

Studies of changes in electrical resistance of zinc oxide nanostructures under the influence of variable gaseous environments

M. PROCEK^{1*}, T. PUSTELNY¹, A. STOLARCZYK², and E. MACIAK¹

¹ Department of Optoelectronics, Silesian University of Technology, 2 Akademicka St., 44-100 Gliwice, Poland

² Department of Physical Chemistry and Technology of Polymers, Silesian University of Technology, 9 Strzody St., 44-100 Gliwice, Poland

Abstract. The paper deals with the investigations concerning the influence of the changing gas environment on electrical resistance of zinc oxide (ZnO) nanostructures. The investigated structures are wide-gap semiconductors with the morphology of ZnO flower-shaped agglomerates of nanostructures. The resistance changes of these nanostructures were tested under the influence of various gases such as nitrogen dioxide (NO₂), hydrogen (H₂), ammonia (NH₃) and also of humidity changes of carrier gases. To clarify the mechanisms of physicochemical processes in ZnO nanostructures during their interaction with gaseous environments, investigations were performed in two different carrier gases, viz. in synthetic air and in nitrogen. The study was carried out at a structure temperature of 200°C.

Key words: zinc oxide (ZnO), flower-like nanostructures, gas sensor, wide gap semiconductors, electric properties of semiconductors.

1. Introduction

Presently, an important problem which attracts the attention of metrologists and technologists is the way of obtaining more and more sensitive and inexpensive gas sensors. The gas sensors are commonly applied in many domains of life, including the industry and households. Sensor structures' designing requires the knowledge of physicochemical phenomena occurring during the contact of the sensing structure with the measured gas.

Since many years, the most popular and well known structures sensitive to the presence of gases have been the semiconductive ones. Very popular semiconductors applied for this purpose are metal oxides, which are semiconductors with a wide band gap, such as: SnO₂, TiO₂, WO₃, ZnO and others [1–4].

In spite of the large popularity of wide-gap semiconductors, the solutions based on them, as well as the considerable investigations concerning them, the phenomena occurring during their interaction with gases are still not fully recognized. Therefore, an ultimate formalism permitting to describe accurately the mechanism of the occurrence of the measurement signal in thin (both smooth and porous) layers has still not been found [5].

In recent years a considerable progress in the domain of nanotechnology has been achieved, thanks to which researchers have access to new methods of obtaining nano- and microstructures. Various new forms of nano- and microstructures have become available, differing both in their morphology and chemical composition, as well as in the kind of crystalline lattice. Many nanostructures are investigated in terms of their application in gas sensors. The graphene and its compounds, such as the graphene oxide and the reduced graphene oxide may be served as an example [6–8]. Recently,

also nanostructures of wide-gap semiconductors are intensively studied in order to apply them in the sensors of gases and vapours [9]. The potential of sensors based on nanostructures relies on: their developed surface, the multiplicity of connections between the crystallites and the possibility of their easy doping by metal nanoparticles [10]. Theoretical considerations concerning interactions of semiconductor nanoparticles with gaseous molecules are, so far, much less advanced in comparison with those dealing with thin layers.

In the present paper nanoparticles of ZnO, which is a n-type wide-gap semiconductor, are presented and characterized. The morphology and chemical composition of the investigated nanostructures are tested and discussed. Responses of these structures to gases such as: NO₂, H₂, and NH₃, as well as to changes of the humidity, are introduced and compared. Researches have been carried out in two different carrier gases, namely in synthetic air and in pure nitrogen.

2. Theoretical part

Changes of the electrical conductance in planar semiconductor structures are mainly caused by changes in the concentration of charge carriers. The molecules of gases affect the semiconductor structure through its surface. The gas adjacent to the surface may be physically or chemically adsorbed. The adsorption of gas leads to changes of the concentration of the charge carriers in semiconductor – an atom or particle of gas may add or remove an electron from the conduction band and also leads to filling up of trap surface states. In case of porous layers, a double Schottky barrier between the grains is supposed to exist [11]. The potential barrier at the connection of the grains, as well as the amount of free carriers and their spatial distribution, depend on the gas affecting the surface of the semiconductor. Therefore, the electric conduction

*e-mail: marcin.procek@polsl.pl

of a semiconductor structure depends also on the kind and concentration of the gas [12].

