodes sprayed a film of zinc oxide using reactive magnetron sputtering on UVN-71PZ. The target was sprayed in a working mixture of oxygen and argon (60 % O_2 + 40 % Ar) with a working pressure of the mixture in a vacuum chamber of 1 Pa, heating the substrate (100 ± 3) °C and the target power of 0.35 kW per 6 minutes. At an average deposition rate for such conditions of 100 nm/min, the film thickness was (600 ± 30) nm. The formed zinc oxide film has a resistance of 10^6 Om · cm, which leads to shorting of the electrodes, due to a decrease in resistance when exposed to ultraviolet radiation. Test samples were annealed in oxygen for 60 min at 250 °C to increase the resistance. The resistivity of annealed films increases to 109 Om · cm. Resistance was measured by the four-probe method. The obtained samples of sensitive elements (Fig. 1, *a*) were monitored for porosity and punctures using a scanning probe microscope (Fig. 1, *b*). The capacitance was monitored using an E7-20 immitance meter with a measuring signal voltage of 1 V and a frequency of 500 kHz. The limits of the relative error of the measuring signal voltage E7-20 at a frequency of 500 kHz ± 3 % in the range of more than 100 mV. The immitance meter E7-20 allows recording the dielectric loss tangent (tg δ) and capacitance change (Δ*C*) with an accuracy of ± 0.01 pF at a frequency of 500 kHz. Without exposure to radiation, the capacitance of the sensitive element was 630 pF, the tangent of the dielectric loss angle was 0.03, the temperature coefficient of the capacitance was measured directly when the sensitive element was heated in the range of 20–85 °C, and was 0.8 % of the capacitance of 630 pF.



a *b*

Fig. 1. Macro photograph of the obtained sample of the sensitive element on the photodielectric effect (scale ~ 1:17) (*a*); surface of the sensing element (*b*)

Measurement of the influence of electrical parameters. In Fig. 2 shows a scheme for measuring the capacitance of a sensitive element when exposed to radiation with a wavelength λ = 200–800 nm. For irradiation of the sensing element used sources of radiation that are part of the spectrophotometer SF-2000 (СФ-2000) in the wavelength range 200–395 nm is a deuterium lamp of the company Hamamatsu L6308, in the range from 395 to 800 nm — a halogen lamp Philips Capsuleline G4 CL. The working gap of the spectrophotometer was 1 nm for ultraviolet radiation and 1.5 nm for visible radiation. In this case, the sensitive element can be considered as a planar capacitor. The capacity of the planar capacitor is determined by the known formula

$$C = \varepsilon_0 \varepsilon \frac{S}{d}, \qquad (1)$$

where S is leaf area, d is gap between the leaves, ε_0 is electric constant, ε is relative dielectric constant.

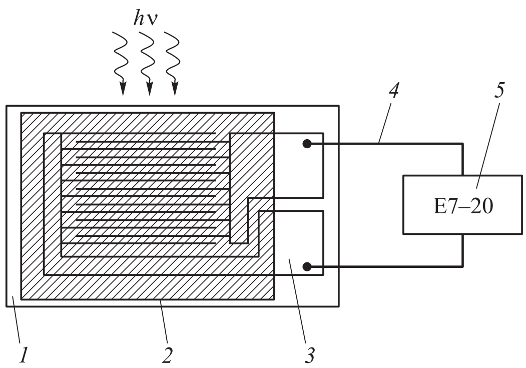


Fig. 2. Diagram for registering changes in the capacitance of a sensitive element under the action of light:

1 is glass substrate mark KV (КВ); *2* is zinc oxide film; *3* is electrodes; *4* is conductive leads; *5* is LCR meter E7-20

From formula (1) it follows that the capacity of the planar capacitor depends on the area of the plates, the gap between them and the relative dielectric constant of the material filling the gap between the plates. During the experiment, the area of the plates (290 mm^2) and the gap between them (20 μm) remained unchanged, the capacitance changed only due to a change in the relative dielectric constant of zinc oxide, through the action of light sources.

