Influence of small concentrations of NO₂ on resistance of ZnO and TiO₂ nanostructures

M. Procek¹, T. Pustelny¹, A. Stolarczyk², E. Maciak¹

¹⁾ Department of Optoelectronics, at the Silesian University of Technology, 2 Akademicka St., 44-100 Gliwice, POLAND; ²⁾ Department of Physical Chemistry and Technology of Polymers, at the Silesian University of Technology, 9 Strzody St., 44-100 Gliwice, POLAND

Abstract

This work presents a resistance structures with sensor layers based on nanostructures elaborated on the base of titanium dioxide (TiO₂) and zinc oxide (ZnO). The structures were tested concerning their sensitivities to the effects of nitrogen dioxide in atmosphere of a synthetic air. The ZnO and TiO₂ nanostructures played the role of sensor layers. Investigations have proved that elaborated resistance structures with a ZnO and TiO₂ layers are sensitive to the presence of nitrogen dioxide (NO2) in atmosphere of a synthetic air. The resistance of the structure amounted to about 20 Ω for ZnO structures and to about 200 Ω for TiO₂ structures. The investigations confirmed that a resistance structures with ZnO and TiO₂, exposed to the effect of nitrogen dioxide in atmosphere of synthetic air changes their resistances relatively fast. This indicates that such structures might be practically applied in sensitive sensors of nitrogen dioxide ensuring a short time of response.

1. Introduction

Nowadays, a lot of attention has been devoted to monitoring the quality of air [1] and environment [2] and to the detection of explosives by detecting their vapours [3][4]. In 2005 the Kyoto Treaty came into force, concerning the constraint of the emission of some gases (including - nitrogen oxides) into the atmosphere in order to restrict the greenhouse effect [5]. For this reason to detecting gases extremely sensitive gas sensors should be applied permitting the detection and determination of small concentrations on the level of single ppm (parts per million) and even ppb (parts per billion) in the atmosphere of air. Such gas sensors are also applied in medical diagnostics [6] and chemical industry, food industry and other domains.

Very important group of toxic gases are

nitrogen oxides (No_x) and their concentration in the air ought to be controlled due to their considerable pernicious effects. NO_x are also components of the vapours of such explosives as TNT, RDX, nitroglycerin [3]. An important group of sensors which are used in the determination of the concentration and the detection of NO_x are sensors based on semiconducting metal oxides with a wide forbidden energy gap, such as TiO₂, SnO₂, WO₃, In₂O₃, ZnO, Fe₂O₃ and combination of those semiconductors [7-10]. Sensors based on these materials can be applied in various types of gas sensors, such as resistance sensors, optical sensors and gravimetric sensors.

Titanium dioxide (TiO₂) has been applied already for many years in photo- and electrochemical systems (e.g. in photo-catalysis, in solar cells [11]). Attempts have been made to apply TiO₂ for the detection of gases, including: NH₃, CO, H₂, H₂S, vapours of alcohols, humidity and others [12-17]. A well-known and widely applied material is also zinc oxide (ZnO) [18]. In recent years the application of ZnO has been widely investigated due to its piezoelectric, optoelectronic, acoustoelectronic and sensoric properties [11][16].

In the domain of gas sensors the most often resistance sensors are used, operating thanks to electrical conductance changes of the semiconductor caused by the adsorption of atoms and molecules on its surface. Sensoric properties of such of sensors can be modified by adequate doping. Gas sensors based on wide bandgap semiconductors require, however an elevated temperature of operation typical within the range of 200–400°C, or their activation by means of UV radiation [11].

In every kind of gas sensors the critical problem is the adequate choice of the sorbent – the material which permits to scan the change of signals caused by changes of the concentration of the gas in the gas mixture. The best known and widely applied sensors are thin-layer ones, obtained in various ways. Besides that also the effect of various admixtures of transition metals is known, which improves the sensitivity and selectivity of these sensors. The sensitivity of thin-layer sensors depends on the area of the sorbent surface. The metrology requires a continuous increasing of the sensitivity and response time of the sensors at simultaneously reduction of their dimensions and consumption of energy. This can be achieved by influencing properly the morphology and topology of the adsorbing element surface In recent years much interest has been devoted to nano- and microparticles forming a developed sorption structure, the surface are of which is much larger than that of thin layers. Various methods of obtaining nano-particles of TiO2 and ZnO have been developed, among then the hydrothermal method, the sol-gel method, the chemical vapour deposition (CVD) method and solution grown method [18][19].

