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Conductometric sensor for hydrogen peroxide vapors detection

G.H. Shahkhatuni, V.M. Aroutiounian, V.M. Arakelyan, M.S.Aleksanyan, G.E. Shahnazaryan

Yerevan State University, 1 Alex Manoukian str., 0025, Yerevan, Republic of Armenia
E-mail: gevshahkhatuni@ysu.am

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Abstract. ZnO doped with 2 at.% La gas sensitive thin film was deposited on the Multi-Sensor-Platforms by the rf magnetron sputtering method using ZnO doped with 2 at.% La ceramic target prepared by us. Palladium catalytic particles were deposited by ion beam sputtering method on the surface of the sensing layer. The sensitivity of semiconductor film to low concentration of hydrogen peroxide vapors was measured at different operating temperatures. It was found that the ZnO+2 at.% La film has shown high sensitivity to low concentration of hydrogen peroxide vapors at different operating temperature started from room temperature.

Keywords: gas sensor, hydrogen peroxide, thin film, magnetron sputtering, ZnO

1. Introduction

Hydrogen peroxide is a weakly acidic, colourless liquid, miscible with water in all proportions. Hydrogen peroxide (H_2O_2) was discovered by Thenard in 1818 and has been used industrially since the mid-19th century. Now prepared primarily by anthraquinone autoxidation, hydrogen peroxide is used widely to prepare other peroxygen compounds and as a nonpolluting oxidising agent. Because pure hydrogen peroxide is unstable and has explosion risk, it is usually in a water solution. It is the simplest peroxide and is commercially available in aqueous solution over a wide concentration range. Hydrogen peroxide is a manufactured chemical, although small amounts of hydrogen peroxide gas may occur naturally in the air. Low exposure of H_2O_2 may occur from use at home; higher exposures may occur from industrial use. Exposure to hydrogen peroxide can cause irritation of the eyes, throat, respiratory airway and skin. Drinking concentrated liquid can cause mild to severe gastrointestinal effects [1-3].

Hydrogen peroxide has a wide application fields in different area and it can used as an antiseptic and anti-bacterial agent for medical uses; for industrial and domestic waste water disinfection and sterilization; in chemical industry as reagent in making organic and inorganic peroxides, sodium perborate and percarbonate, a bleach used in laundry detergents; in manufacturing epoxides, hydroquinone, catechol, ethylene glycol, glycerol and other organic products; as a bleaching agent for oils, fats, furs, leather, textiles, pulp and paper; in mining industry for extraction uranium from ores; as a reagent in analytical chemistry and oxidizing agent in a laboratory organic synthesis; in rocketry (particularly in high concentrations as high-test peroxide as a monopropellant) and in bipropellant systems; as an reserve oxygen source on submarines; to bleach human hair and so on [4].

It is widely used also in pharmaceutical applications for its disinfectant properties. These applications include the disinfection of dental and surgical instruments as well as contact lenses.

Hydrogen peroxide vapors are also used for the production of drugs for cleaning the environment from the microbes [5].

So, due to such a wide application fields of hydrogen peroxide (with a liquid and vapor form) and its toxicity the high demand for hydrogen peroxide vapor sensors with optimized parameters grows year by year.

Metal oxide semiconductors gas sensors have been widely studied due to their low costs, high sensitivity, selectivity and stability, easy production and so on. As the typical n-type metal oxide semiconductors, zinc oxide (ZnO) with a wide band-gap ($3.37 eV$) has been widely used in conductometric gas sensors because of its low cost, nontoxicity, stability and easy-achieved real-time response in gas sensing application. However, pure zinc oxide exhibits low sensitivity and poor selectivity as well as high resistance. Therefore, it is necessary to add appropriate dopant in poor metal oxide for improving the gas sensing properties [6,7].

In this work, (ZnO) doped La solid solution was synthesized by solid phase reaction and obtained nanostructured thin film by rf magnetron sputtering method. The gas sensing performances of the gas-sensitive thin films were evaluated in detecting comparatively low-concentration of hydrogen peroxide vapors. The sensing mechanisms of hydrogen peroxide vapors on metal oxide surface were also discussed in detail.