To register the change in the capacitance of the sensitive element under the action of radiation, an immittance meter E7-20 was connected to the terminals at a voltage of the measuring signal of 1 V and a frequency of 500 kHz.

As the wavelength shifts to the ultraviolet region, the capacitance of the sensitive element decreases from 480 to 385 pF, which corresponds to a change in dielectric constant from 3.68 to 3, the minimum value of the capacitance 385 pF falls at 372 nm (Fig. 3). In the radiation range of 372–390 nm, the capacitance of the sensitive element has a characteristic growth from 385 to

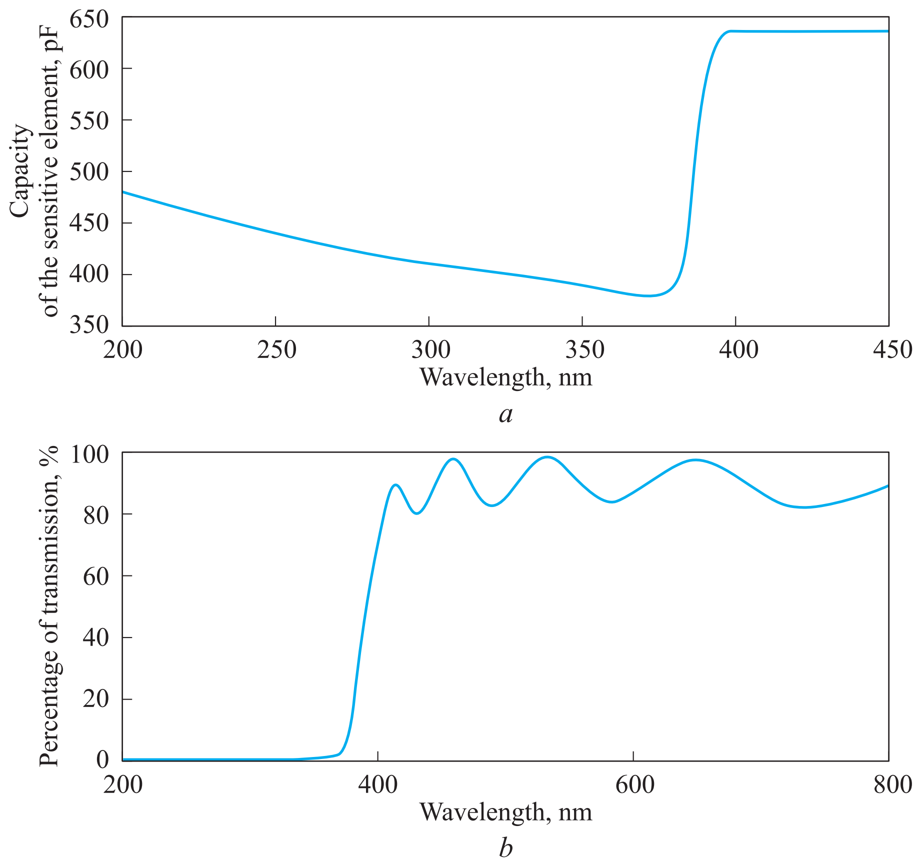


Fig. 3. A graph of the dependence of the capacitance of the sensitive element on the radiation wavelength (*a*); transmission spectrum of a thin film of zinc oxide with a thickness of (600 ± 30) nm (*b*)

635 pF, which corresponds to a change in dielectric constant in the range of 3.0–4.9, with an increase in wavelength over 390 nm, the capacitance of the sensitive element did not change and was 635 pF. At the same time, tg δ in the studied ranges practically did not change and remained within 0.03, the temperature of the sensitive element was recorded with a resistance thermometer and was 24.5 °C throughout the experiment. The obtained measurement results correlate with the transmission spectrum of a thin zinc oxide film (Fig. 3, *b*) of the same thickness obtained in a single technological cycle with the sample under study.