The present paper presents the results of investigations concerning resistance sensors based on nanoparticles of ZnO and TiO_2 , viz. nanorods, nanotubes, nanobelts, as well as complex nanostructures. Further on the methods of synthesizing such nanostructures will be presented, and also the results of investigations concerning gas sensors constructed by their applications.

2. Synthesis of nanostructures

2.1. Nnanoparticles of ZnO

In technological processes the following materials were used: $Zn(NO_3)_2 \bullet 6H_2O$ (produced at POCH), NaOH (POCH), etylenodiamine EDA (Fluka) and ethanol (Aldrich). In order to obtain various morphologies two syntheses were preformed:

Synthesis A: In a teflon vessel 0.600 g NaOH and 0.440 g $Zn(NO_3)_2 \bullet 6H_2O$ were solved in 3 ml of deionized (at the ratio of Zn^{+2} ions to OH⁻ ions equal to 1:10). Then 30 ml ethanol, 5 ml deionized water and 5 ml EDA were added. The solution was placed for 30 minutes in an ultrasonic bath and next passed to an autoclave. The reaction was run at a temperature of 180°C for two hours. After the reactor on the autoclave had been cooled down, the obtained sediment was centrifuged, repeatedly rinsed in deionized

water and ethanol. The zinc oxide was dried for 12 hours under reduced pressure (15 mbar) at room temperature.



Fig.1. SEM image of ZnO from synthesis A

Synthesis B: The process was similar to that of synthesis A, but at different ratio of the base, viz. 1.2 g NaOH (ration of the ions Zn^{+2} : OH equal to 1:20) and the mixture was kept longer in the ultrasonic bath (40 minutes).



Fig.2. SEM image of ZnO from synthesis B

After the syntheses the obtained structures were depicted by means of a scanning electron microscope (SEM) SUPRA 35, produced by ZEISS. As is to be seen in Figs 1 and 2, in result of these syntheses two different morphologies of ZnO were achieved. These are, respectively, nanotubes with various dimensions (synthesis A) and flower-shaped agglomerates of nanowires (synthesis B). It has been perceived that in synthesis B the obtained structures are more homogeneous, i.e. agglomerates with a diameter of several μ m. The effect of synthesis A is a mixture of nanotubes with various dimensions and granules with a diameter of several score to several hundreds nm.

2.2 Nanoparticles of TiO2

Nanofibres of TiO_2 were obtained by means of the hydrothermal method [17]. For this

purpose the following materials were used: anataze (porduced by Sigma Aldrich), KOH (POCH), ethanol (POCH) and deionized water.



Fig.3. SEM image of TiO₂ calcined in 350°C





Into a teflon vessel 0.5 g anatase and 20 ml of 10-mole sodium hydroxide solution were introduced. The suspension was stirred for 10 minutes at room temperature and then passes into the autoclave. The reaction was run for 72 h at temperature of 150°C, stirring the mixture all the time. After its removal from the autoclave the sediment was decanted, repeatable rinsed with deionized water and next with 0.1 mol HCl solutions until an acid reaction of the filtrate was achieved. The residual hydrochloric acid was rinsed in deionized water until a chemically inert pH was reached. The resulting titanium acid IV was passed into a quartz crucible, preliminarily dried for one hour at a temperature of 70°C. Then the titanium acid was divided into three batches and again subjected for one hour to thermal calcinations treatment at various temperature viz. 350°C and 450°C.

Similarly as in the case of ZnO, the obtained structures were depicted by means of SEM and presented in Figs 3 and 4. These images indicate that the temperature of calcination influences the length and homogeneity of the temperature of calcination influences the length and homogeneity of the obtained fibers.

