Hydrogen Peroxide Vapours Sensors Made From ZnO<La> and SnO_2<Co> Films

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***Abstract*—Thin film hydrogen peroxide vapours sensors made from ZnO<La> and SnO_2<Co> were manufactured by the high-frequency magnetron sputtering method. Response of the prepared sensors was investigated at different concentrations of hydrogen peroxide vapours and temperatures of the sensor work body. It was found that the La-doped ZnO sensors exhibit a sufficient response at 10 ppm of hydrogen peroxide vapours at the operating temperature of 220 °C. Good response to 100 ppm of hydrogen peroxide vapours at the work body temperature of 150 °C was shown for Co-doped SnO_2 sensors.**

Keywords - sensor; hydrogen peroxide vapours; semiconductor; metal oxide; thin film.

I. 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 in large concentrations under certain conditions (for example, in the presence of transition metals) can decompose fast and can be explosive. H_2O_2 is subsumed under the category of matters 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 the air after completion of disinfection cycle are very important. From this point of view, development and manufacturing of systems sensitive to H_2O_2, able to determine its concentration in the environment is a very actual problem and attracts interest of chemists, physicians, industrial engineers, etc.

Now the electrochemical sensors are wide used [1]-[3]. However, note that the process of chemical decontamination can be carried out in two different ways: the first is the wet approach using water or any other H_2O_2 solution and the second one is the dry method using H_2O_2 in vapour phase. Therefore, the development and manufacturing of stable and reproducible sensors sensitive to H_2O_2 vapours are required.

An H_2O_2 vapours phase checking is also crucially significant in connection with counterterrorism efforts. An amperometric sensor for detection of H_2O_2 vapours made of an agarose-coated Prussian-blue was investigated [4]. A single-wire optical sensor for H_2O_2 vapours was manufactured [5]. The chemiresistive films made of organic p-type semiconductors metalized phthalocyanines (MPcs, where M = p-, d-, and f-block elements) are also sensitive to H_2O_2 vapours [6].

The aim of the present paper is a development of the technology, manufacturing and investigation of solid-state H_2O_2 vapours sensors made from nanostructured semiconductor metal oxide films.

In Section I, the necessities in the development of the H_2O_2 sensors and, in particular, sensors sensitive to H_2O_2 vapours are briefly described. In Section II, the manufacture technology of sensors made from semiconductor doped with metal oxide ZnO<La> and SnO_2<Co> nanostructures is described. The results of investigations of its sensitivity to H_2O_2 vapours are presented. In Section III, the conclusions are made and the directions of the future work are described.

II. EXPERIMENTAL RESULTS AND DISCUSSION

Ceramic targets made from ZnO doped with 1at.% La and SnO_2 doped with 2at.% Co were synthesized by the method of solid-phase reaction in air. The annealing was carried out at 1300 °C and 500 °C-1100 °C for the compacted samples of ZnO<La> and SnO_2<Co>, respectively.

Prepared semiconductor ZnO<La> and SnO_2<Co> targets with a diameter ~ 40 mm and thickness ~ 2 mm were used for deposition of nanosize films using the high-frequency magnetron sputtering method. Multi-Sensor-Platforms (purchased from TESLA BLATNÁ, Czech Republic) are used as substrates. The power of the magnetron generator unit was 60 W. Duration of the sputtering process was equal to 15 and 20 minutes for ZnO<La> and SnO_2<Co>, 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

 ISBN: 978-1-61208-543-2

in air was carried out at temperature 250 °C to obtain film homogeneity and eliminate mechanical stress.

The sensors manufactured by us are resistive, i.e., its operation is grounded on changes of resistance of gas sensitive semiconductor layer under the influence of H_2O_2 vapours caused by an exchange of charges between molecules of the semiconductor film and absorbed H_2O_2 vapours.

Response of prepared sensors made from doped metal oxide films under the influence of H_2O_2 vapours was measured using a home-made system [4]. Samples were placed in a hermetic chamber. A corresponding quantity of the H_2O_2 water solution with certain concentration was placed in the chamber to reach a required concentration of H_2O_2 vapours. Measurements of the manufactured sensors response were carried out at different concentrations of H_2O_2 vapours (from 10 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.

The sensor resistance variance under the H_2O_2 vapours influence was measured using a special home-made computer program. A typical curve demonstrating changing of the sensor resistance under the influence of H_2O_2 vapours at invariable temperature of the work body is presented in Figure 1.

