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SnO_2 and ZnO Detectors of Hydrogen Peroxide Vapors

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Abstract:
Thin-film hydrogen peroxide vapors sensors made from SnO_2<Co> and ZnO<La> were manufactured by the high-frequency magnetron sputtering method. Thicknesses of deposited doped metal oxide films were measured and its morphology was investigated. Response of the prepared sensors was measured at different concentrations of hydrogen peroxide vapors and temperatures of the sensor work body. It was found that both Co-doped SnO_2 and La-doped ZnO sensors exhibit a sufficient sensitivity to 10 ppm of hydrogen peroxide vapors at the operating temperature 200 °C and 220 °C, respectively. It was established that the dependencies of the sensitivity on hydrogen peroxide vapors concentration at the work body temperature 150 °C have a linear character for prepared structures and can be used for determination of hydrogen peroxide vapors concentration.

Key words: sensor, hydrogen peroxide vapors, semiconductor, thin film, metal oxide.

Introduction

Hydrogen peroxide (H_2O_2) is used in such fields as medicine, pharmacology, food and textile industry due to a wide spectrum of its antibacterial properties, low toxicity, ecological purity (the residue of H_2O_2 decompose on neutral water and oxygen). However, insufficiently, pure H_2O_2 at large concentrations is explosive under certain conditions (for example, in the presence of transition metals). Therefore, concentrated solutions of H_2O_2 can cause burns in the case of the contact with skin, mucous membranes and respiratory tract. H_2O_2 is subsumed under the category of matters, that are dangerous for man with certain maximum permissible concentration. Therefore, the correct selection of the H_2O_2 concentration during the sterilization of equipment technological surfaces and also control of the H_2O_2 content in air after completion of disinfection cycle are very important. From this point of view, 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 determination 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 employed are applied in these sensors. Advantage of these sensors is a simplicity of their manufacturing, good response, 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 H_2O_2 (certain concentration) and the second one is the dry method using H_2O_2 in vapor phase [7]. Therefore, the development and manufacturing of stable and reproducible sensors sensitive to hydrogen peroxide vapors (HPV) are extremely required. The HPV phase checking is also crucially significant in connection with counterterrorism efforts.

The most used method is based on the determination of the concentration of HPV after cooling down and being absorbed in water. An amperometric sensor for detection of HPV made of an agarose-coated Prussian-blue modified thick-film screen-printed carbon-electrode transducer was investigated [8]. Near infrared spectrophotometry was used for monitoring of concentration of HPV 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 HPV [10]. The chemiresistive films made from organic p-type semiconductors phthalocyanines metalized with elements of p-, d-, and f-blocks were also sensitive to HPV [11].

The aim of the present paper is development of technology, manufacturing and investigations of solid-state HPV sensors made from semiconductor metal oxide nanostructured films.

Material and Measurements Methods

Ceramic targets made from metal oxide SnO_2 doped with 2 at.% Co and ZnO doped with 1 at.% La were synthesized by the method of solid-phase reaction in air in a programmable furnace Nabertherm, HT O4/16 with a controller C 42. The annealing of the compacted samples SnO_2<Co> was carried out at 500 °C (five hours), 700 °C (five hours), 1000 °C (five hours) and 1100 °C (five hours) consecutive. The following program of annealing for the compact samples of ZnO<La> was choosen: rise of temperature from room temperature up to 1300 °C for three hours, the soaking at this temperature during four hours, the further decrease in temperature for three hours prior to room temperature. Then, the synthesized compositions were subjected to mechanical treatment in air in order to eliminate surface defects. Thus, smooth, parallel targets with a diameter ~ 40 mm and thickness ~ 2 mm were manufactured.

Prepared semiconductor SnO_2<Co> and ZnO<La> targets had sufficient conductance and were used for deposition of nanosize films. Multi-Sensor-Platforms (purchased from TESLA BLATNÁ, Czech Republic) are used as substrates. Using heat resistance the chip can be kept at constant temperature. The platform integrates a temperature sensor (Pt 1000), a heater and interdigitated electrode structures in platinum thin film on a ceramic substrate. Heater and sensor are covered with an insulating glass layer. Gas sensitive layer made from SnO_2 doped with 2 at.% Co or ZnO doped with 1 at.% La was deposited onto the non-passivated electrode structures using the high-frequency magnetron sputtering method. That way the Multi-Sensor-Platform is converted into gas sensors.