When developing a sensitive element on the photodielectric effect, it is desirable that the range of capacitance change (ΔC) is as large as possible, then the measuring circuit will be easier to record the radiation of small power. For this purpose, the influence of the electrical voltage of the measuring signal on the output characteristic of the sensitive element was studied. The graph (Fig. 4) shows that with a decrease in the measuring voltage from 1 to 200 mV, the difference between C_{min} and C_{max} decreases. With an increase in the voltage of the measuring signal of more than 1 V, the probability of shorting the electrodes increases.

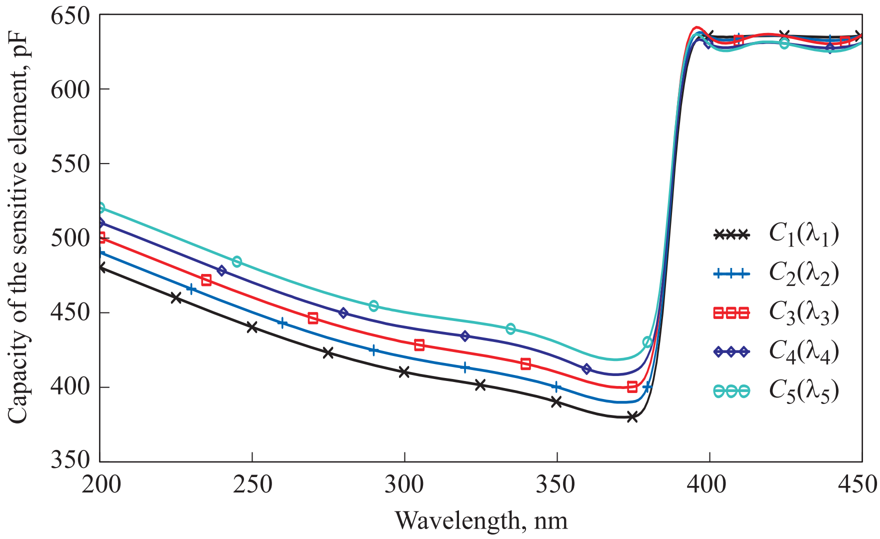


Fig. 4. A graph of the dependence of the capacitance of the sensitive element on the radiation wavelength for different values of the voltage of the measuring signal: $C_1(\lambda_1)$ at 1 V; $C_2(\lambda_2)$ at 800 mV; $C_3(\lambda_3)$ at 600 mV; $C_4(\lambda_4)$ at 400 mV; $C_5(\lambda_5)$ at 200 mV

In photoexcitation mode, increasing the frequency while maintaining the measuring signal voltage of 1 V reduces the average capacitance value of the sensitive element (Fig. 5). The observed frequency dispersion of the tangent of dielectric loss angle (Fig. 6) is associated primarily with the polarization of the space charge. The origin of the space charge in a thin zinc oxide film is explained by the presence of defects in the crystal lattice, since during magnetron sputtering the film has an *X*-ray amorphous phase besides the crystalline [12].

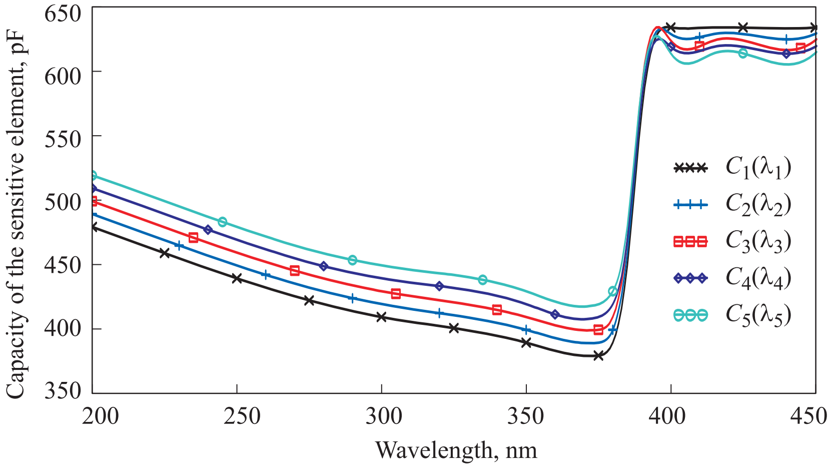


Fig. 5. A graph of the dependence of the capacitance of the sensitive element on the radiation wavelength for different values of the measuring signal frequency: $C_1(\lambda_1)$ at 1 mHz; $C_2(\lambda_2)$ at 750 kHz; $C_3(\lambda_3)$ at 500 kHz; $C_4(\lambda_4)$ at 300 kHz; $C_5(\lambda_5)$ at 200 kHz

