Optical investigations of ZnO layers affected by some selected gases in the aspect of their application in optical gas sensors

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Abstract. The paper presents the results of investigations of zinc oxide (ZnO) layers as a potential sensing material, being affected by certain selected gaseous environments. The investigations concerned the optical transmission through thin ZnO layers in wide spectral ranges from ultraviolet to the near infrared. The effect of the gaseous environment on the optical properties of zinc oxide layers with a thickness of ∼400 nm was analyzed applying various technologies of ZnO manufacturing. Three kinds of ZnO layers were exposed to the effect of the gaseous environment, viz.: layers with relatively slight roughness (RMS several nm), layers with a considerable surface roughness (RMS some score of nm) and layers characterized by porous ZnO structures. The investigations concerned spectral changes in the transmission properties of the ZnO layers due to the effect of such gases as: ammonia (NH_3), hydrogen (H_2), and nitrogen dioxide (NO_2) in the atmosphere of synthetic air. The obtained results indicated the possibility of applying porous ZnO layered structures in optical gas sensors.

Key words: ZnO semiconductor, gas sensors.

1. Introduction

Monitoring the state of the atmosphere is of essential importance in the analysis of the natural environment, in the course of technological processes as well as in domestic installations, particularly with regard to the safety of the users and the professional teams of the operating personnel. Sensor structures sensitive to the selected gaseous environment ought to be characterized by a high sensitivity, a short time of response and a possibly low temperature of operation [1, 2]. At present extensive investigations are under way aiming at the development of sensor structures sensitive to the given gaseous environment, based on semiconductor materials with a wide energy band gap [3], as well as on organic semiconductors [4]. An attractive semiconducting material with a potential possibility of application in gas sensors is zinc oxide (ZnO) [5–9]. The undoped zinc oxide due to occurrence in it of oxygen vacancies and interstitial zinc atoms, is the n-type semiconductor. ZnO is characterized by an energy band on the level $\Delta E_g \approx 3.3$ eV [10–12]. It is an optically transparent material in the visible range of the electromagnetic spectrum. The short wavelength absorption edge $\lambda_g \approx 380$ nm [13, 14]. The physical properties of ZnO predispose it to apply in optoelectronic sensor structures, in which the effect of the gaseous environment will change electrical properties of ZnO, and thus also change the optical properties (including the spectral transmission of light through the structures). The application of optical systems for the purpose of detecting certain selected gaseous environments is particularly desirable in areas in which considerable electromagnetic disturbances occur, and

where sensor structures utilizing the changes of electric properties cannot be fully applied, e.g. because of the danger of explosion. In some special cases sensor structures must operate adequately at near room temperature. The present paper quotes the results of investigations of thin ZnO layers on glass substrates within the range of their spectral properties of transmission with regard to the detection of some selected gases, operating at a relatively low temperature of the order $T \approx 120°C$.

Among frequently applied methods of getting ZnO there are also such technologies as: cathode sputtering, magnetron sputtering in the modes RF and DC, electron-beam sputtering (E-Beam), molecular beam epitaxy (MBE), pulsed laser deposition (PLD), metal organic vapour deposition (MOVD), chemical vapour deposition (CVD), sol-gel method [10, 15]. Such a wide range of applied technologies permits to get zinc oxide layers with various physical properties, varying in the topography of the surface. The obtained ZnO layers may be characterized by a topography of the surface within a wide range of changes, from a relatively slight roughness of the surface (RMS only a few nanometers), through layers with a considerably developed very rough surface (RMS some score to several scores nanometers) up to layers with a complex porous structure. Porous ZnO layers may occur in form of nanograins, in which the size of nanograins is on the level from a few scores and even several hundred nanometers. ZnO layers may take the form of nanostructures with complex shapes, e.g. nanorods, nanotubes, nanopropellers, nanoflowers, nanodots and nanotops, as shown in [16–21]. What more, they differ in their sensibility to effects of the gaseous environment.

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The aim of the paper was to determine the influence of the topography of the ZnO surface on the sensory properties of the layers in some selected gaseous environments, viz. hydrogen (H_2), ammonia (NH_3) and nitrogen dioxide (NO_2) in synthetic air (20% oxygen and 80% nitrogen). The investigations were focused on the optical properties of the manufactured layers, especially – their optical transmission.

2. Measurement setup

The influence of the selected gaseous environments on changes of the optical properties and the spectral characteristics of transmission in planar structures were investigated making use of spectrophotometry within the range from ultraviolet to infrared light: UV-VIS-IR. The tested ZnO layers were deposited on plates of quartz glass or BK7 glass. The structures were placed in a measuring chamber with quartz windows permitting to measure the spectral characteristics of the transmission of light in the atmosphere of the selected gaseous environment. The investigations were run applying the spectrometer HR2000+ES, the light sources of the type DT-mini-2-GS (produced by Ocean Optics), and a PC computer for recording and the acquisition of data. The temperature of the structure was stabilized by a digital controller Shimaden FP93 with an accuracy of $T = \pm 0.1°C$. The temperature of the sensor structure was measured by the PT100 thermistor, situated on the surface of the ZnO layer. During experiment test temperature of ZnO structure was equal to $T = 120°C$. It allowed to minimize the impact of humidity on the results of the study of ZnO structures in selected gaseous environments. In all investigations the humidity of applied synthetic air was H≈5%.