2.Experimental

Ceramic target based on ZnO doped with $2 at.\% La$ was synthesized by solid-phase reaction method [8]. The powders of initial oxide (ZnO and La_2O_3) were weighed in the appropriate quantities. This mixture was carefully intermixed and pressed by forming a tablet. The pressed $ZnO<La>$ tablet was annealed in the programmable furnace Nabertherm, HT $O_4/16$ with the $C42$ controller. The annealing was carried out at high temperature (500 °C to 1100 °C). Then the ceramic target was subjected to mechanical treatment for eliminating surface defects. So, the semiconductor solid solution as a target for rf magnetron sputtering was prepared.

Gas sensitive nanosized thin film was obtained by the high-frequency magnetron sputtering method using prepared semiconductor $ZnO<La>$ target. The Multi-Sensor-Platform (purchased from TESLA BLATNÁ, Czech Republic) was used as a gas sensor substrate. On the alumina substrate are located Pt interdigitated ohmic contacts and around the contacts there are heater ($Pt1000$) and temperature sensor. The heater and temperature sensor are covered with an insulating glass layer (see Fig.1). When gas sensitive film is deposited on the active area of the platform the Multi-Sensor-Platform is converted into gas sensor (see Fig. 2).

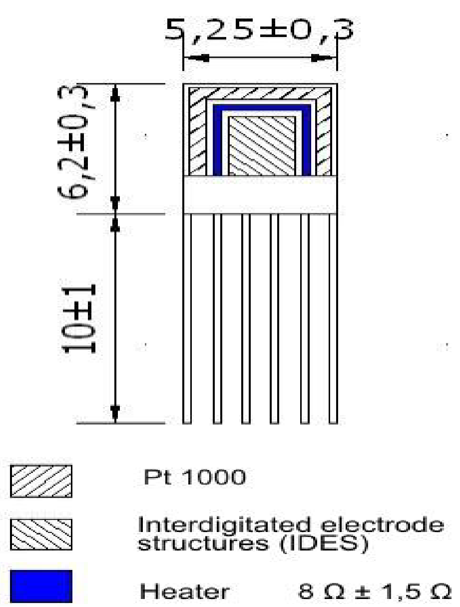


Fig. 1. The schematic image of the Multi-Sensor-Platform (with mm unit).

It is known that different noble metal particles on the metal oxide surface can act as catalysts [9]. In order to improve the sensitivity and the rate of response on the active surface of the sensor were deposited Pd catalytic particles by ion-beam sputtering method.

During the sputtering of nanosized thin film the power of high-frequency magnetron generator unit was $60W$. The substrate temperature during sputtering was 200^0C and duration of the sputtering process was 20 minutes. After deposition of the sensitive layer on the surface of this layer were deposited palladium catalytic particles by ion-beam sputtering method. The deposition time was 3 seconds. In the final stage the sensor structure was annealed in the air at temperature of 250^0C during 3 hours to obtain homogeneous films, eliminate mechanical stress and improve sensor stability.