Semiconductor structures operating in the natural environment are exposed to considerable concentrations of oxygen (about 21%) and humidity. It is, therefore, important to find out how much changes in the conductivity of semiconductor structures depend on the changes in the concentration of O₂ and H₂O in the air. The concentration of oxygen in the atmosphere may be assumed to be rather constant. The content of humidity in the air is, however, unstable and subjected to considerable changes depending on temperature changes, rainfall, atmospheric fronts and the vicinity of water region.

The interaction between the semiconductor structure and the oxidizing gases differs from its reaction with the reducing gases [11, 13]. Reducing gases react with the oxygen, which was earlier adsorbed by the structure. In oxide semiconductors, the reducing gases may also react with the oxygen of the crystalline lattice. The result of these reactions is a decrease of the barrier of the surface potential in the semiconductor and a decrease of the electrical resistance on the surface.

Oxidizing gases are adsorbed on the same active centres, on which the oxygen is adsorbed, competing with it. When the adsorption of oxidizing gas is stronger than the adsorption of oxygen, the barrier of the potential increases, resulting in an increase of the electrical resistance of the structure.

Electrons may also tunnel through short distances between the grains (or nanoparticles) of the semiconductor structure even when the boundaries of the grains are not completely shaped (the distances between the grains remain relatively small). In such case, the tunnel current is attenuated by the surface potential of the grains, which results in similar contribution to a change of the resistance as the barrier effect.

Two basic paths of the current flow are to be distinguished in an oxide semiconductor, viz.: through the potential barrier in the case of grains (nanoparticles) contact and by tunnelling, when the grains do not contact each other directly, but are in close proximity [11]. In the theory of semiconductor sensors, the notion “receptor function” is used (describing the response of single crystallite to gas), as well as the notion “transducer function” (describing the impact of the common interaction of the nanostructures with the gases on the connections between crystallites) [12].

3. 3. Experimental part

3.1. Characterization of the investigated ZnO nanostructures. The method of the synthesis of the tested material has been dealt with in detail in the authors’ earlier paper [14]. The morphology of the investigated ZnO structures was illustrated by the scanning electron microscope (SEM – INSPECT S50 produced by the FEI Ltd.) image which is shown in Fig. 1.

This image indicates that the obtained ZnO structure occurs in a form of flower-like agglomerates of nanotubes with a high homogeneity. The observed agglomerates have a diameter of about 3 to 5 μm. Single nanotubes contained in the agglomerates have the length of single microns, and their diameter is estimated to be from several to scores of nanome-

tres. The chemical composition of the investigated structures was confirmed by Raman spectroscopy tests, carried out immediately after the synthesis (measurements were carried out on NT-MDT NTEGRA SPECTRA platform, with red laser λ = 633 nm stimulation). These tests proved that the investigated structure is a chemically pure zinc oxide with a typical Raman spectrum for ZnO nanostructures (Fig. 2) [15].