3. Sensor performance

Transducer system is a four comb electrode array with period of 10 µm. It was made of gold in photolithograpfic lift-off process on glass substrate with dimensions 20 x 30 mm. The way of constructing a similar transducer, though made on silicon substrate, and its characteristics have been described in [20]. The sorbants were deposited by drop-coating method. The previously prepared nanoparticles were dispersed in pure ethanol (POCH) stirring it for 15 minutes using for this purpose a magnetic mixer until a homogeneous suspension was achieved. In the process of depositing the sorbents mask was used, so that only the required areas were covered. Immediately after the dispersion the prepared suspension were passed to the proper area of the resist. The whole was stirred for 30 minutes in the furnace with a temperature of 70°C to let the ethanol completely evaporate. Then the resist was carefully removed. A ready system with four sensors is to be seen in Fig. 5., in which on the channels CH1-CH4: CH1-TiO₂ calcined at 350°C; CH2-TiO₂ calcined at 450°C; CH3-ZnO A, and CH4-ZnO B have been plotted.



Fig. 5. Ready sensor made from nanoparticles on cobe electrode. Channels: CH1 – TiO_2 350; CH2 – TiO_2 450; CH3 – ZnO A; CH4 – ZnO B

The use of four-channel sensor matrix ensures simultaneous testing of four materials under identical conditions to ensure comparability of results.

4. Details of measurements

The sensitivity of elaborated structures to the effect of NO_2 in synthetic was tested on the teststand which was previously described in work [20]. In all these measurements the atmosphere was synthetic air (20% O_2 and 80% N_2). The tests were run at a continues flow of synthetic air amounting to 500ml/min.

The resistance of the respective transducer

with sensor layer was measured by means of the appliance AGILENT 34970, with an accuracy of \pm 0.5·10⁻³ Ω . It is to be admitted that the obtained structures are characterized a surprising low resistance of merely 15-200 Ω . It is entire resistance concerning both the sensor structure and the thin layer of gold, of which the transducers were made. The measurements were taken at a stabilized temperature of the substrate, rate of 115°C in order to eliminate the excess humidity from the sorptive surface and to aid the resorption of NO₂. The resistance of the transducers measured various were at concentrations of NO_2 within the range of 0-400 ppm. The cycle of measurements comprised an alternative introduction of pure synthetic air (by 30 minutes) and next a gaseous mixture concerning NO_2 in synthetic air (also by 30 minutes) into the test chamber, increasing successively the concentration of NO2. The measurements were performed at two different values of humidity of air, viz. RH = 5% and RH = 50%.



Fig.6. Sensor response on NO₂ influence, T=115°C, humidity RH=5%. for: a) ZnO where black and grey plots represents data from synthesis A and B respectively; b) TiO₂ where black and gray plots represents data from calcination in 350°C and 450°C respectively

5. Influence of NO₂ on structures

As to be expected, the resistance of

semiconductor sensors increases when the synthetic air contains NO2 (Figs 6 and 7). In reaction with the surface molecules this gas is subjected to chemisorption, which affects the number of charge carriers in the area adjacent to the surface. The growing resistance informs us that this sensor layer is getting impoverished in the amount of electrons, in resent of which the adsorbed gas molecules are forming traps localized in the forbidden band of semiconductor. As has already been mentioned, all the obtained structures display a surprising poor resistance; probably there dominates a mechanism of conduction through the surface states. The resistance of the produced materials is contained within the range from about 15 to about 200 Ω on the distance between electrodes rate of 10 um.

5.1. ZnO structures

Basing on the results concerning ZnO structures (Fig. 6a) in a dry mixture (RH \approx 5%), it is seen that in spite of considerably differing morphologies of the structures, the values of their resistance are approximately the same. It is, however, evident that various morphologies differ in their sensitivity to NO₂.

In the case of ZnO from the synthesis B (Fig. 6a - grey line) a reaction can be seen (perceptible due to the different level of noise) already at a concentration of 40 ppm NO₂. In the case of ZnO – synthesis B (Fig. 6a – black line) an increase of the resistance is to be observed only at a concentration of 100 ppm (not earlier). In the case of ZnO impregnates rather slowly, lagging even in 30 minutes. But, instead, a rapid drop of the resistance is to be observed after letting in fresh air. It should be mentioned that values of changes of the resistance depends in the case of ZnO structures on the concentration of NO₂, which implies the possibility of scaling such a sensor and determining the actual concentrations. The sensor operates worse at a higher content of steam in the mixture amounting to RH $\approx 50\%$ (Fig. 7a). Then we witness a reduction of its sensitivity and encounter problems connected with its proper behavior. This becomes particularly evident in the case of ZnO synthesis B (Fig. 7a - grey line), where resistance juices occur at concentrations of about 40 ppm and 200 ppm, probably due to the sedimentation of moisture in the pores of the material, which leads to a reduction of the resistance and changes in the impedance of the contacts. In the case of

ZnO – synthesis A (Fig. 7a – black line) the threshold of detectability drops by a half in comparison with a dry mixture.



