MANUFACTURING AND INVESTIGATIONS OF HYDROGEN PEROXIDE VAPORS SENSOR

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1. Introduction

Hydrogen peroxide (H_2O_2) is subsumed under the category of matters that are dangerous for man with certain maximum permissible concentration. Therefore, the development of sensors for determination of the H_2O_2 concentration in the environment is important and attracts interest of chemists, physicians, industrial engineers, etc. The H_2O_2 stable sensors can be used in analytical chemistry, in various fields of the industry (food, textile, pharmaceutical), for an environmental control, in clinical diagnostic for prompt and reliable specification of diagnoses of different diseases and check of a course of treatment.

Several techniques have been developed for a reliable and sensitive detection of H_2O_2, such as chemiluminesce, fluorimetry, liquid chromatography, spectrophotometry and fluorescence. These techniques are complex, expensive and time consuming. Now the electrochemical sensors are wide used [1-6]. A large range of materials such as ferric hexacyanoferrate (Prussian blue) and other metal hexacyanoferrates, redox proteins, metallophthalocyanines and metalloporphyrins, transition metals and metal oxides have been applied in these sensors. Advantages of these sensors are simplicity of manufacturing, good response and a capability of control in a real time. In recent years, nanotechnology progress is promoted advance in the field of manufacturing of the H_2O_2 electrochemical sensors. For example, carbon nanotubes and graphene can be used either as substrates with high specific area for catalytic materials or as electrocatalysts by themselves. Note that process of chemical decontamination can be carried out in two different ways: the first is the wet approach using water or any other solution of H_2O_2 (certain concentration) and the second one is the dry method using H_2O_2 in vapor phase [7]. The correct selection of the H_2O_2 concentration during the sterilization of the equipment technological surfaces and also control of the H_2O_2 content in air after completion of disinfection cycle are very important. Therefore, the development and manufacturing of stable and reproducible sensors sensitive to H_2O_2 vapors are extremely required. The H_2O_2 vapor phase checking is also crucially significant in connection with counterterrorism efforts. The most used method is based on the determination of the concentration of H_2O_2 vapors after cooling down and being absorbed in the water. An amperometric sensor for detection of H_2O_2 vapors made of an agarose-coated Prussian-blue modified thick-film screen-printed carbon-electrode transducer was investigated [8]. Near infrared spectrophotometry was used for the monitoring of the concentration of H_2O_2 vapors in the course of sterilization [9]. It was reported about manufacturing of organic core/sheath nanowires with waveguiding core and chemiluminogenic cladding and manufacturing of organic single-wire optical sensor for H_2O_2 vapors [10]. The chemiresistive films made from organic p-type semiconductors phthalocyanines metalized with elements of p-, d-, and f-blocks were also sensitive to H_2O_2 vapors [11].

The aim of the present paper is development of technology, manufacturing and investigations of solid-state hydrogen peroxide vapors sensors made from semiconductor metal oxide nanostructured ZnO<La> films.

2. Experimental

Ceramic targets made of metal oxide ZnO doped with 1 at.% La were synthesized by the method of solid-phase reaction in the air in the programmable furnace Nabertherm, HT O4/16 with the

controller C 42. The following program of annealing for the compact samples of ZnO<La> was chosen: rise of temperature from room temperature up to 1300 °C for three hours, soaking at this temperature during four hours, further decrease in temperature for three hours prior to room temperature. Then, the synthesized compositions were subjected to mechanical treatment in the air in order to eliminate surface defects. Thus, smooth parallel targets with a diameter ~ 40 mm and thickness ~ 2 mm were manufactured.