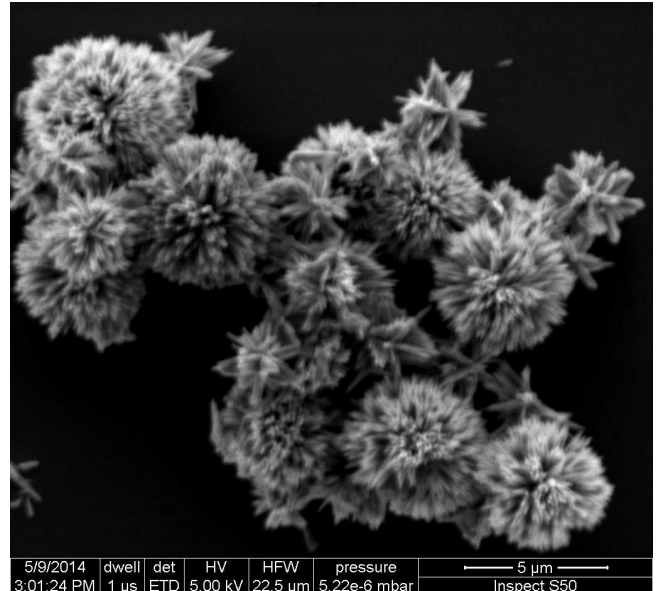


Fig. 1. Scanning electron microscope (SEM) image of investigated ZnO structure

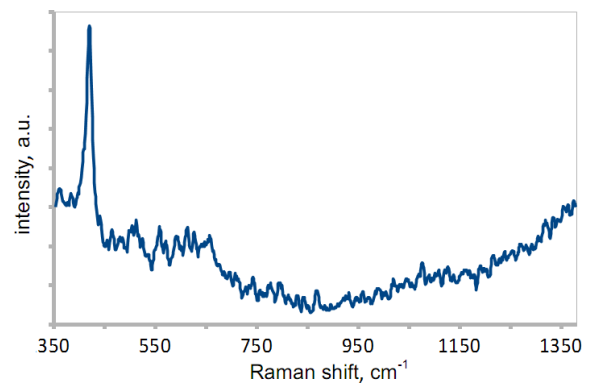


Fig. 2. Raman spectrogram for the investigated ZnO structure

3.2. Preparation of the transducer for resistance measurements. In order to measure the resistance of ZnO nanostructures, these structures were deposited on an interdigital transducer. The transducer is made from a thin gold layer, with thickness of 100 nm, on an oxidized silicon substrate with a size of 10×10 mm. The thickness of the SiO₂ layer, on the substrate surface, is of 1 μm. The distances between the electrodes of the transducer and the width of the electrodes amount to 5 μm. The adequate shape of the electrodes was attained by applying a proper photolithography process. The SEM image of transducer electrodes with deposited ZnO nanostructures is shown in Fig. 3.

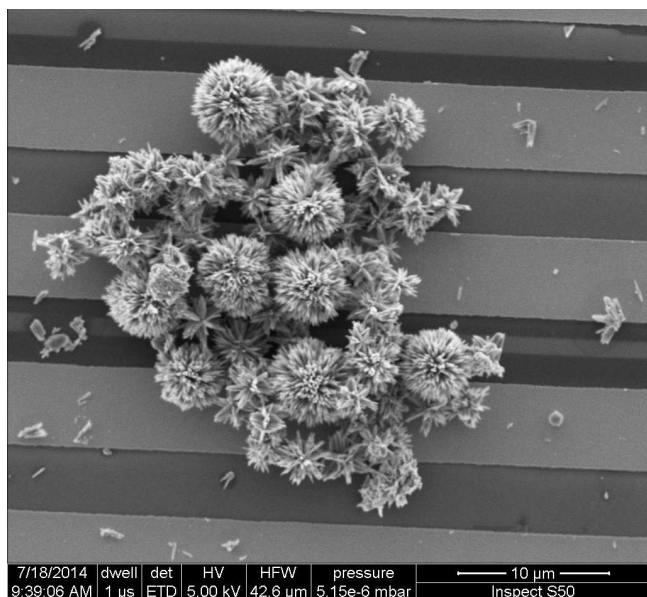


Fig. 3. SEM image of transducer with deposited ZnO nanostructures

The tested ZnO nanostructures were deposited on the transducer by applying a drop-coating method. Pulverized nanostructures were dispersed in the hexane by using an ultrasonic bath. The obtained suspension was dropped on the transducer and then allowed to dry. Excessive material, not adhering to the electrodes, was removed by means of compressed air. Ultrasonic dispersion in hexane was found to be more effective than mechanical dispersion in ethanol. Through the use of a non-polar hexane, the transducer is more evenly covered, the structure has a better adhesion to the substrate and operates more stable than a sensor tested in our previous works [14, 16].