5.2. TiO₂ structures

The results concerning TiO_2 structures (Fig. 6b and 7b) show that in spite of their similar morphologies they display a different resistance depending on the temperature of calcination. All the results obtained in the case of TiO_2 display a sufficient sensitivity to NO_2 already at a concentration of 40 ppm and justify the conclusion that the threshold of detection is below the tested range of concentrations. nanoparticles of TiO_2 react promptly to the occurrence of NO_2 , and changes of the resistance differ in the entire considerably from the level of noise.

 NO_2 is desorbed slowly, so that the sensor does not mange to desorb it entirely in the course of 30 minutes, which results in the fact that the resistance of the structure displays a slight tendency to increase during the time in which it is being measured (including of the characteristics). The sensitivity sensors based on TiO₂ layers is not interrogated by an elevated humidity (Fig. 7b). The response of the sensor in the case of humid mixture is even better than in the case of a dry one. When the mixture is dry, the values of changes in the resistance of the sensors depend on the concentration of NO_2 . Such a dependence has not been observed in the case of dry mixtures, in which the sensor can be scaled roughly for the purpose of determining adequately the concentration of NO_2 . A higher resistance and greater changes of the resistance can be observed in the case of nanorods and nanobelts of TiO₂ calcined at a temperature of 350° C.

6. Conclusions

The present paper proves that sensor structures of ZnO and TiO2 react to slight concentrations of NO₂ already at 115°C. Such a low temperature contributes to a reduced consumption of energy by the sensors. The results of investigations indicate that TiO₂ is more sensitive to nitrogen dioxide both in a dry and a humid atmosphere. The sensoric properties of ZnO deteriorate when the gas mixture is moist, and the threshold of detection is twice lower. Humidity does not affect so much the sensitivity and threshold of detection of TiO₂, but do not allow to determine concretely the concentration of NO_2 . The influence of humidity on the operation of the sensors is a general problem in the technology of sensors. Attempts are being made to restrict this effect by applying dehumidifiers. The rate of the response of TiO₂ to the occurrence of NO_2 is shorter than that of ZnO. The latter is, however, characterized by a faster resorption. In the case of TiO_2 nanostructures the threshold of the detection of NO_2 is below the level of 40 ppm and may even lie lower the only a few ppm.

ZnO structures are characterized by a rapid desorption of NO_2 and may be applied for a quick disappearance detection of this gas. For this reason, matrix of sensors consisting of TiO₂ and ZnO permits to determine in a relatively short time both the moments of the occurrence and the fading of NO₂ in the gas mixture.

In the paper it has also been shown that the sensitivity of the sensors depended to a large extent on the morphology of the surface, which is particularly evident when the morphologies of ZnO differ considerably from each other.

It is to be stressed that the presented structures were pure semiconducting materials without any admixtures. By applying admixtures the sensoric properties can be still improved.

Acknowledgements

The work was partially sponsored by the National Centre for Scientific Researches and Development NCBiR within the grant OR00017912.

The participation of M.Sc. Marcin Procek was sponsored by means of the European Social Fund, comprised in the Project "SWIFT" POKL. 08.02.01-24-005/10.