The tested structures were heated up to the required temperature $T = 120°C$ by means of a heater placed just under the investigated sensor structure, permitting the recording of the spectral characteristics of the transmitted light. The adequate composition of the gas mixture passed into the measuring chamber was controlled automatically by a programmed feeder.
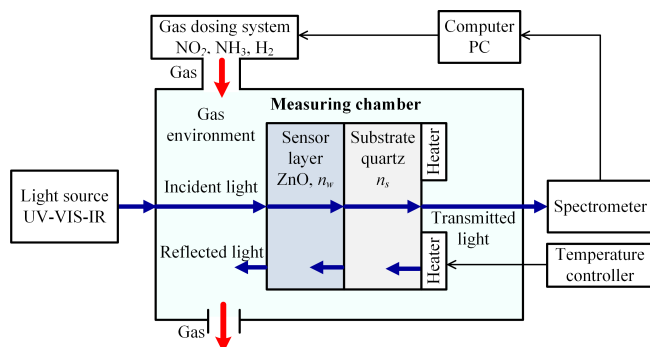

Fig. 1. Diagram of the measuring stand testing the sensor structure

The gas batching system allowed to perform tests in chosen atmospheres consisting of up to six gases within a wide flow rate from some milliliters per minute (ml/min.) to several thousand ml/min., at a wide temperature rate of the structure

and the gases, at a controlled duration of "poisoning" the structure and its "detoxication", at a selected humidity and selected measurement cycles (Fig. 1). During experiments the ZnO structures were tested in selected gas environment: hydrogen, nitrogen dioxide or ammonia. The presented results concern gases with a preset concentration contained in the atmosphere of synthetic air. All the results quote further on in this paper, concerning the properties of the transmission of the tested ZnO layers, have been corrected so that they would not take into consideration a light transmission in the glass or quartz substrates.

3. Experimental results

The ZnO layers were divided into three kinds, depending on the roughness of the surface and its porosity. The investigations presented in the paper were performed for various ZnO structures. The structures investigated for the given kind of ZnO are manufactured in this same technological process.

3.1. ZnO layers with an undeveloped surface. The first kind – thin ZnO layers with an undeveloped surface and relatively slight roughness on the level RMS ≈ 5 nm. Formally, the technology of the layers was optimized to be applied as waveguide layers in planar optical waveguides. The obtained layers were characterized by a low coefficient of attenuation of the optical signal – the coefficient of attenuating the optical modes propagating in the layers amounted to about $\alpha \sim 3$ dB/cm. Such layers have among others, been presented in [22, 23]. ZnO films were deposited on a substrate, e.g. glass BK7 or quartz. The results presented below refer to ZnO layers produced by applying the technology of reactive sputtering in the RF mode, making use of the ceramic target ZnO (99.99% purity). The depositing processes were realized in an atmosphere of oxygen O_2 (30%) and argon Ar (70%) on the heated substrate. The pressure during the deposition amounted to $P_{Ar+O2} = 1.0$ Pa (the partial pressure of the oxygen to $P_{O2} = 0.3$ Pa). After the deposition on BK7 glass the structures were annealed using the Rapid Thermal Annealing (RTA) method at: $T = 400°C$ in N_2 by $t_{N2} = 10$ min. and $T = 500°C$ in O_2 by $t_{O2} = 10$ minutes.

The surface topography of the layer, achieved by means of the AFM method, is to be seen in Fig. 2a, and its cross-section obtained by means of scanning electron microscopy (SEM) in Fig. 2b.

The light transmission across the ZnO layer in the spectral range UV-VIS-IR has been presented in Fig. 3. The absorption edge is equal $\lambda_{g1} \approx 380$ nm and the energy band gap is $E_{g1} = 3.25$ eV. The first kind of ZnO layers – with an undeveloped surface (relatively smooth) with thickness of $d_w = 300$ nm, was exposed to NH_3 – ammonia with 500 ppm (parts per million) in cycles of $t_z = 15$ minutes poisoning (gas NH_3 in synthetic air) and $t_o = 15$ minutes detoxication. The tests of the effect on the gaseous environment were carried out at the temperature of the ZnO structures $T_z = 120°C$. The response of the ZnO layer to the cycles of poisoning with NH_3 and detoxication in synthetic air is to be seen in Fig. 4.