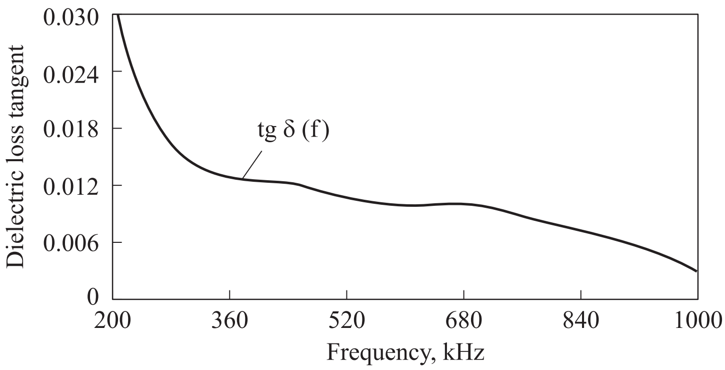


Fig. 6. A graph of change of dielectric loss tangent versus frequency

Measurement of the sensitivity of the element. The main and most important characteristics of radiation receivers include the sensitivity and wavelength corresponding to the maximum sensitivity λ_{max}. The sensing element was irradiated with radiation in the wavelength range of 200–800 nm, according to the scheme (see Fig. 2), at a measuring signal voltage of 1 V and a frequency of 500 kHz, the element temperature was controlled throughout the experiment, it was 24.5 °C. In Fig. 7 shows the dependence of the sensitivity of the element on the radiation wavelength.

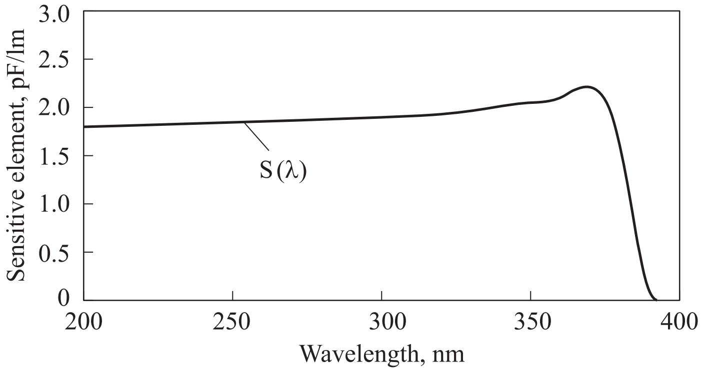


Fig. 7. Spectral sensitivity characteristics

It is clear from the graph (see Fig. 7) that as the wavelength shifts to the ultraviolet region, the sensitivity of the element increases, the maximum spectral sensitivity falls at λ = 372 nm, which corresponds to the sensitivity value S = 2.2 pF/lm. This is explained by the highest value of intrinsic absorption of zinc oxide at this wavelength [13, 14]. In the wavelength range of more than 390 nm, the sensitivity decreases to almost zero. Integral sensitivity in the range of 200–390 nm is 2 pF/lm.

Conclusion. Technology has been developed for producing a sensitive element on a photodielectric effect. The sensitive element has an integral sensitivity of 2 pF/lm to the wavelength range of 200...390 nm, the highest sensitivity of 2.2 pF/lm element shows to monochromatic radiation with a wavelength λ = 372 nm.

It has been experimentally proven that in thin films of zinc oxide obtained by magnetron sputtering, a change in the dielectric constant in the range of 3.0–4.9 is observed due to exposure to ultraviolet radiation in the wavelength range of 200–390 nm.