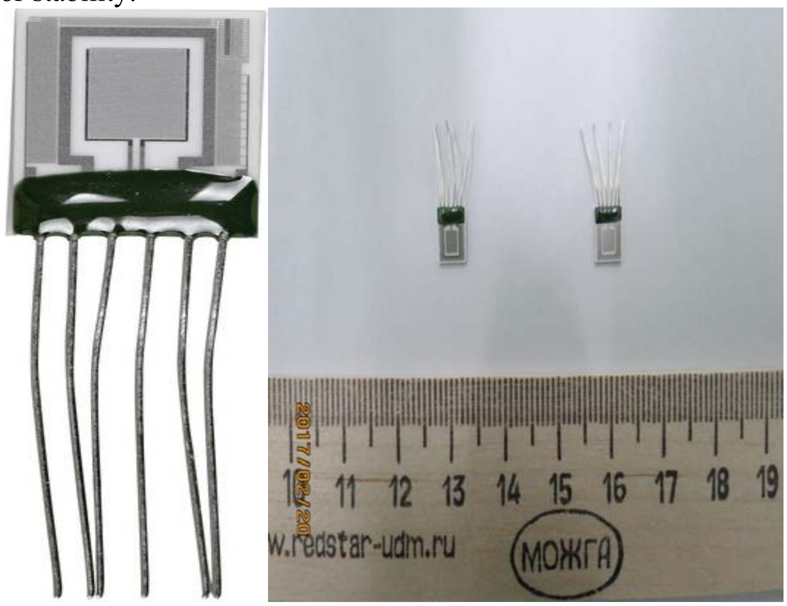


Fig. 2. Photos of gas sensors based on Multi-Sensor-Platform.

3.Results and discussion

3.1. Gas sensing mechanism

The sensor manufactured by us is a type of resistive or conductometric. It means that its operation is grounded on changes in the resistance or the conductance of gas sensitive semiconductor layer under the influence of target gas due to an exchange of charges between molecules of both the semiconductor film and adsorbed target gas. For n-type semiconductor the majority charge carriers are electrons and upon interaction with a reducing gas an increase in conductivity occurs. In case of an oxidising gas the depletion of charge carrying electrons of sensing layer is take place resulting in a decrease in conductivity. For p-type semiconductor the majority charge carriers are positive holes. In this case the opposite effects are observed with the material and showing an increase in conductivity in the presence of an oxidising gas. All these cases are presented in Table 1 [10-12].

Table 1

Typo of semiconductor	Oxidising Gases	Reducing Gases
n-type	Resistance increase	Resistance decrease
p-type	Resistance decrease	Resistance increase

It is known that hydrogen peroxide is an oxidising gas and the ceramic target (ZnO doped with $2at.\%La$) shows n-type behavior. As known there are ions, such as O_2^-, O^- and O^{2-} on the surface of semiconductor films.

They originate due to electrons which are captured by adsorbed oxygen on the surface of oxide:

$$O_2(gas) \leftrightarrow O_2(ads) \quad (1)$$

$$O_2(ads) + e^- \leftrightarrow O_2^-(ads) \quad (2)$$

$$O_2^-(ads) + e^- \leftrightarrow 2O^-(ads) \quad (3)$$

$$O^-(ads) + e^- \leftrightarrow O^{2-}(ads) \quad (4)$$

The exchange of charges takes place between these surface oxygen species and target gas molecules. So, at the presence of H_2O_2 vapors the reaction between semiconductor surface and H_2O_2 molecules takes place. At first on the semiconductor surface hydrogen peroxide molecules split into water and oxygen molecules (see Reaction (5)), then oxygen molecules take electrons from lattice becoming oxygen ions (see Reaction (6)). A variation of the sensor resistance or electrical conductivity takes place as a result of such exchange of electrons. This variation of conductivity was fixed as sensor response.

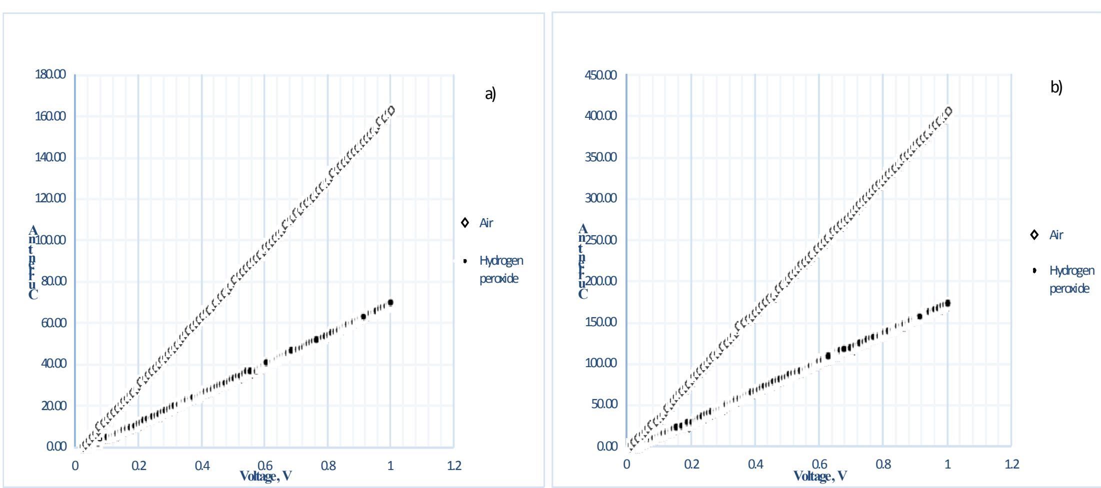
$$2H_2O_2 \rightarrow 2H_2O + O_2(gas) \quad (5)$$