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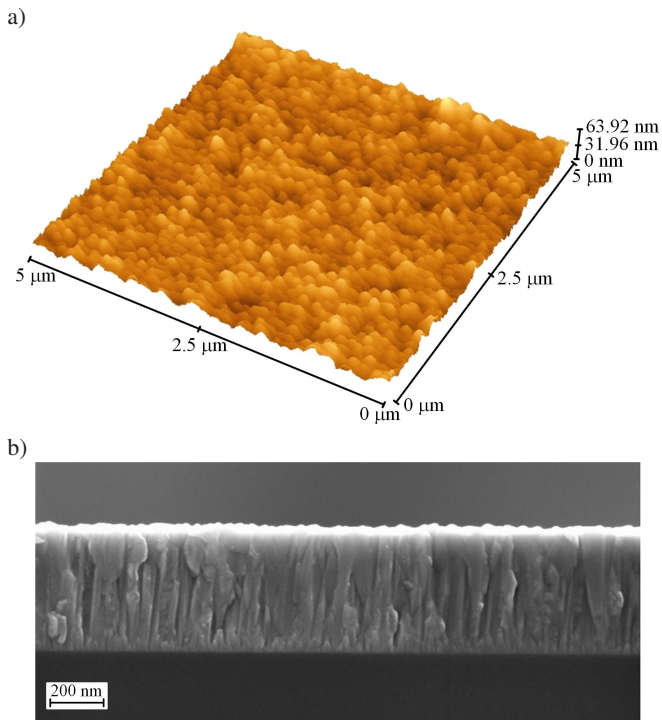
a)

b)

Fig. 2. Topography of ZnO layer with an undeveloped surface: a) image of AFM; b) cross-section of layer (SEM picture)
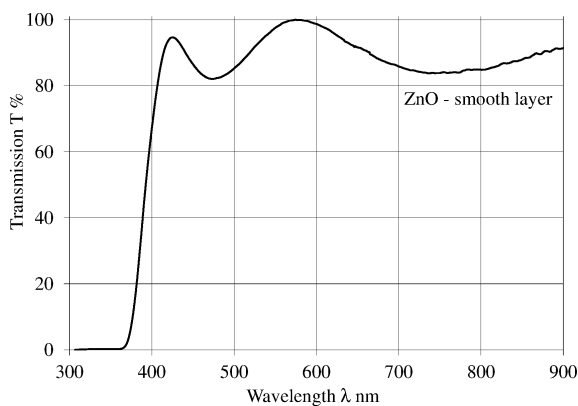

Fig. 3. Characteristics of the spectra transmission of the ZnO layer with a smooth surface in synthetic air with NH_3 with concentration 500 ppm
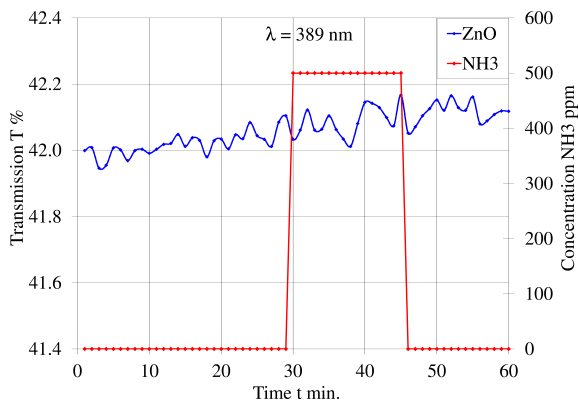

Fig. 4. Light transmission cross the ZnO layer expose to NH_3 with concentration of 500 ppm in synthetic air for a wavelength $\lambda = 389$ nm

This structure was then exposed to the effect of a gaseous environment containing H_2 with a concentration of $c = 3\%$ in cycles $t_z = 15$ minutes poisoning and $t_o = 15$ minutes detoxication (synthetic air).

In the course of exposing smooth ZnO layers with an undeveloped surface to ammonia (NH_3) and hydrogen (H_2) no changes in the transmission of the optical signal due to "poisoning" by these gases were recorded. The results quoted above are also reflected in the characteristics of transmission at the wavelength $\lambda = 389$ nm concerning both gases presented in Figs. 4 and 6. Thus, it may be concluded that zinc oxide layers with an undeveloped surface (RMS ~ 5 nm) are not sensitive to the investigated gases. Their application as sensor layers is absolutely unjustifiable. These layers can be used as optical waveguides [20].
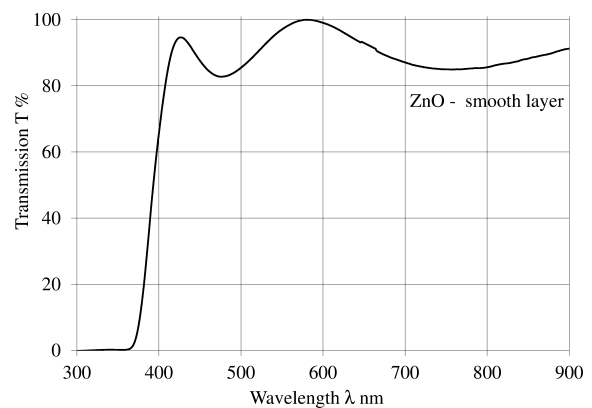