Prepared semiconductor ZnO<La> targets had sufficient conductance and were used for deposition of films using the high-frequency magnetron sputtering method. An alumina or Multi-Sensor-Platforms (purchased from TESLA BLATNÁ, Czech Republic) were used as substrate for nanosize films. In last case, when the Multi-Sensor-Platforms were used as substrates, the chip can be kept at constant temperature using heat resistance. The platform integrates a temperature sensor (Pt 1000), a heater and interdigitated electrode structures in platinum thin film on a ceramic substrate. The heater and sensor are covered with an insulating glass layer. Gas sensitive layer made of ZnO doped with 1 at.% La was deposited onto the non-passivated electrode structures. This way the Multi-Sensor-Platform is converted into gas sensors. The following working conditions of the high-frequency magnetron sputtering were chosen: the power of the magnetron generator unit was 60 W; the substrate temperature during sputtering was 200 °C; the sputtering process was carried out during 15 and 30 minutes for preparing films with different thickness. The sensing device was completed through the ion-beam sputtering deposition of palladium catalytic particles (the deposition time was 3 seconds). The interdigited titanium contacts were deposited (the deposition time was 50 minutes) by ion beam sputtering method on the surface of the sensing layers when the alumina substrate was used. Further annealing of the manufactured structures in the air was carried out at temperature 250 °C to obtain homogeneous films and eliminate mechanical stress. The thicknesses of the deposited doped metal oxide films were measured by Ambios XP-1 profilometer. Morphology and chemical composition of the deposited ZnO<La> films were studied by scanning electron microscopy (SEM) using Mira 3 LMH (Tescan) and energy-dispersive X-ray spectroscopy using Quantax 200 with XFlash 6|10 detector (Bruker) with resolution of 127 eV, respectively. Response of the prepared sensors made of doped metal oxide films under the influence of H_2O_2 vapors was measured in YSU using a home-made system [12]. Sensors were placed in a hermetic chamber. A certain quantity of H_2O_2 water solution was placed in the chamber to reach a corresponding concentration of H_2O_2 vapors. Measurements of the manufactured sensors response (the sensor resistance changes under the H_2O_2 vapors influence) were carried out at different concentrations of H_2O_2 vapors. The sensor on alumina substrate is put on the heater which allows raising temperature of the sensor working body up to 350 °C. A platinum heater on a front side of the sensor on Multi-Sensor-Platforms ensures a necessary temperature of the work body. All measurements were carried out at sensor applied voltage 0.5 V.

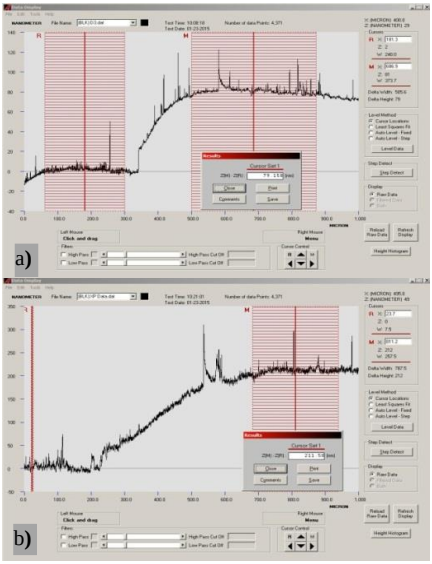

Fig. 1. The thicknesses measurement resultes for ZnO doped with 1 at.% La films with sputtering duration of 15 (a) and 30 minutes (b).

Investigations of the sensitivity of the prepared sensors to H_2O_2 vapors with concentration below than 100 ppm were carried out at University of Chemistry and Technology (Prague). In particular, the temperature dependence of sensitivity to 100 ppm H_2O_2 vapors was investigated. Measurements of the sensitivity of the ZnO<La> sensors to 10 ppm H_2O_2 vapors were carried out by the following way. Firstly, an atmosphere containing 10 ppm of H_2O_2 vapors was prepared in a laboratory model of an isolator. This H_2O_2 vapors concentration decreased by spontaneous decomposition of H_2O_2. When a reference device (Dräger Sensor® H_2O_2 HC) could not detect any H_2O_2 vapors, the sensor was inserted into the model isolator. Then, sensor responded immediately. When the maximum response was reached, the sensor was taken out into an atmosphere without any traces of H_2O_2 vapors. This process was repeated three times.

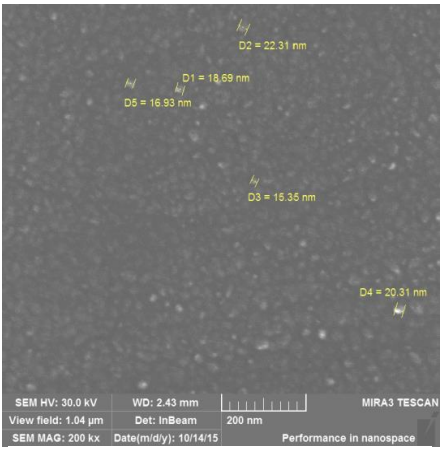

Fig. 2. SEM images for ZnO doped with 1 at.% La films.

3. Results and discussion

The thickness of the ZnO doped with 1 at.% La films prepared during 15 and 30 minutes was equals 80 nm and 210 nm, respectively (Fig. 1). Results of the study of morphology for the deposited doped metal oxide films are presented on the Fig. 2. The average size of nanoparticles was equal 18.7 nm. The sensor manufactured by us is resistive, i.e., its operation is grounded on changes in the resistance of gas sensitive semiconductor layer under the influence of H_2O_2 vapors due to an exchange of charges between molecules of the semiconductor film and adsorbed H_2O_2 vapors. A variation of the sensor resistance takes place as a result of such exchange of charges. This variation of resistance was fixed as sensor response.