3.3. Preparation for the measurements. In order to change the temperature of the tested structure, the silicon plate with the transducer was immobilized on the heater, which was a thick-layer resistor on an alumina substrate (Al_2O_3). The heater with transducer was immobilized on a holder with feedthroughs, which are chromium-nickel pins. For the purpose of fastening the transducer to the heater and immobilizing the heater on the holder, thermally resistant glue, which does not emit gases in elevated temperature, was used. Electric connections between the transducer electrodes and the holder pins were realized by wire-bonding technique (using the device 53XX-BDA made by F&K DELVOTEC), applying a gold wire with a diameter of $25 \mu\text{m}$. The temperature was measured by a PT100 gauge. Wires leading from this gauge and from the heater were attached to the adequate pins of the holder. Thus, the structure prepared on the holder was tightly closed by stainless steel cover equipped with quick gas connectors. The holder with its cover constitutes the measuring chamber in the form of chip, which can be put in commercially available sockets.

3.4. Details of the measurements. The effective resistance of the investigated structure was measured by means of the

device Agilent 34970a. Measurements and control of temperature were implemented by the control unit FP 93 (produced by Shimaden). The gas was dosed by a gas server provided with gas flow mass controllers. This server allows for precise mixing of gases in selected proportions and thus to control the concentration of the tested gases. This device includes also a gas humidifier and a humidity meter. The gases were supplied from cylinders containing the proper calibration gas mixtures. The measurements were taken at a stabilized structure temperature of $200.0 \pm 0.2^\circ\text{C}$ and a constant gas flow of 500 ml/min . In the experiments two different carrier gases were applied, viz. the synthetic air ($80\% \text{ N}_2 + 20\% \text{ O}_2$) and the pure nitrogen (N_2). The sensor structures were checked concerning their response to the following gases: NO_2 , H_2 , NH_3 and also to humidity changes of carrier gases. The measurement cycles comprised an alternate passing into the measuring chamber pure carrier gas (for 10 minutes) and the tested gas with a present concentration in the carrier gas (for 10 minutes).

The concentration of the tested gas in each subsequent cycle was increased. The humidity of the gas mixture was measured at room temperature ($\text{RT} = 23^\circ\text{C}$). For measurement control and data acquisition a PC, with an adequate software in the LabVIEW environment, was used. In the course of measurements of the resistance of the structure, resistance was checked in every two seconds.

4. Results and discussion

As an example of oxidizing gas, NO_2 was chosen. Concentrations of NO_2 amounted to 20, 100, 200, 400 parts per million (ppm) respectively. The results of the effect of NO_2 on the investigated ZnO structure have been gathered in Fig. 4. The resistance of the structure affected by NO_2 increases in the case of both of carrier gases (synthetic air and nitrogen). As it can be seen, the changes of the resistance are proportional to the changes of the concentration of the investigated gas. Depending on the carrier gas used, there is a difference in the dynamics of the changes of the resistance. In the air atmosphere the structure was detoxicated from NO_2 , which is proved by the drop of resistance to its basic level. In case of the nitrogen atmosphere, the structure was detoxicated much slower, because the carrier gas did not contain any oxygen (which could compete with NO_2 for adsorption centres) and, thus, no return of the resistance of the structure to its basic level can be observed (Fig. 4).

The hydrogen was investigated as the first one from the group of reducing gases. The influence of hydrogen (H_2) on the investigated structure was measured at concentrations of 1, 2, 3, and 4 %. The results of these measurements are presented in Fig. 5. The structure proved to be more sensitive to hydrogen in the air atmosphere than in the nitrogen atmosphere. Interestingly, the resistance changes under the influence of hydrogen in different carrier gases had an opposite direction. In the air atmosphere the resistance grows, whereas in the nitrogen atmosphere it decreases.