Fig. 5. Characteristics of the spectra transmission of a smooth ZnO layer in synthetic air with $c = 3\%$ concentration of H_2
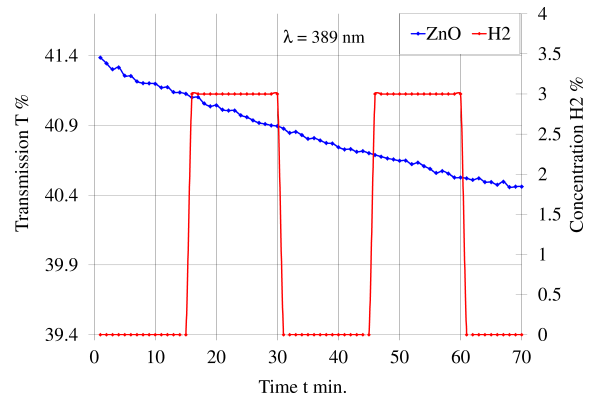

Fig. 6. Light transmission cross the ZnO layer expose to H_2 with concentration of 3% in synthetic air for a wavelength $\lambda = 389$ nm

3.2. ZnO layers with a rough surface. The second kind of structures comprised of ZnO layers with a rough surface. The ZnO layer is characterized by a developed surface but it is not porous like the third kind of the ZnO layer presented in next section. The surface of the ZnO layer contained nanopyramides with a height of several to some scores of nanometers. The image of its topography obtained by means of the method AFM is to be seen in Fig. 7. The layers were deposited by reactive magnetron sputtering from the ZnO target upon an unheated substrate of glass BK7. After their deposition on the glass substrate these layers were not subjected to annealing.
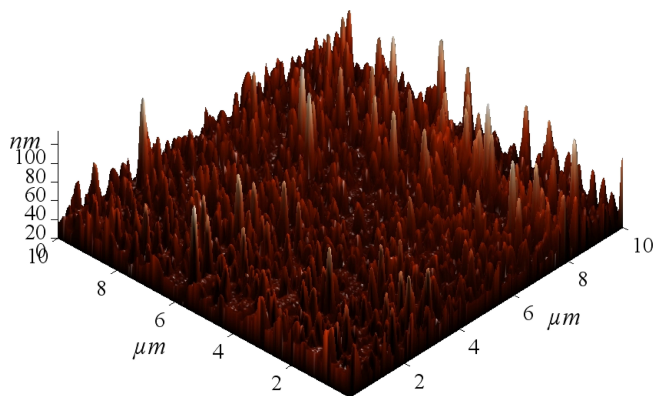
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Fig. 7. Topography of a ZnO layer with a rough surface, obtained by applying the AFM method

The ZnO layers with a rough surface, $\sim$790 nm thick, were exposed to NH$_3$ –ammonia in cycles: $t_z = 20$ minuts poisning (NH$_3$) with concentrations of $c = 250$ ppm or $c = 500$ ppm in synthetic air, and detoxication (synthetic air: 20% – O$_2$ and 80% – N$_2$). Investigations were performed at a temperature of the ZnO layer $T_z = 120°$C. Figure 8 presents changes in the spectral transmission of ZnO layer in the spectral range: UV-VIS-IR. The edge of absorption is equal $\lambda_{g2} \approx 370$ nm and energy band gap at the level $\Delta E_{g2} \approx 3.35$ eV. Inves-
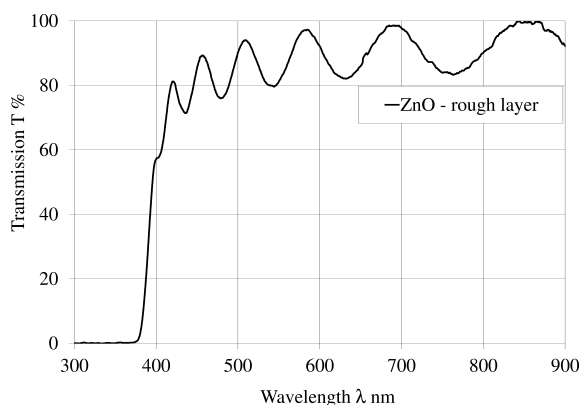

Fig. 8. Spectral characteristics of the rough ZnO layer in synthetic air
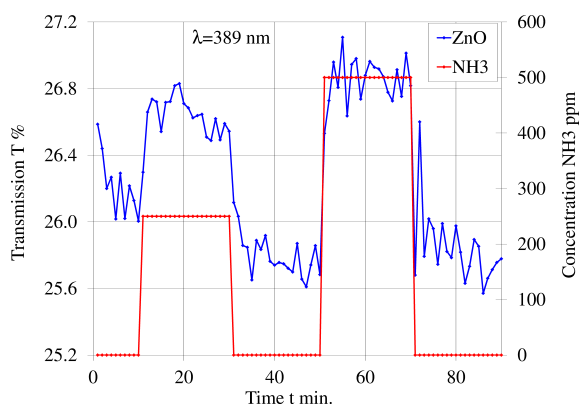

Fig. 9. Light transmission through the ZnO layer with a rough structure exposed to NH$_3$ with concentrations of 200 ppm and 500 ppm in synthetic air for a wavelength $\lambda = 389$ nm

tigations displayed a change in the transmission of light in the range near ultraviolet, and at an increasing concentration of NH$_3$ the transmission of light through the ZnO layer also increases, as is to be seen in Fig. 9.