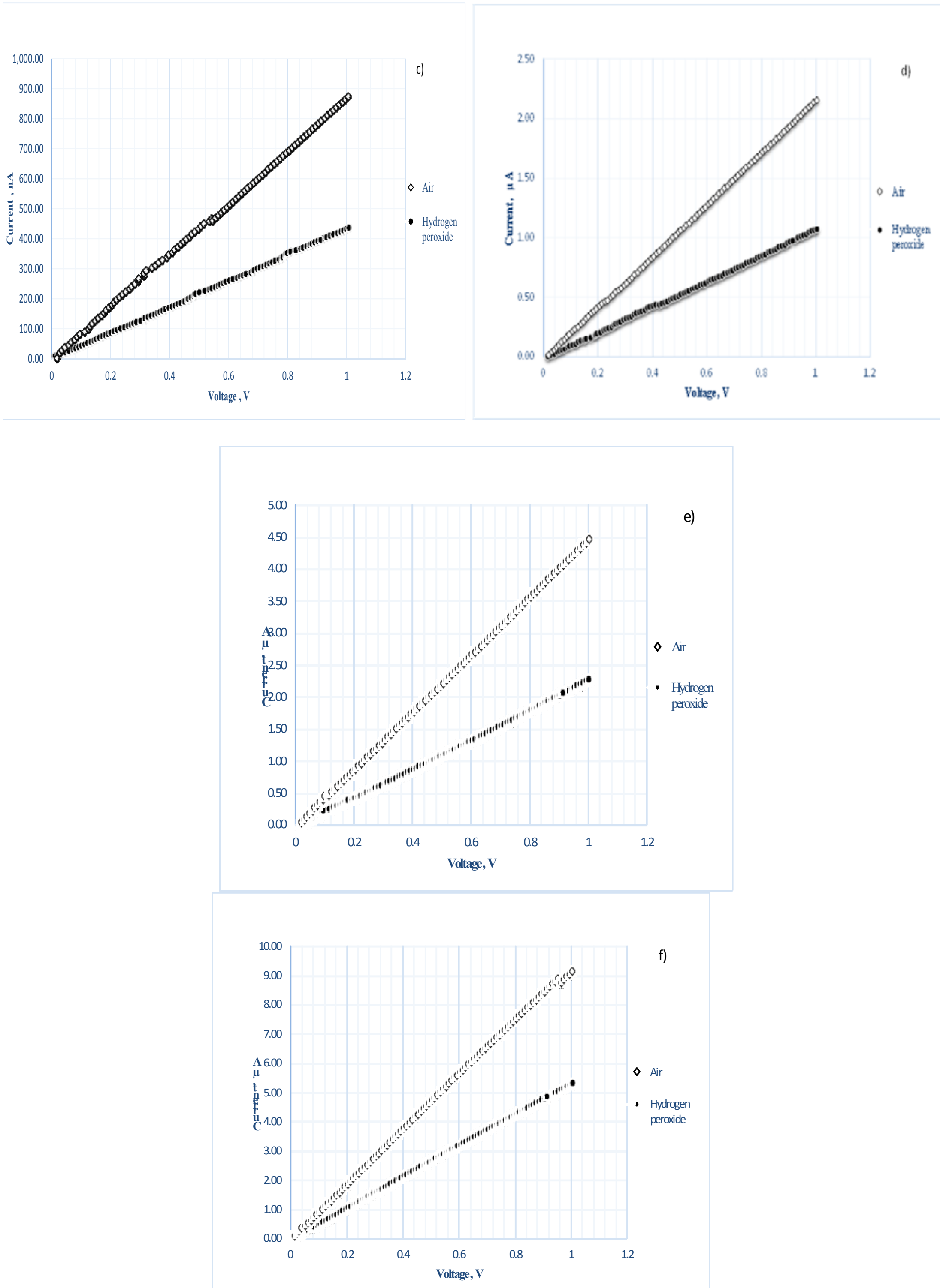
$$O_2(gas) + e^- \rightarrow O_2^-(ads) \quad (6)$$