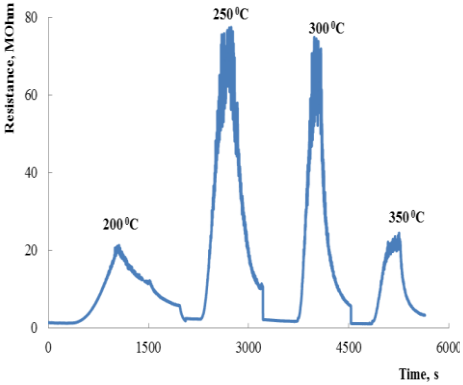

Fig. 3. The resistance variation of the ZnO<La> (80nm) sensor under the influence 1800 ppm of H_2O_2 vapors at different work body temperatures.

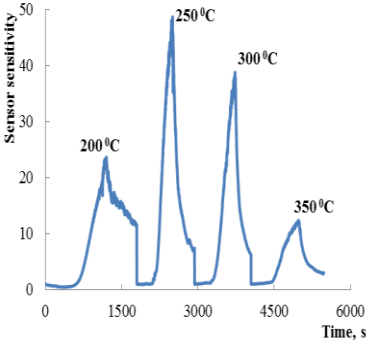

Fig. 4. The ZnO<La> (210 nm) sensor sensitivity to 1800 ppm of H_2O_2 vapors at different work body temperatures.

The sensor resistance variation under the influence of H_2O_2 vapors at invariable temperature of the work body was measured using a special home-made computer program. Results of such measurements are presented on the Fig. 3 for ZnO<La> (80 nm) sensors. The response and recovery times were determined as the time required for reaching the 90% resistance changes from the corresponding steady-state value of each signal and were equals on the average 6 and 10 minutes respectively at the pointed temperatures. The sensor sensitivity was determined as the ratio R_{vapors}/R_{air}, where R_{vapors} is the sensor resistance in the presence of H_2O_2 vapors in the air and R_{air} is the sensor resistance in the air without H_2O_2 vapors. The sensitivity of ZnO<La> (210 nm) sensor at different work body temperatures is presented on the Fig. 4. Note that the resistance of prepared sensors has changed in order of magnitude under influence of H_2O_2 vapors already at operation temperature 100 °C. However in such temperature a long time was needed for recovery of sensors parameters. Pulsed increasing of work body temperature is needed for decreasing of the recovery time of investigated sensors.

The sensitivity of the prepared sensors is decreased, when the working body temperature excesses some certain value (about 250 °C). An amount of matter, adsorbed on a surface and generally held by Van der Waals forces (physical adsorption), is decreased with the increase of temperature. More intensive exchange of electrons between the absorber and the absorbed matter takes place when the stronger chemical nature bond is established between them, originates at capping of electronic shells of both adsorbent and adsorbate atoms. Amount of chemisorbed matters increases with the temperature growth. Desorption prevails over the adsorption when a temperature is increased above certain value and, therefore, the sensor sensitivity is decreased. As it has already been noticed, H_2O_2 concerns to materials dangerous for man with certain maximum permissible concentration. The permissible limit of exposure 1.0 ppm has established by Occupational Safety and Health Administration (OSHA, USA) [10, 11]. It is immediately dangerous for life and health when its concentration reaches 75 ppm [13]. Therefore, the investigations of the prepared sensors sensitivity to H_2O_2 vapors with concentration below than 100 ppm were also carried out at University of Chemistry and Technology (Prague). The results of measurements of response to 100 ppm of H_2O_2 vapors at invariable temperature of the work body are presented on the Fig. 5 for the ZnO<La> sensors preparing on the Multi-Sensor-Platforms substrates. Results of these measurements show, that the structure made of ZnO<La> exhibits a response to 100 ppm of H_2O_2 vapors at the operating temperature starting at 100 °C. The ZnO<La> sensor exhibited enough response (sensitivity was equal ~ 2) to 100 ppm of H_2O_2 vapors at the operating temperature 200 °C. The investigations of the ZnO<La> sensors sensitivity to very low concentrations (0-10 ppm) of H_2O_2 vapors were carried out. The sensitivity to 10 ppm of H_2O_2 vapors was equal ~ 2 for the ZnO<La> sensors at the work body temperature 220 °C. Note that the DrägerSensor® H_2O_2 HC reference device was not sensitive to 10 ppm of H_2O_2 vapors (Fig. 6). The results of investigations of the sensitivity at different concentrations of H_2O_2 vapors are presented on the

