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Gas Sensors Based on ZnO Structures

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The paper presents the results of investigations concerning sensor structures based on porous layers of zinc oxide (ZnO) sensitive to a selected gaseous environment. The investigations comprised analyses of the influence of the gaseous environment on the optical properties of a sensor structure, in particularly on the change of the spectral characteristics of optical transmission within the range of ultraviolet light and in the visible range. These presented investigations were carried out in such a gaseous environment as nitrogen dioxide NO_2 in synthetic air.

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1. Introduction

The actual development of our industrial civilization requires a monitoring of the gaseous environment with respect to the protection of human health and the protection of the natural environment, as well as in industrial plants in the course of technological processes [1–3]. Sensor structures sensitive to some selected gaseous environment ought to be characterized by a high sensitivity, a good selectivity and repeatability [4]. At present for sensor application much attention is paid to searches and investigations of new semiconductive materials, including oxide semiconductors with a wide energy band gap [5, 6].

An interesting material displaying considerable possibilities of application in sensor structures sensitive to some chosen gases is zinc oxide [7, 8]. Investigations are particularly devoted to the production of sensor structures in which the active ZnO layer has a large surface, which has the form of nanostructures, e.g. nanograins, nanorods and flower-shaped agglomerates, etc. [9, 10]. Such materials are characterized by a relatively high value of the energy gap, amounting to $E_g \approx 3.2$ eV [11–13]. ZnO is transparent in the visible range of the spectrum; therefore it can be applied in optical and optoelectronic structures. Its edge of absorption overlaps the range of near ultraviolet [14, 15]. The application of ZnO in sensor structures sensitive to gaseous environment is due to the fact that the external environment may change optical properties of ZnO sensor layer. Thus also the optical properties are subject to changes, as is to be dealt with in this paper.

2. Measurement setup

The tested sensor structures of zinc oxide (ZnO) were deposited on a quartz substrate making use of the technology of cathode sputtering. The thickness of the deposited ZnO layers amounted to about $d_w = 400$ nm. Experimental tests concerning the response of ZnO sensor structures in the atmosphere of selected gases in synthetic air were carried out spectrophotometrically in the range from near ultraviolet over visible range to the range of near infrared (UV–VIS–IR). The behavior of light is the visible range and the adjacent range at the boundary of materials with different refractive indices has been illustrated schematically in Fig. 1. Some part of the energy of the incidence wave is reflected at the interface with different refractive indices n_c and n_w. The part of the optical energy is transmitted through the tested structure, but in the tested ZnO layer there occurs also the so-called effect of the interference of light in the thin layer.

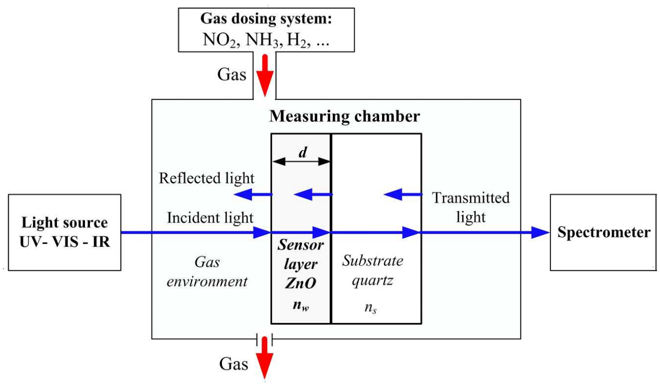

Fig. 1. Diagram of the measurement setup.

The measurement setup where the behavior of the ZnO-based sensor structures in some selected gaseous environment were tested consists of a measurement chamber (in which the tested structure is placed), the source of light, spectrometer and a system of batching the gas.

The temperature of the tested structures were controlled and stabilized on the required level by means of a digital controller. The structures are heated by heater positioned just under the structure. This heater must be constructed in such a way that permits to measure

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the spectral characteristics of transmission of the investigated structures. For the purpose of recording the optical signals the measurement systems were provided with the spectrometer HR2000+ES (produced by Ocean Optics Co.). As the source of light the DT-mini-2-Gs (also from Ocean Optics Co.) was applied. The acquisition of data and automatic control were realized by a computer of the class PC. The gas is passed into the measurement chamber through a batcher system, which permits to program the composition of the gas mixture, the duration of the respective cycles and the volume of the flowing gas. The batching stand consists of a programmer with a controller electronically checking the flux of gas. The gas flows from the cylinders into the controller through a set of external valves and reducers. The batching system can be programmed in order to adjust the values of the concentration of given gas in the atmosphere of synthetic air (20% O_2, 80% NO_2) and to adjust the duration of the cycles of poisoning t_z and detoxication t_0, as well as the flow rate of the gas V through the measurement chamber.

3. Results of experimental investigations

In the course of the first stage of investigations the topography of surface of ZnO sensor structures was tested. The structures revealed to have a very complex and much developed surface, and thus also a large active area.