The power of the magnetron generator unit was 60 W. The substrate temperature during sputtering was 200 °C. Duration of the sputtering process was equal to 20 minutes and 15 minutes for SnO_2<Co> and ZnO<La>, respectively. The sensing device was completed through the ion-beam sputtering deposition of palladium catalytic particles (the deposition time ~ 3 seconds). Further annealing of the manufactured structures in 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 (see Fig. 1).

Morphology and chemical composition of the deposited SnO_2<Co> and 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 prepared sensors made from doped metal oxide films under the influence of HPV 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 HPV. Measurements of the manufactured sensors response (the sensor resistance variance under the HPV influence) were carried out at different concentrations of HPV (from 100 ppm up to 4000 ppm). A platinum heater on a front side of the sensor ensures a necessary temperature of the work body. The sensor work body temperature was being varied from room temperature up to 350 °C.

Investigations of the sensitivity of the prepared sensors to HPV with concentration below than 100 ppm were carried out at University of Chemistry and Technology (Prague). In particular, the temperature dependence of

sensitivity to 10 ppm HPV was investigated. For these measurements atmosphere in “Peroxybox” system developed in that Institute in Prague was controlled (0-10 ppm H_2O_2 and 20-23% RH) and the sensor’s temperature was changed. The final sensitivity was calculated as the response of sensor in “Peroxybox” system divided by response of sensor in air.

Measurements of the sensitivity of the ZnO<La> sensors to 10 ppm HPV were carried out by the following way. Firstly, an atmosphere containing 10 ppm of HPV was prepared in a laboratory model of an isolator. This HPV concentration decreased by spontaneous decomposition of H_2O_2. When a reference device (Dräger Sensor® H_2O_2 HC) could not detect any HPV, 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 HPV. This process was repeated three times.

Experimental Results and Discussion

The thickness of the SnO_2 doped with 2 at.% Co and ZnO doped with 1 at.% La films was equals 160 nm and 30 nm, respectively.

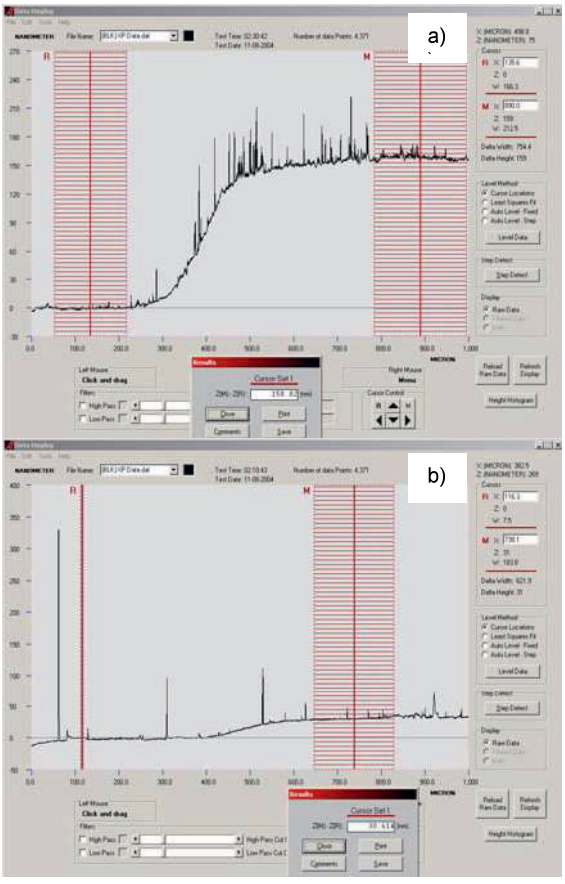

Fig. 1. The thicknesses measurement resultes for SnO_2 doped with 2 at.% Co (a) and ZnO doped with 1 at.% La (b) films.

Results of the study of morphology for the deposited doped metal oxide films are presented on the Fig. 2. Average size of nanoparticles was equals 18.7 nm for both compositions.