The ZnO layers with a rough surface were affected by ammonia NH$_3$ – at a wavelength $\lambda \approx 390$ nm, and of an ammonia concentration of 500 ppm the change of the optical tramsmission was on the level $T \sim 1.2\%$. The response time of the tested structure to its "poisoning" amounted to about $t_z \sim 180$ seconds, similar to the time of its detoxication ($t_o \sim 180$ s).

3.3. Porous ZnO layers. The third kind of the structures consists of porous ZnO layers, characterized by a granular nanostructure, the size of the grains being in the range from a score to several hundred nanometers.

The zinc oxide porous layers were manufactured in two steps: first, a porous Zn film was deposited by reactive magnetron sputtering method from the Zn target under 80 W DC power in an atmosphere of 17% oxygen and 83% argon. The total pressure of the gas mixture during deposition was $P \approx 0.2$ Pa and the base pressure prior to deposition was of the order of $P \approx 14 \cdot 10^{-6}$ Pa. The second step was ex-situ annealing in an oxygen flow at a temperature of $T \approx 400°$C, performed in order to form ZnO.

An image of the porous ZnO layer obtained by means of SEM has been presented in Fig. 10. The physical properties of porous ZnO layers as well as the technology of deposition have been dealt with in [24, 25].

These porous ZnO structures were exposed to certain selected gaseous environments, such: ammonia – NH$_3$, nitrogen dioxide – NO$_2$, hydrogen – H$_2$. The carrier gas was synthetic air (20% O$_2$, 80% N$_2$). All investigations were performed at a temperature of the ZnO structure amounting to $T_z = 120°$C.

The technology of porous ZnO layers was optimized in order to get layers with the most developed surface. The ZnO layer is characterized by a deep porous structure consisting of ZnO nano-grain, its dimensions is of one or a few dozen nanometers. Thanks to porous structure of ZnO, active surface of sensor is developed significantly. The surface would be affected by the gaseous environment in the most possible degree. The layers were manufactured with the purpose of being applied as active layers in optical gaseous sensor structures. The thickness of the porous structures of zinc oxide amounted to $d_w = 400$ nm.

The porous ZnO structure was exposed to NH$_3$ with concentration of $c = 250$ ppm or $c = 500$ ppm in synthetic air, in cycles of poisoning and detoxication lasting $t = 20$ minutes. Figure 11 shows the characteristics of the spectral transmission through a porous ZnO layer in the range: UV-VIS-IR. Measured edge of absorption is $\lambda_{g3} \approx 300$ nm which correspond to energy band gap $\Delta E_{g3} \approx 4.00$ eV. The performed investigations have proved that the porous sensor layer of ZnO exposed to ammonia NH$_3$ in synthetic air increases its transmission, particularly in the ultraviolet range, as is to be seen in Fig. 12. The analysis of changes in the transmission at a wavelength $\lambda = 380$ nm has been presented in Fig. 12.
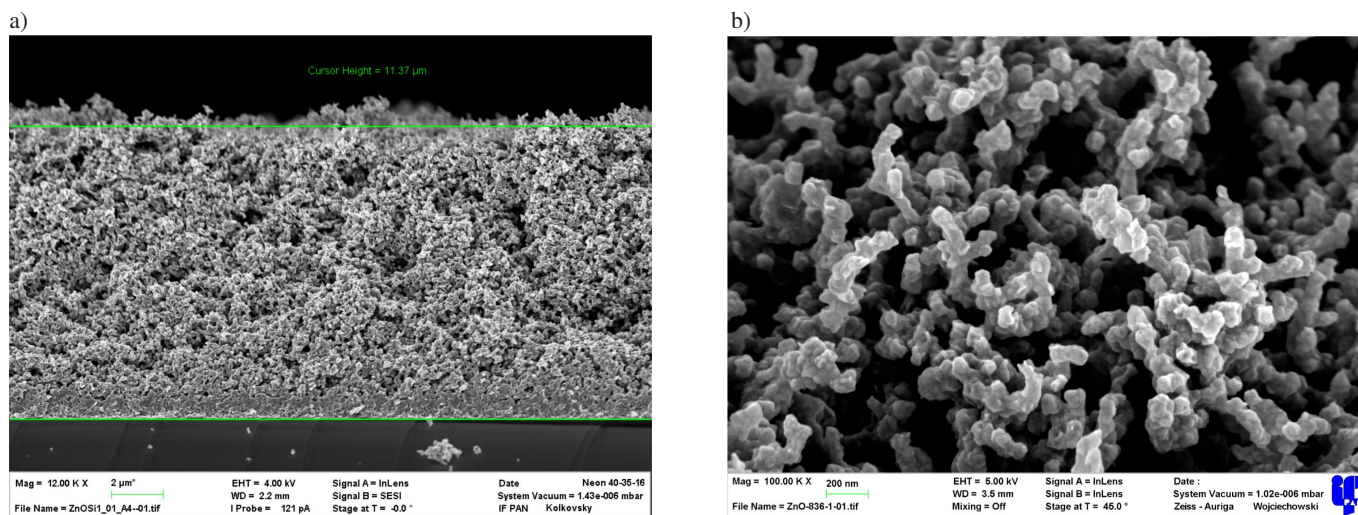
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a)

b)