The determined value of the root mean square of surface roughness amounts to $S_q = 72.8$ nm. The image of the ZnO sensor structure, obtained by applying the atomic force microscopy (AFM) method, is to be seen in Fig. 2.

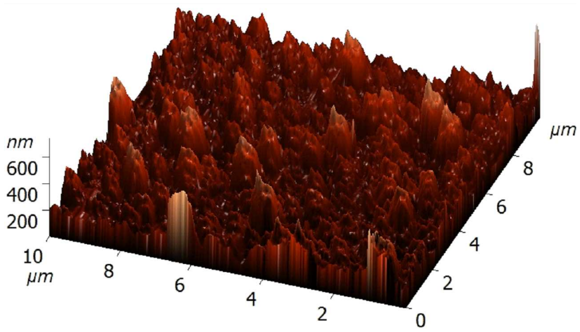

Fig. 2. Topography of the surface of ZnO sensor structure.

In the next stage the spectral characteristics of transmission T were determined spectrophotometrically concerning the ZnO sensor structures.

In the course of determining the spectral characteristics of transmission as the signal of reference the quartz substrate was determined (without the ZnO layer). These investigations proved that the spectral characteristics of zinc oxide (ZnO) were determined on the quartz substrate. After that the spectral transmission characteristic of ZnO layer was measured that in the wavelength range above $\lambda = 370$ nm the structure is transparent, as shown in Fig. 3. Because the ZnO in the structure presented in Fig. 3 was porous, in this characteristics the maximum and minimum values of interference which may occur in thin layers are not visible (due to the lack of resonances in this structure).

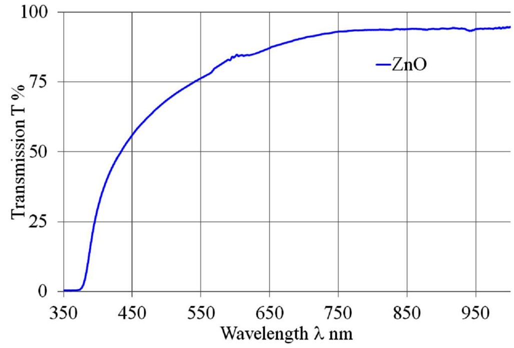

Fig. 3. Spectral characteristics of the transmission of porous ZnO.

The investigated sensor structure was exposed to nitrogen dioxide NO_2 with concentrations amounting in the subsequent cycles of poisoning respectively to $C_{NO2} =$ 500 ppm, $C_{NO2} = 1000$ ppm, $C_{NO2} = 1500$ ppm or $C_{NO2} = 2000$ ppm in cycles lasting $t_z = 30$ min. The layer was detoxicated in an atmosphere of synthetic air $C_{air} = (20\%\ O_2,\ 80\%\ N_2)$ in cycles lasting $t_0 = 30$ min between the cycles of poisoning. During the investigations the gas was flowing through the measurement chamber in the toxication cycle $V_g = 100\ cm^3/min$. Temperature of the structure was during the experiments stabilized on the level of $T_z = 120\,°C$.

The changes of the spectral transmission characteristic of the ZnO sensor structures within the ultraviolet and visible range of light ($\lambda = 350$–550 nm) under the influence of the NO_2 gaseous environments are presented in Fig. 4.

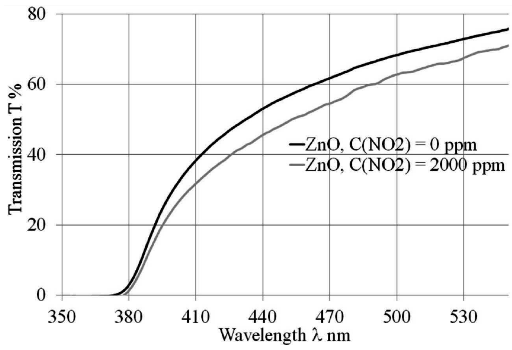

Fig. 4. The spectral transmission of sensors structures under influence of NO_2 environments.

The analysis of the obtained results of investigations indicated that in the course of poisoning the sensor structure by NO_2, the value of its optical transmission T decreases in the range of blue light (Fig. 4).

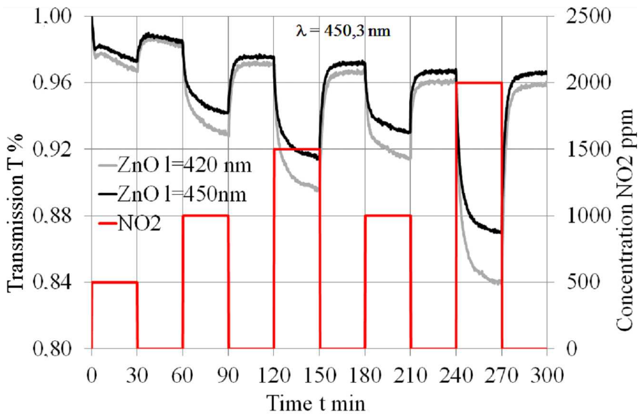

Fig. 5. Changes in the transmission T at wavelengths of $\lambda = 420$ nm and $\lambda = 450$ nm as a function of changes in the gaseous environment.