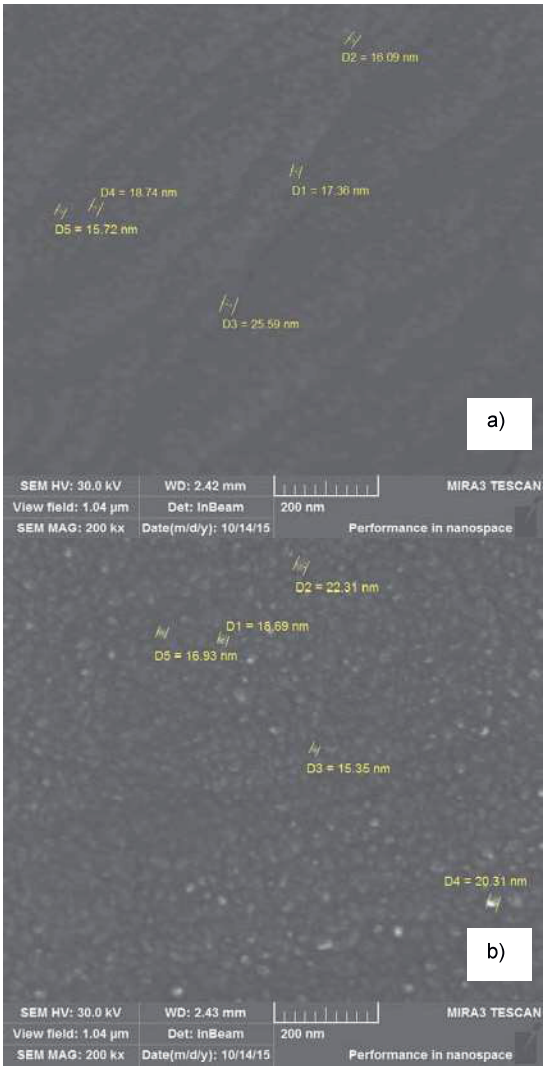

Fig. 2. SEM images for SnO_2 doped with 2 at.% Co (a) and ZnO doped with 1 at.% La (b) films.

The sensors manufactured by us are resistive, i.e., its operation is grounded on changes in the resistance of gas sensitive semiconductor layer under the influence of HPV due to an exchange of charges between molecules of the semiconductor film and adsorbed HPV. A variation of the sensor resistance is takes place in result of such exchange of charges. This variation of resistance was fixed as sensor response.

The sensor resistance variance under the HPV influence was measured using a special home-made computer program. Typical curve demonstrating changing of the sensor resistance under the influence of HPV at

invariable temperature of the work body is presented on the Fig. 3.

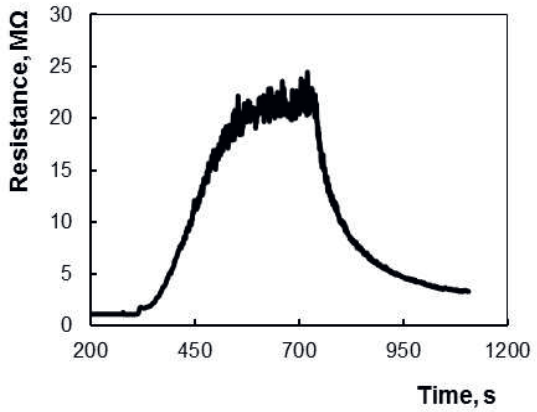

Fig. 3. Resistance variation of the ZnO<La> sensor under the influence 1800 ppm of HPV, work body temperature 350 °C.

The sensor sensitivity was determined as the ratio R_{HPV}/R_{air}, where R_{HPV} is the sensor resistance in the presence of HPV in air and R_{air} is the sensor resistance in air without HPV. The sensor sensitivity at different work body temperatures is presented on the Fig. 4.

As can see from these dependences, the sensitivity of the sensors is decreased for both structures, when the working body temperature excesses some certain value (300 °C and 250 °C for ZnO<La> and SnO_2<Co> sensors, respectively). 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. The desorption prevails over the adsorption when a temperature is increased above certain value and, therefore, the sensor sensitivity is decreased. Temperature, above which the sensitivity decrease occurs, for sensors made of structure ZnO<La> greater than for sensors made of structure SnO_2<Co>. It is most probably that the chemical bond between molecules of ZnO and H_2O_2 is stronger, than between molecules of SnO_2 and H_2O_2. This is testified also by the fact that the recovery time for sensors made of SnO_2<Co> is less than recovery time for ZnO <La> sensors.

Note that the prepared sensors resistance has changed in order of magnitude under influence of HPV already at operation temperature 100 °C. However in such temperature a long period of time was needed for recover of sensors parameters. Pulsed increasing of work body temperature is needed for decreasing of the recovery time of investigated sensors.