Fig. 10. Porous structure of the ZnO layer – SEM image: a) cross-section, b) surface
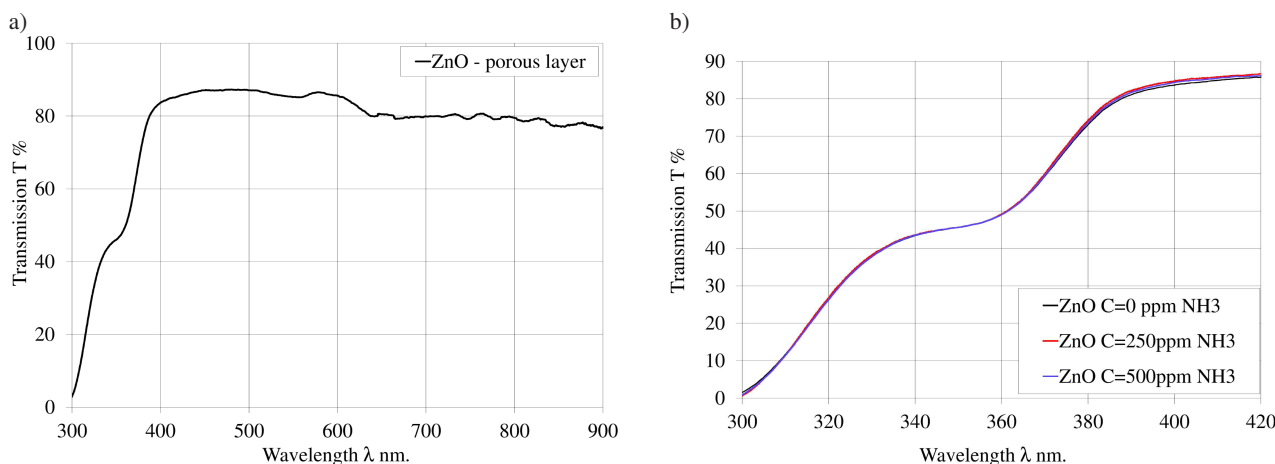
a)

b)

Fig. 11. Characteristics of the spectral transmission cross the porous ZnO layer in the optical range: a) UV-VIS-IR in synthetic air, b) UV after action of NH_3 in synthetic air
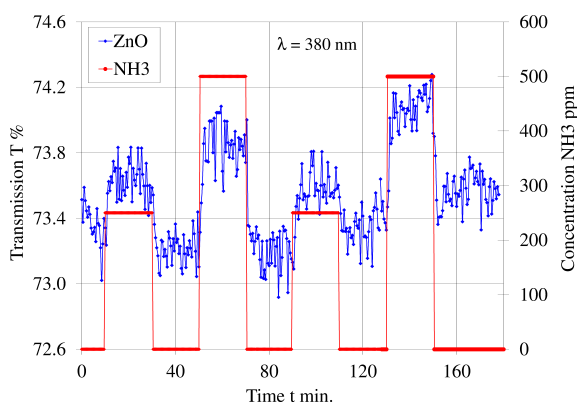

Fig. 12. Changes in the optical transmission of the porous ZnO layer exposesed to NH_3 at a wavelength $\lambda = 380$ nm

For the wavelength around 380 nm the slope of light absorption characteristic is the steepest. For this wavelength we observed also the highest changing of transmission light through the ZnO sensors layer during poisoning and detoxifi-

cation process by NH_3 we observed also the highest changing of transmission light of ZnO sensors structures during poisoning and detoxification by selected gases.

The change of the transmission of light amounted to $\Delta T \approx 1\%$ at a wavelength $\lambda = 380$ nm and a NH_3 concentration of $c = 500$ ppm. The times of response of the structure to poisoning and detoxication were $t_{oz} \sim 90$ seconds, each.

The next stage of investigation was the determination of the response of the sensor structure with a porous ZnO layer to hydrogen H_2.

