Influence of small concentrations of NO$_2$ on resistance of ZnO and TiO$_2$ nanostructures

M. Procek$^1$, T. Pustelny$^1$, A. Stolarczyk$^2$, E. Maciak$^1$

$^1$ 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 (TiO$_2$) 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 TiO$_2$ nanostructures played the role of sensor layers. Investigations have proved that elaborated resistance structures with a ZnO and TiO$_2$ layers are sensitive to the presence of nitrogen dioxide (NO$_2$) in atmosphere of a synthetic air. The resistance of the structure amounted to about 20 $\Omega$ for ZnO structures and to about 200 $\Omega$ for TiO$_2$ structures. The investigations confirmed that a resistance structures with ZnO and TiO$_2$, 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]. 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 TiO$_2$, SnO$_2$, WO$_3$, In$_2$O$_3$, ZnO, Fe$_2$O$_3$ 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 (TiO$_2$) 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 TiO$_2$ for the detection of gases, including: NH$_3$, CO, H$_2$, H$_2$S, 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 area of which is much larger than that of thin layers. Various methods of obtaining nano-particles of TiO$_2$ 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. Nanoparticles of ZnO

In technological processes the following materials were used: Zn(NO$_3$)$_2$•6H$_2$O (produced at POCH), NaOH (POCH), etylenediamine 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$_3$)$_2$•6H$_2$O were solved in 3 ml of 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 μm. 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 TiO$_2$

Nanofibres of TiO$_2$ were obtained by means of the hydrothermal method [17]. For this
purpose the following materials were used: anatase (produced by Sigma Aldrich), KOH (POCH), ethanol (POCH) and deionized water.

3. Sensor performance

Transducer system is a four comb electrode array with period of 10 μm. It was made of gold in photolithographic 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 sorbents 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-TiO$_2$ calcined at 350°C; CH2-TiO$_2$ calcined at 450°C; CH3-ZnO A, and CH4-ZnO B have been plotted.

4. Details of measurements

The sensitivity of elaborated structures to the effect of NO$_2$ in synthetic was tested on the test-stand 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 ± 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 were measured at various concentrations of NO₂ 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 NO₂ 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%.

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 μm.

5.1. ZnO structures

Basing on the results concerning ZnO structures (Fig. 6a) in a dry mixture (RH ≈ 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 ≈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.

Fig. 7. Sensor response on NO\textsubscript{2} influence, T=115°C, humidity RH=50%. for: a) ZnO where black and gray plots represents data from synthesis A and B respectively; b) TiO\textsubscript{2} where black and gray plots represents data from calcination in 350°C and 450°C respectively

5.2. TiO\textsubscript{2} structures

The results concerning TiO\textsubscript{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\textsubscript{2} display a sufficient sensitivity to NO\textsubscript{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\textsubscript{2} react promptly to the occurrence of NO\textsubscript{2}, and changes of the resistance differ in the entire considerably from the level of noise.

NO\textsubscript{2} is desorbed slowly, so that the sensor does not manage 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 TiO\textsubscript{2} 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\textsubscript{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\textsubscript{2}. A higher resistance and greater changes of the resistance can be observed in the case of nanorods and nanobelts of TiO\textsubscript{2} calcined at a temperature of 350°C.

6. Conclusions

The present paper proves that sensor structures of ZnO and TiO\textsubscript{2} react to slight concentrations of NO\textsubscript{2} already at 115°C. Such a low temperature contributes to a reduced consumption of energy by the sensors. The results of investigations indicate that TiO\textsubscript{2} 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 TiO\textsubscript{2}, but do not allow to determine concretely the concentration of NO\textsubscript{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 TiO\textsubscript{2} to the occurrence of NO\textsubscript{2} is shorter than that of ZnO. The latter is, however, characterized by a faster resorption. In the case of TiO\textsubscript{2} nanostructures the threshold of the detection of NO\textsubscript{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\textsubscript{2} and may be applied for a quick disappearance detection of this gas. For this reason, matrix of sensors consisting of TiO\textsubscript{2} and ZnO permits to determine in a relatively short time both the moments of the occurrence and the fading of NO\textsubscript{2} 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.

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Main author:

MSc. Macin Procek
Silesian University of Technology
ul. Akademicka 2
44-100 Gliwice
tel. 32 237 12 63
e-mail: Marcin.Procek@polsl.pl