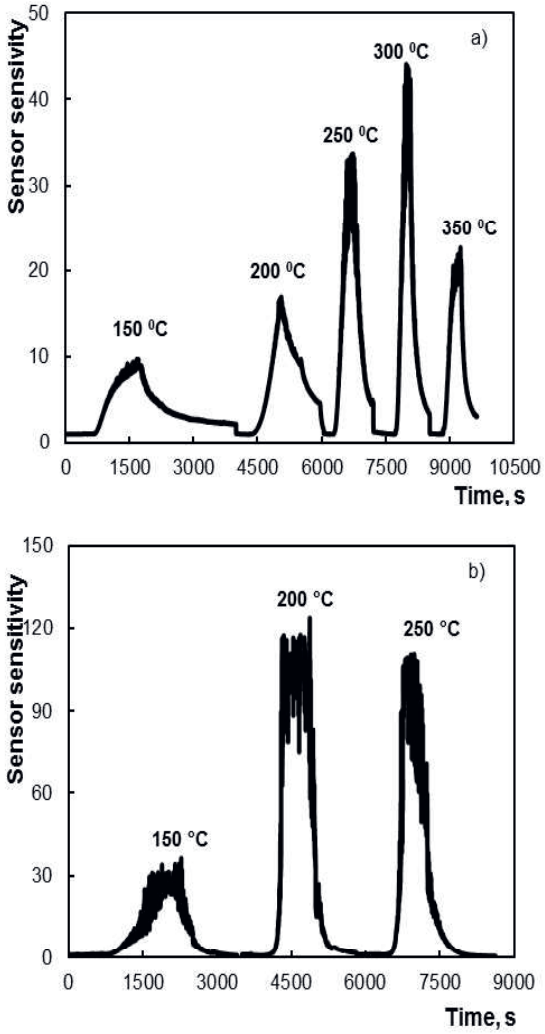

Fig. 4. The ZnO<La> sensor sensitivity to 1800 ppm of HPV (a) and the SnO_2<Co> sensor sensitivity to 100 ppm of HPV (b) at different work body temperatures.

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 HPV with concentration below than 100 ppm were also carried out.

The results of measurements of the SnO_2<Co> sensor response to 75 ppm of HPV at invariable temperature of the work body are presented on the Fig. 5. As the dependence indicates, the structure SnO_2<Co> exhibited enough response (sensitivity was equal ~ 2) to 75 ppm of HPV at the operating temperature 200 °C.

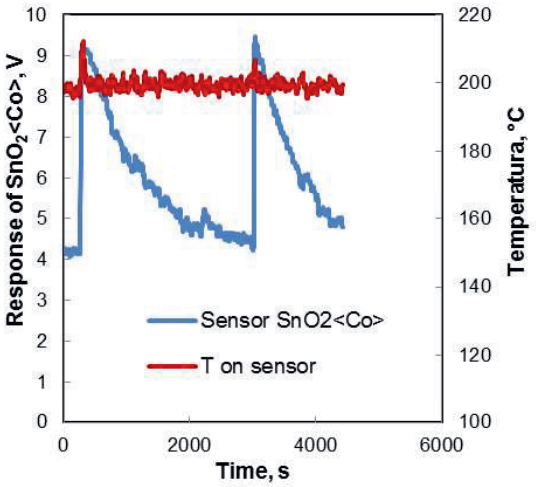

Fig. 5. SnO_2<Co> sensor response to 75 ppm of HPV, work body temperature 200°C.

Investigations of the SnO_2<Co> and ZnO<La> sensors sensitivity to very low concentrations (0-10 ppm) of HPV were carried out at University of Chemistry and Technology (Prague).