The porous ZnO layer with the thickness $d = 400$ nm was deposited on a plate of glass BK7. The hydrogen used in these investigations had a concentration of: 1%, 2%, 3% (in synthetic air) in the respective cycles of poisoning lasting $t = 20$ minutes each. Also the process of detoxication (in synthetic air) took $t = 20$ minutes. The spectral characteristics of the transmission of light concerning this structure have been presented in Fig. 13a. In the case of porous ZnO layers, the characteristics of transmission do not contain any minimum

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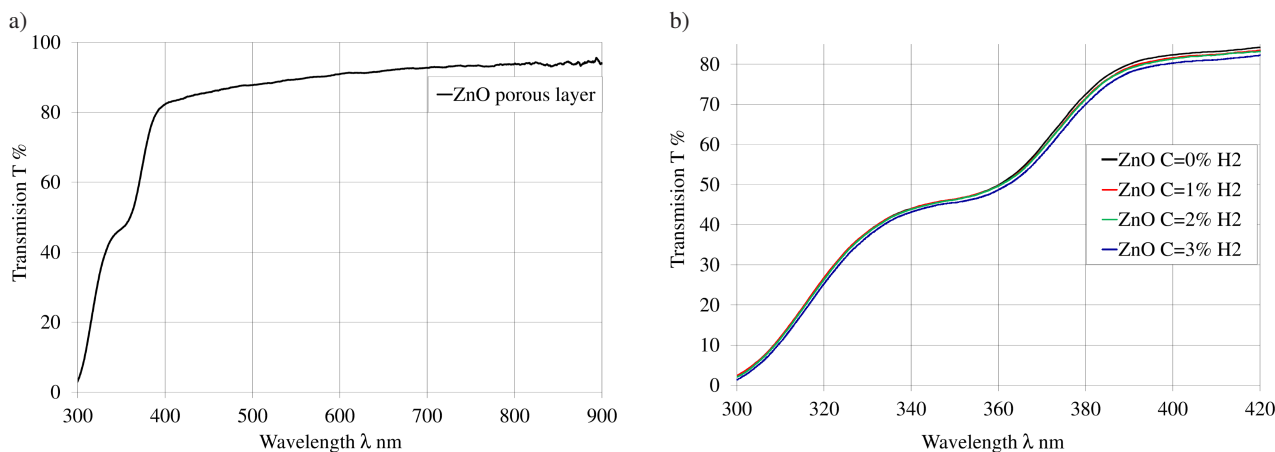
a)

b)

Fig. 13. Spectral characteristics of the porous ZnO layer in the range: a) UV-VIS-IR in synthetic air; b) UV-VIS in synthetic air with concentration $c = 2\%$ of H_2

nor maximum values of interferences, because due to their porosity in the structures no interference of light was observed. The performed investigations indicate that structure with porous ZnO layer exposed to hydrogen (H_2) in synthetic air decreases its transmission T, particularly in the ultraviolet range and in blue light (Fig. 13b).

Figure 14 presents a cycle of measurements of a porous ZnO layer affected by H_2 in synthetic air.

The change in the transmission of light amounted $\Delta T \approx 1.5\%$ at a wavelength $\lambda = 389$ nm and a H_2 concentrations of $c = 3\%$ (Fig. 14). The investigations have also proved that the time of response of the structure to poisoning lasted about $t_{oz} \sim 90$ seconds, whereas the detoxication time of the porous ZnO layer amounted to almost $t_{oo} \sim 120$ seconds.

Finally, investigations concerning porous ZnO layers exposed to nitrogen dioxide (NO_2) were performed. A porous ZnO layer with a thickness of $d = 400$ nm was exposed NO_2 with concentration of 500 ppm, 1000 ppm, 1500 ppm, 2000 ppm in synthetic air. The investigations were run in equal cycles of poisoning and detoxication $t_{zo} = 30$ minutes. Temperature of the ZnO structure was $T = 120°C$. The spectral characteristics of the light transmission in the range: UV-VIS-IR of the tested layer are to be seen in Fig. 15a. The performed investigations indicate that a structure with a porous ZnO layer 400 nm thick, exposed to NO_2 in synthetic air, displays a lower optical transmission T for higher NO_2 concentrations, particularly in the range UV and blue light, as shown in Fig. 15b.
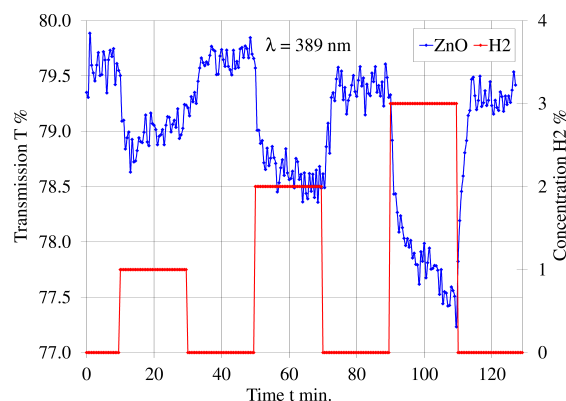
Fig. 14. Changes of transmission of the structure with porous ZnO exposed to H_2 in synthetic air (at wavelength $\lambda = 389$ nm)
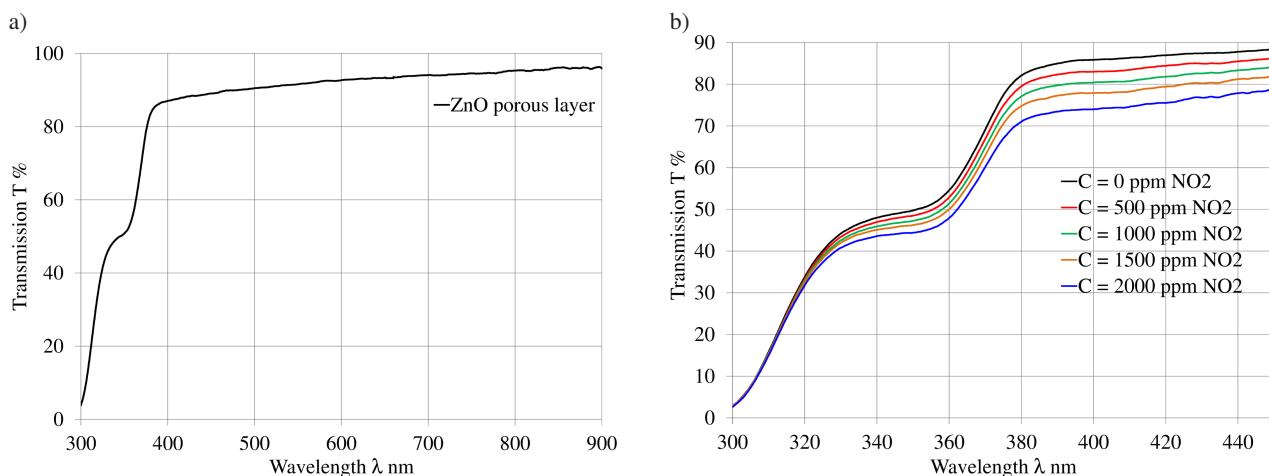
a)