The changes in the transmission of the optical signal within the visible range — blue light with a wavelength of $\lambda = 420$ nm and $\lambda = 450$ nm recorded under the influence of the sensor structure, are presented in Fig. 5. The quantity of changes depends on the concentration of the gas (NO_2) to which the sensor structure was being exposed. Thus, for instance, when the gas is concentrated on the level $C = 2000$ ppm, the change of transmission at the wavelength $\lambda = 450$ nm is on the level $\Delta T \approx 9\%$ (Fig. 5 — black line). At a wavelength in the range $\lambda = 420$ nm is on the level $\Delta T \approx 12\%$ (Fig. 5 — gray line). An important feature of the elaborated ZnO sensor structures sensitive to some gaseous environment is the detoxication of the structures and a return of their properties (the values of the transmission T for given wavelength) to the state preceding the exposure to NO_2. The performed investigations proved that the optical transmissions of the elaborated sensor structures in the process of detoxication relatively soon attain their states previous to their poisoning in a time of about $t_0 \approx 8$ min.

4. Summary

The performed investigations have proved the influence of the external gaseous environment on the optical properties of sensor structures based on porous zinc oxide layers. From the viewpoint of applying porous ZnO layers in optoelectronic sensor structures sensitive to some selected gaseous environment, of much importance is the fact that in the course of exposing the ZnO structure on action of the gaseous NO_2 in an atmosphere of synthetic air, the optical parameters of the structures — their spectral characteristics of transmission, undergo changes. Changes caused by the interaction of the sensor structures with given gaseous environment are reproducible. Basing on these investigations it may be concluded that already in near future it will be possible to apply ZnO layers in sensor structures for the detection of selected gases in atmospheric air.

Acknowledgments

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References

[1] X. Liu, S. Cheng, H. Liu, S. Hu, D. Zhang, H. Ning, *Sensors* **12**, 9635 (2012).

[2] W.P. Jakubik, M. Urbańczyk, E. Maciak, T. Pustelny, *Bul. Pol. Acad. Sci., Techn. Sci.* **56**, 133 (2008).

[3] T. Pustelny, I. Zielonka, C. Tyszkiewicz, P. Karasiński, B. Pustelny, *Opto-Electron. Rev.* **14**, 161 (2006).

[4] O. Lupan, V.V. Ursaki, G. Chai, L. Chow, G.A. Emelchenko, I.M. Tiginyanu, A.N. Gruzintsev, A.N. Redkin, *Sensors Actuat. B* **144**, 56 (2010).

[5] K. Gut, *Bull. Pol. Acad. Sci, Techn. Sci.* **59**, 395 (2011).

[6] T. Anderson, F. Ren, S. Pearton, B.S. Kang, H.T. Wang, Ch.Y. Chang, J. Lin, *Sensors* **9**, 4669 (2009).

[7] T. Pustelny, P. Struk, *Opto-Electron. Rev.* **20**, 201 (2012).

[8] T. Pustelny, E. Maciak, Z. Opilski, M. Bednorz, *Opt. Appl.* **37**, 187 (2007).

[9] D. Calestania, M. Zhaa, R. Moscaa, A. Zappettinia, M.C. Carottab, V. Di Natalеb, L. Zanottia, *Sensor Actuat. B* **144**, 472 (2010).

[10] T. Pustelny, M. Procek, E. Maciak, A. Stolarczyk, S. Drewniak, M. Urbańczyk, M. Setkiewicz, K. Gut, Z. Opilski, *Bul. Pol. Acad. Sci., Techn. Sci.* **60**, 853 (2012).

[11] Ü. Özgür, Ya.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Doan, V. Avrutin, S.J. Cho, H. Morkoc, *J. Appl. Phys.* **98**, 041301 (2005).

[12] K. Gut, K. Nowak, *Europ. Phys. J., Spec. Top.* **154**, 89 (2008).

[13] M.A. Borysiewicz, E. Dynowska, V. Kolkovsky, J. Dyczewski, M. Wielgus, E. Kaminska, A. Piotrowska, *Phys. Status Solidi A* **209**, 2463 (2012).

[14] P. Struk, T. Pustelny, Z. Opilski, *Acta Phys. Pol. A* **118**, 1239 (2010).

[15] P. Struk, T. Pustelny, K. Gołaszewska, E. Kamińska, M. Borysiewicz, M. Ekielski, A. Piotrowska, *Opto-Electron. Rev.* **19**, 462 (2011).