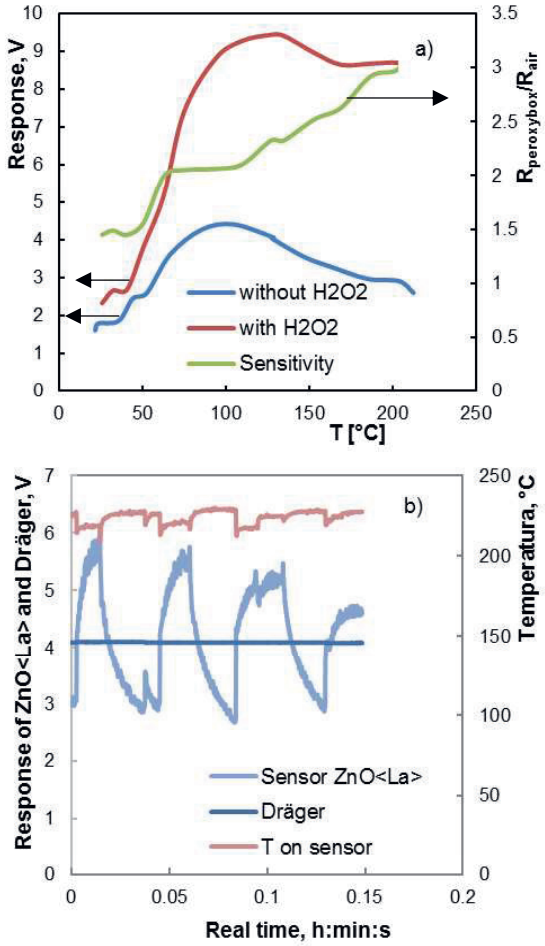

Fig. 6. The temperature dependence of sensitivity to 10 ppm HPV for SnO_2<Co> sensor (a) and ZnO<La> sensors response to 10 ppm of HPV, work body temperature 220°C (b).

Results of these measurements show, that the structure made of SnO_2<Co> exhibits a response to 10 ppm of HPV at the operating temperature starting at 50 °C (Fig. 6a). Sensitivity to 10 ppm of HPV was equal ~ 3 for the SnO_2<Co> sensors at the work body temperature 200 °C. The sensitivity to 10 ppm of HPV 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 is not sensitive to 10 ppm of HPV (Fig. 6b).

The results of investigations of the prepared sensors sensitivity at different concentrations of HPV are presented on the Fig. 7.

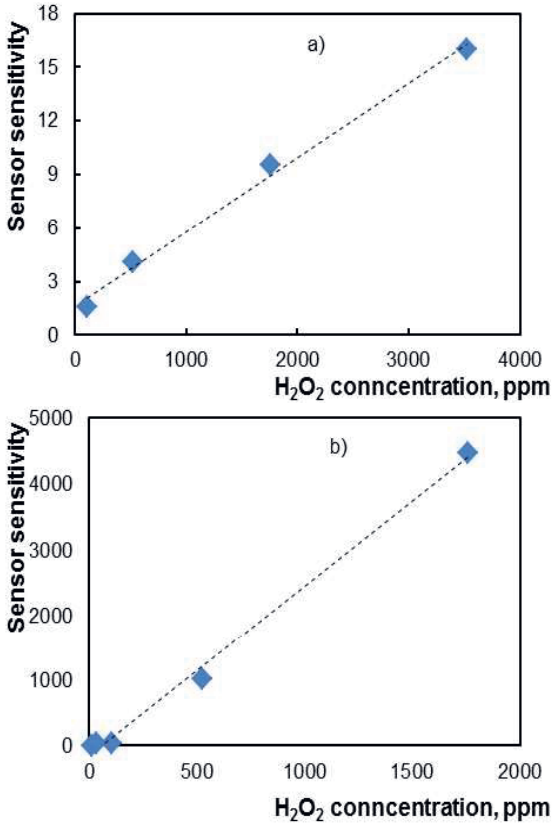

Fig. 7. The dependence of sensor sensitivity on HPV concentration at operating temperature 150 °C for ZnO<La> (a) and SnO_2<Co> (b) sensors.

As can see, these dependencies of sensors sensitivity on HPV concentration have a linear character and can be used for determination of HPV concentration.

Conclusions

The technology for the manufacture of semiconductor sensors made from ZnO doped with 1 at.% La and SnO_2 doped with 2 at.% Co nanostructured films was developed. Sensitive SnO_2<Co> and ZnO<La> layers were deposited onto the Multi-Sensor-Platforms using the high-frequency magnetron sputtering method. The thicknesses of the deposited doped metal oxide films were equals 160 nm

and 30 nm for SnO_2<Co> and ZnO<La> compositions, respectively. Average size of nanoparticles was equals 18.7 nm for both structures. Specimen detecting HPV were manufactured and investigated. The sensitivity of the prepared sensors was measured at different temperatures of the sensor work body and concentrations of HPV. It was found that both Co-doped SnO_2 and La-doped ZnO sensors exhibit a good response to HPV at the operating temperature starting at 100 °C. Sensors made from SnO_2<Co> and ZnO<La> were sufficient sensitive to 10 ppm of HPV. It was established that the dependencies of the sensitivity on HPV concentration at the work body temperature 150 °C have a linear character for prepared structured and can be used for determination of HPV 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.

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