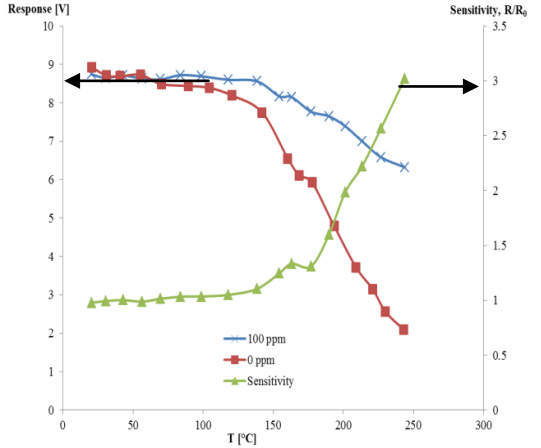

Fig. 5. The temperature dependence of sensitivity to 100 ppm H_2O_2 vapors for ZnO<La> sensor.

Fig. 7 for prepared made of ZnO<La> sensors. As can see, this dependence of sensors sensitivity on H_2O_2 vapors concentration has a linear character and can be used for determination of H_2O_2 vapors concentration.

3. Conclusions

The technology for the manufacturing of semiconductor sensors made from ZnO doped with 1 at.% La nanostructured films was developed. Sensitive ZnO<La> layers were deposited onto alumina substrate and the Multi-Sensor-Platforms using the high-frequency magnetron sputtering method. Thicknesses of deposited doped metal oxide films were measured and its morphology was investigated. The thicknesses of the deposited ZnO<La> films were equals 80 nm and 210 nm. The aaverage size of nanoparticles was equals 18.7 nm for both structures. Specimens detecting H_2O_2 vapors were manufactured and investigated. The sensitivity of the prepared sensors was measured at different temperatures of the sensor work body and concentrations of H_2O_2 vapors. It was found that La-doped ZnO sensors exhibit a good response to H_2O_2 vapors at the operating temperature starting at 100 °C. Sensors made of ZnO<La> were sufficient sensitive to 10 ppm of H_2O_2 vapors at the work body temperature 220 °C. It was established that the dependencies of the sensitivity on H_2O_2 vapors concentration at the operation temperature 220 °C have a linear character for prepared structured and can be used for determination of H_2O_2 vapors concentration. Our future work will be directed on the long-time stabilization of sensors parameters and the improvements of such characteristics as operation speed and recovery time.

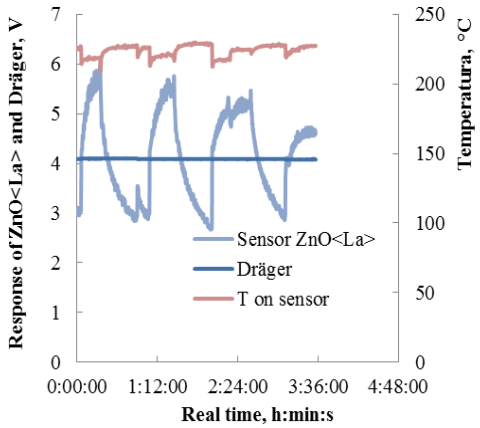

Fig. 6. ZnO<La> sensors response to 10 ppm of H_2O_2 vapors, work body temperature 220°C.

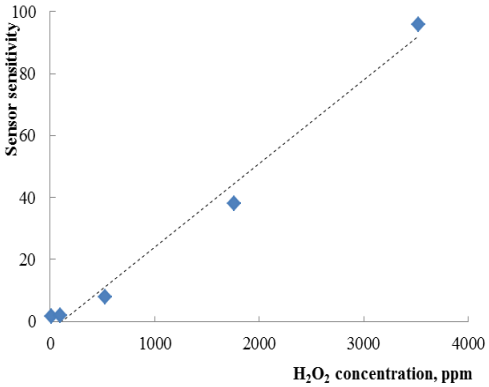

Fig. 7. The sensitivity dependence on H_2O_2 vapors concentration at operating temperature 220 °C.

Acknowledgments: This investigation was supported by the Swiss National Science Foundation FNSNF within the framework of the SCOPES DecoComp project. Authors express gratitude to Dr. V. Kuzanyan for help in the measurements of thickness of our samples.

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