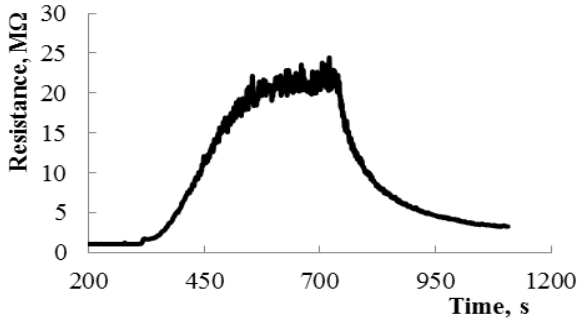

Figure 1. Resistance variation of the ZnO<La> sensor under the influence 1800 ppm of H_2O_2 vapours, work body temperature of 350 °C.

As a result of such measurements, the sensor response was determined as the ratio R_{vapors}/R_{air}, where R_{vapors} is the sensor resistance in the presence of H_2O_2 vapours in air and R_{air} is the sensor resistance in air without H_2O_2 vapours. The SnO_2<Co> sensor response to 100 ppm of H_2O_2 vapours at the work body temperature of 150 °C and 200 °C is presented in Figure 2. The temperature of the sensor work body remains constant during of the each measurement.

Investigations of the ZnO<La> sensors sensitivity to 10 ppm of H_2O_2 vapours were carried out at University of Chemistry and Technology (Prague). Firstly, an atmosphere containing 10 ppm of H_2O_2 vapours was prepared in a laboratory model of an isolator. This H_2O_2 vapours concentration decreased by spontaneous decomposition of H_2O_2. When a reference device (DrägerSensor® H_2O_2 HC) could not detect any H_2O_2 vapours, the sensor was inserted into the model isolator. Then, the sensor responded immediately. When the maximum response was reached, the sensor was taken out into an atmosphere without any traces of H_2O_2 vapours. This process was repeated three times. Results of these measurements are presented in Figure 3.

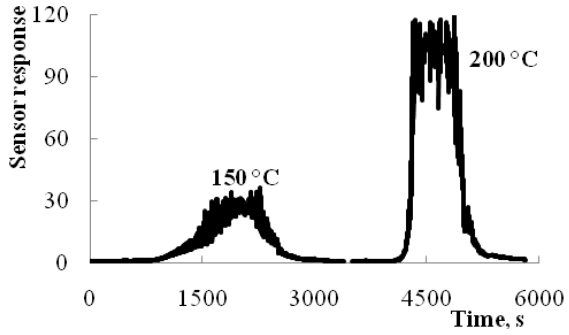

Figure 2. The SnO_2<Co> sensor response to 100 ppm of H_2O_2 vapours at different work body temperatures.

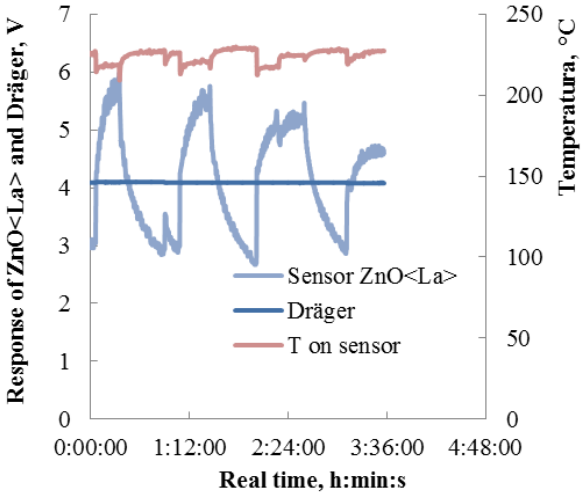

Figure 3. ZnO<La> sensors response to 10 ppm of H_2O_2 vapours.

Note that the DrägerSensor® H_2O_2 HC reference device is not sensitive to 10 ppm of H_2O_2 vapours. The ZnO<La> sensors were sufficiently sensitive to 10 ppm of H_2O_2 vapours at the work body temperature of 220°C, i.e. the sensors manufactured by us allow detection of H_2O_2 vapours concentrations which are not exceeding the maximum permissible value.

III. Conclusion and Future Work

The technology for semiconductor nanostructure sensors made from ZnO doped with 1at.% La and SnO_2 doped with 2at.% Co was developed. Specimen detecting H_2O_2 vapours were manufactured and investigated. Sensors made from ZnO<La> were sensitive to 10 ppm of H_2O_2 vapours. Sensors made from SnO_2<Co> exhibited good response to 100 ppm of H_2O_2 vapours at the operating temperature starting at 100°C. Our future work will be directed on the long-time stabilization of sensors parameters and the

 ISBN: 978-1-61208-543-2

improvements of such characteristics as operation speed and recovery time.

ACKNOWLEDGMENT

This investigation was supported by the Swiss National Science Foundation FNSNF within the framework of the SCOPES DecoComp project.

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 ISBN: 978-1-61208-543-2