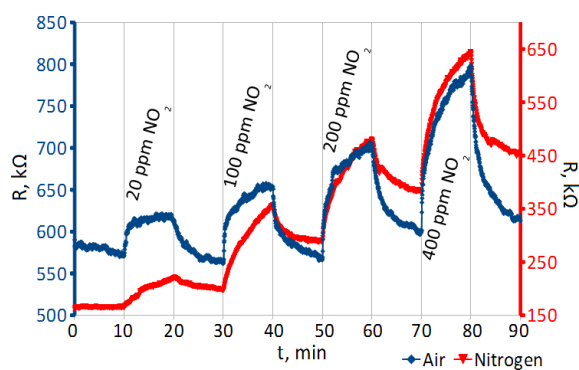


Fig. 4. The changes of the resistance of ZnO nanostructures caused by NO₂ in the air and in the nitrogen. The temperature of the structure was $T = 200^{\circ}\text{C}$, the relative humidity at 23°C in the air was $\text{RH} = 5.7\%$ and in the nitrogen it was $\text{RH} = 6.4\%$

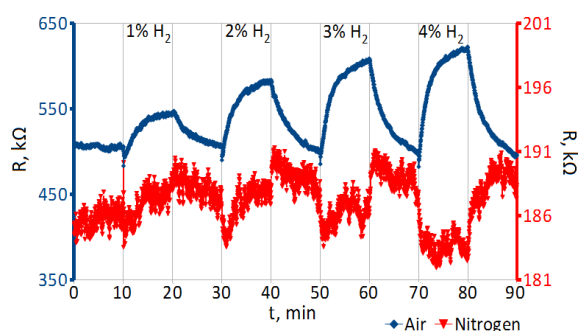


Fig. 5. The changes of the resistance of ZnO nanostructures caused by H₂ in the air and in the nitrogen. The temperature of the structure was $T = 200^{\circ}\text{C}$, the relative humidity at 23°C in the air was $\text{RH} = 5.7\%$ and in the nitrogen it was $\text{RH} = 6.4\%$

The next investigated reducing gas was NH₃. Its influence on the ZnO structure has been presented in Fig. 6. NH₃ concentration amounted to 9.5, 23.9, 47.7 and 95.4 ppm respectively. It is evident that the character of changes of the resistance differs depending on the applied carrier gas. However, it should be noted that the cylinder with a calibration mixture of NH₃ contained synthetic air. Hence, the suspicion that when the nitrogen was the carrier gas, the observed changes of the resistance were mainly due to the presence of oxygen which was passed to the measurement chamber with NH₃. The result is more competent in air conditions, where resistance of the structure decreased in the presence of NH₃. Such a result is characteristic for reducing gases.

From the viewpoint of practical applications, a very important problem is the influence of humidity on the tested structure. In order to investigate the effect of humidity on the change of the resistance an experiment was carried out, during which the dry gas and the humid gas were passed alternately into the measuring chamber. The level of humidity of the humid gas amounted to 16%, 25%, 41% and 56% respectively. The results of this experiment have been presented in Fig. 7. It can be seen that in both of these cases an increase of the humidity causes a decrease of the resistance of the structure. In an atmosphere of the synthetic air, the changes are higher than in an atmosphere of the nitrogen.

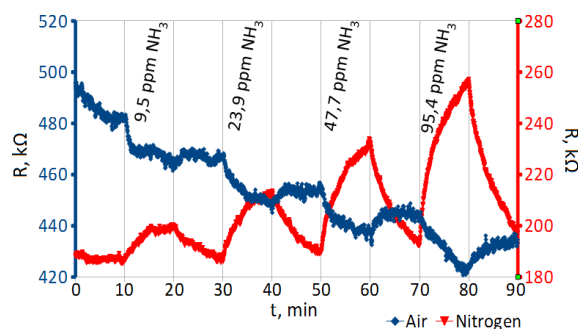


Fig. 6. The changes of the resistance of ZnO nanostructures caused by NH₃ in the air and in the nitrogen. The temperature of the structure was $T = 200^{\circ}\text{C}$, the relative humidity at 23°C in the air was $\text{RH} = 5.7\%$ and in the nitrogen it was $\text{RH} = 6.4\%$

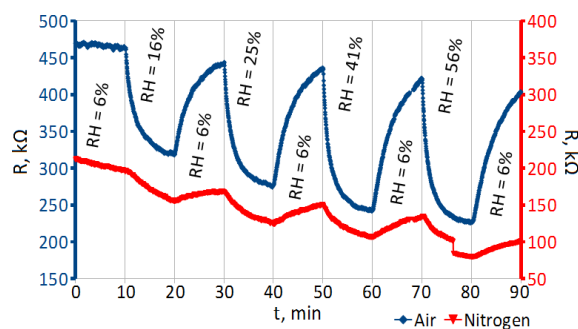


Fig. 7. The changes of the resistance of ZnO nanostructures caused by humidity changes in the air and in the nitrogen. The temperature of the structure was $T = 200^{\circ}\text{C}$, the relative humidity was measured at 23°C