b)

Fig. 15. Spectral transmission through porous ZnO laer in the range: a) UV-VIS-IR (in synthetic air); b) UV and blue light (exposed to NO_2 in synthetic air)

Figure 16 presents an exemplary cycle of measurements, in which a porous ZnO layer was subjected to the effect of NO_2 in synthetic air.
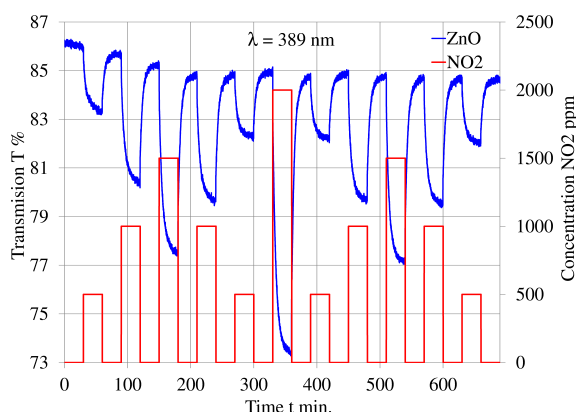

Fig. 16. Changes of transmission of the structure with porous ZnO exposed to NO_2 in synthetic air (at wavelength $\lambda = 389$ nm)

The change in the transmission of light at the wavelength $\lambda = 389$ nm amounted to $\Delta T \approx 12\%$ at a concentration of $c = 2000$ ppm of NO_2 (Fig. 16) The investigations have also shown that the response time of the structure to poisoning and detoxication was about $t_{oz} \sim 10$ minutes. With regard to their application in sensor structures, of essential importance is the fact that the properties of the ZnO structure are reversible – after the process of poisoning the structure its regeneration is caused by the flow of synthetic air in order to recover its sensing properties. The response of the structure with a porous ZnO layer is also repeatable; the cycles of poisoning involve the same change of transmission at the given concentration of the gas, as can be seen in Fig. 16.

4. Conclusions

As had been expected, the performed investigations confirm that the best sensor properties characterize the structures with the most developed surface, i.e. structures based on porous ZnO. Presented experimental results shows the ZnO layer with small roughness optimized for planar waveguide application (ZnO layer with undeveloped surface) do not change their optical transmission under influence of following gases: H_2, NH_3. Along with an increase in surface development of ZnO layer we can observe small changes of spectral transmission especially in UV and blue light range during poisoning NH_3 and detoxification steps. The biggest changes of spectral transmission of light during influences of selected gases (H_2, NH_3, NO_2) were observed for porous ZnO layers. The maximum changes of spectral transmission of light were observed in UV and blue light range where slope of spectral transmission characteristic is the highest (very close to edge of light absorption).

The investigations have proved also that the values of the absorption edge of λ_g in the manufactured ZnO layers change depending on the topography of their surfaces due to the changing energy band gap ΔE_g. Such large differences

of these values prove explicitly that the electric and electron properties of porous ZnO layers are determined by the electron surface states on the surface of nano- and micrograins. The considerable density of the surface states in porous ZnO leads to the formation of the depletion of electrical conductivity, characterized by considerable curving of the energy edges bands "upwards".

It ought to be stressed that in the present paper ZnO layers with thickness of fraction of micrometer were measured, basing on changes in transmission of light passing the layers transversely (Fig. 1). Changes of the transmission observed experimentally on the level: 1–15% suggest that in the case of applying such layers in optical planar structures, in which the distance of the light effect with the layer amounts even to about 1 cm (being, therefore, several score of thousands times longer than in the tested cases), planar sensor structures may be characterized by a high sensitivity.

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