Measurements have shown that a measuring signal with a voltage of 1 V and a frequency of 500 kHz is optimal for the operation of a sensitive element on the photodielectric effect.

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REFERENCES

[1] Chen C., Xu H., Zhang F., et al. Nanostructured morphology control and optical properties of ZnO thin film deposited from chemical solution. *Mater. Res. Bull.*, 2014, vol. 52, pp. 183–188. DOI: 10.1016/j.materresbull.2014.01.014

[2] Lansiart L., Millon E., Perriere J., et al. Structural properties of ZnO films grown by picosecond pulsed-laser deposition. *Appl. Surf. Sc.*, 2012, vol. 258, no. 23, pp. 9112–9115. DOI: 10.1016/j.apsusc.2011.08.047

[3] Duygulu N.E., Kodolbas A., Ekerim A. Influence of RF power on structural properties of ZnO thin films. *J. Cryst. Growth*, 2013, vol. 381, pp. 51–56.
DOI: 0.1016/j.jcrysgro.2013.07.008

[4] Yao B., Chan Y., Wang N. Formation of ZnO nanostructures by a simple way of thermal evaporation. *Appl. Phys. Lett*., 2002, vol. 81, no. 4, pp. 757–760.
DOI: 10.1063/1.1495878

[5] Yang L., Yang J., Wang D., et al. Photoluminescence and Raman analysis of ZnO nanowires deposited on Si (100) via vapor-liquid-solid process. *Physica E: Low Dimens. Syst. Nanostruct.,* 2008, vol. 40, no. 4, pp. 920–923. DOI: 10.1016/j.physe.2007.11.025

[6] Huang S., Chen Z., Shen X., et al. Raman scattering of single tetrapod-like ZnO nanostructure synthesized by catalyst-free rapid evaporation. *Solid State Commun*., 2008, vol. 145, no. 7-8, pp. 418–422. DOI: 10.1016/j.ssc.2007.11.014

[7] Red'kin A.N., Ryzhova M.V., Yakimov E.E, et al. Aligned arrays of zinc oxide nanorods on silicon substrates. *Semiconductors*, 2013, vol. 47, no. 2, pp. 252–258.
DOI: 10.1134/S1063782613020176

[8] Djurisic A.B., Leung Y.H. Optical properties of ZnO nanostructures. *Small*, 2006, vol. 2, no. 8-9, pp. 944–961. DOI: 10.1002/smll.200600134

[9] Krivchenko V.A., Lopaev D.V., Pashchenko P.V. UV detectors based on nanocrystalline ZnO films. *Prikladnaya fizika* [Applied Physics], 2008, no. 8, pp. 107–111 (in Russ.).

[10] Zima V.N., Korzh I.A., Nikolaenko K.V., et al. [Thin-film ultraviolet sensor]. *REIS–2011*. Omsk, Omskiy NII priborostroeniya Publ., 2011, pp. 441–448 (in Russ.).

[11] Avanesyan V.T., Bordovskii G.A., Potachov S.A. Dielectric characterization of the lone pair oxide structure. *J. Non Cryst. Solids*., 2002, vol. 305, no. 1-3, pp. 44–50.
DOI: 10.1016/S0022-3093(02)01090-6

[12] Belyanin A.F., Krivchenko V.A., Lopaev D.V., et al. Nano-structured ZnO films for microelectronics and optical devices. *TKEA*, 2006, no. 6, pp. 48–55 (in Russ.).

[13] Ozgur U., Alivo Ya.I., Liu C., et al. A comprehensive review of ZnO materials and devices. *J. Appl. Phys.,* 2005, vol. 98, no. 4, pp. 1–103. DOI: 10.1063/1.1992666

[14] Alsultany H., Hassan Z., Ahmed N.M. A high-sensitivity, fast-response, rapid-recovery UV photodetector fabricated based on catalyst-free growth of ZnO nanowire networks on glass substrate. *Opt. Mater*., 2016, vol. 60, pp. 30–37.
DOI: 10.1016/j.optmat.2016.07.004

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