In order to compare the results obtained for all examined analytes, structure responses were estimated. This response is defined as the difference between the resistance of the structure after exposure to an analyte (R_{gas}) and the resistance of structure in the carrier gas immediately before exposure to an analyte (R_0), divided by R_0 :

$$Response = \frac{\Delta R}{R_0} \cdot 100\% = \frac{R_{gas} - R_0}{R_0} \cdot 100\%.$$

Thus, the sensor response is the relative change in resistance expressed as a percentage. Structure responses for all examined analytes are illustrated in the diagram shown in Fig. 8. From the diagram it can be clearly noted that the structure reacts differently to examined analytes in different carrier gases. Reaction to NO₂ in the nitrogen atmosphere was the only case in which the structure response was not proportional to the gas concentration. This is due to the low desorption of the analyte, which causes its accumulation and, as a result, the differences in the relative response of the structure. It may be noted that the aforementioned presence of oxygen in NH₃ calibration mixture causes a response characteristic for the oxidizing gases in the nitrogen atmosphere. Therefore, the result for the NH₃ in the nitrogen is mainly the result of changes of the oxygen concentration, which hides the effect of ammonia on the structure. Positive structure response to the hydrogen (reducing gas) in the air may be surprising, but it is a typical

ZnO reaction to hydrogen at 200°C; at higher temperatures (around 300°C) reaction to hydrogen can be opposite [17].

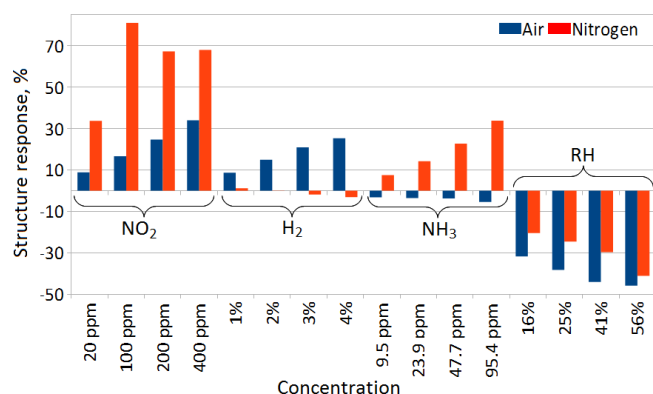


Fig. 8. Juxtaposition of the structure responses for all tested analytes in air and nitrogen atmospheres

5. Conclusions

The paper deals with the influence of NO₂, H₂, NH₃ and changes of the humidity on the resistance of ZnO nanostructures, in the form of flower-shaped agglomerates of nanotubes. The structure proved to be sensitive to all of the investigated gases. The response of the structure differed depending on the investigated gas and the carrier gas. The presence of NO₂ had the greatest influence on the change of the resistance. Thanks to various directions of resistance changes of the sensor structure, one is able to call this structure as the selective one. Changes of resistance of the structure are proportional to concentrations of the investigated gases. Thus, it becomes possible to determine the concentrations of gases on the base of the structure resistance.

In practice, the investigated flower-like ZnO nanostructures can be applied in gas sensors. The investigated structure responds best to gases in the atmosphere of the synthetic air, which is its great advantage. It seems that the structure can be applied to measure environmental gases. Unfortunately, the effect of changes of humidity on the changes of the resistance indicates that in the course of the potential sensor application, gases have to be dried and the humidity of the investigated atmosphere should be stabilized. The structure obtaining method and its deposition on the transducer are processes relatively not technologically complicated and inexpensive. Therefore, this kind of sensor would be a cheap solution. The temperature of 200°C, at which the structure displays favourable metrological properties, is relatively low, and thus the exploitation of a possible sensor would not require a high consumption of energy.

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