Bibliography

- 1. S. Zampolli, I. Elmi, J. Stürmann, S. Nicoletti, L. Dori, G.C. Cardinali, *Selectivity* enhancement of metal oxide gas sensors using a micromachined gas chromatographic column, Sensors and Actuators, B, 105, 400 (2005).
- 2. D.D. Lee, D.K. Lee, *Environmental gas* sensors, IEEE Sensors Journal, 1, 214, (2001).
- D. L. Wang, A. T. Chen, Q. F. Zhang, G. Z. Cao, *Room-Temperature Chemiresistive Effect of TiO₂ Nanowires to Nitroaromatic and Nitroamine Explosives*, IEEE Sensors Journal, 11(6), 1352 (2011).
- 4. A. A. Tomchenko, G. P. Harmer, B. T. Marquis, *Detection of chemical warfare agents using nanostructured metal oxide sensors*, Sensors and Actuators, B, 108, 41 (2005).
- 5. http://en.wikipedia.org/wiki/Kyoto_Pr otocol (present: 29.08.2012r.)
- 6. S. Ehrmann, J. Jungst, J. Goschnick, D. Everhard, *Application of a gas sensor microarray to human breath analysis*, Sensors and Actuators, B: Chemical, 65, 247 (2000).
- Y.X. Yu, D.S. Xu, "Single-crystalline TiO₂ nanorods: Highly active and easily recycled photocatalysts", *Applied Catalysis B: Environmental*, 73, 166 (2007).
- W. Zeng, T.M. Liu, Gas-sensing properties of SnO₂-TiO₂-based sensor for volatile organic compound gas and its sensing mechanism, Physica B: Cond. Mat, 405(5), 1345 (2010).
- L. You, Y.F. Sun, J. Ma, Y. Guan, Highly sensitive NO₂ sensor based on square-like tungsten oxide prepared with hydrothermal treatment, Sensors and Actuators B, 157, 401 (2011).
- 10. W.W. Guo, T.M. Liu, L. Huang, Gassensing property improvement of ZnO by hierarchical flower-like architectures, Materials Letters, 65, 3384 (2011).

- H. Chen, Y. Liu, C. Xie, J. Wu, D. Zeng, Y. Liao, A comparative study on UV light activated porous TiO₂ and ZnO film sensors or gas sensin at room temperature, Ceramics International, 38, 503 (2012).
- J. Gong, Y.H. Li, Z.H. Hu, Z. Zhou, *Ultrasensitive NH₃ Gas Sensor from Polyaniline Nanograin Enchased TiO₂ Fibers*, Journal of Physical Chemistry C, 114, 9970–9974 (2010).
- 13. G.S. Devi, T. Hyodo, Y. Shimizu, Synthesis of mesoporous TiO₂-based powders and their gas-sensing properties, Sensors and Actuators, B: Chemical, 87, 122 (2002).
- C.M. Carney, S.H. Yoo, S.A. Akbar, *TiO₂-SnO₂ nanostructures and their H₂ sensing behavior*, Sensors and Actuators, B, 29, 108 (2005).
- 15. E.D. Gaspera, M. Guglielmi, S. Agnoli, *Au nanoparticles in nanocrystalline TiO*₂-*nio films for SPR-based, selective H*₂S gas sensing, Chemistry of Materials, 22, 3407–3417 (2010).
- D. Barreca, G. Carraro, E. Comini, Novel synthesis and gas sensing performances of CuO-TiO₂ nanocomposites functionalized with Au nanoparticles, Journal of Physical Chemistry C, 115, 10510 (2011).
- L. Gu, K. Zheng, Y. Zhou, J. Li, X. Mo, G.R. Patzke, G. Chen, *Humidity sensors based* on ZnO/TiO₂ core/shell nanorod arrays with enhanced sensitivity, Sensors and Actuators, B, 159 (1), 1-7 (2011).
- T. Pisarkiewicz, T. Kenig, A. Rydosz, W. Maziarz, Solution growth of ZnO sub-micro rods enhanced by electric field, Bulletin of the Polish Academy of Sciences: T. S., 59, 4, 425 (2011).
- L. Huang, T. Liu, H. Zhang, W. Guo, W. Zeng, Hydrothermal synthesis of different TiO₂ nanostructures: structure, growth and gas sensor properties, Journal of Materials Science: Materials in Electronics, 1-6 (2012).
- M. Urbańczyk, E. Maciak, K. Gut, T. Pustelny, W. Jakubik, *Layered thin film nanostructures of Pd/WO_{3-x} as resistance gas sensors*, Bulletin of the Polish Academy of Sciences: T. S., 59, 4, 401 (2011).

Main author:



MSc. Macin Procek Silesian University of Technology ul. Akademicka 2 44-100 Glwice tel. 32 237 12 63

email: Marcin.Procek@polsl.pl