3.2 Experimental results

We investigated the sensitivity of prepared ZnO doped with $2at.\%La$ sensor to H_2O_2 vapors at different operating temperature. The I-V characteristic curves of ZnO doped with $2at.\%La$ sensor in the air and at the presence of $105\,ppm$ H_2O_2 vapors at different operating temperature are presented in Fig. 3 which were measured by Electrochemical Workstation ZIVE SP1 and Keithley 4200-SCS Parameter Analyzer. The electrical current of the ZnO doped with $2at.\%La$ sensor was changed more than twice under the influence of $105\,ppm$ H_2O_2 at operating temperature of 50^0C.

The sensor sensitivity was determined as the ratio of I_{air}/I_{gas}, where I_{air} is the sensor electrical current in the air without target gas and I_{gas} is the sensor electrical current in the presence of target gas with applied voltage of $1V$.




c)
Current , nA
Voltage , V
Air
Hydrogen peroxide
d)
Current, μA
Voltage, V
Air
Hydrogen peroxide
e)
Voltage, V
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Air
Hydrogen peroxide

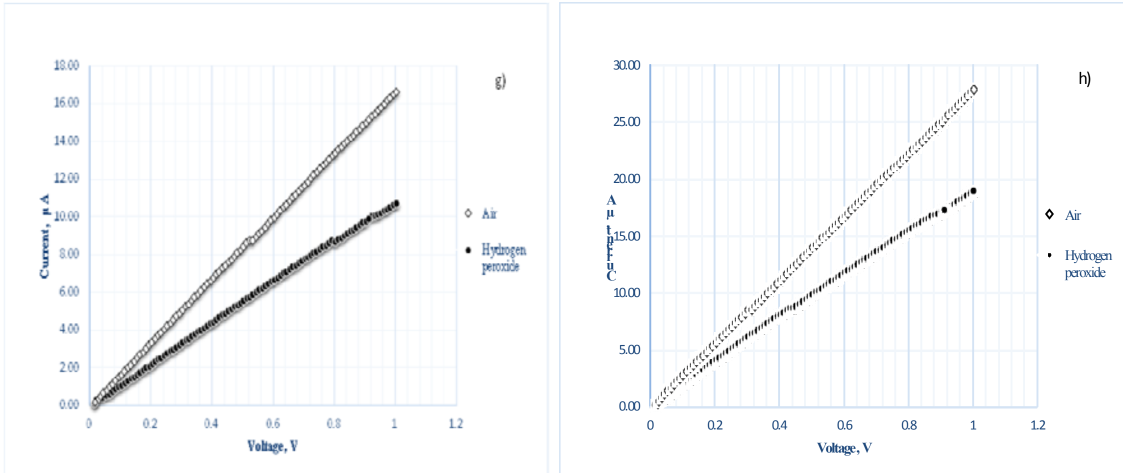

Fig. 3. I-V characteristics of ZnO doped with 2 at.% La sensor in the air and at the presence of 105 ppm H_2O_2 vapors at different operating temperature: a) 25 ^{0}C, b) 50 ^{0}C, c) 75 ^{0}C, d) 100 ^{0}C, e) 125

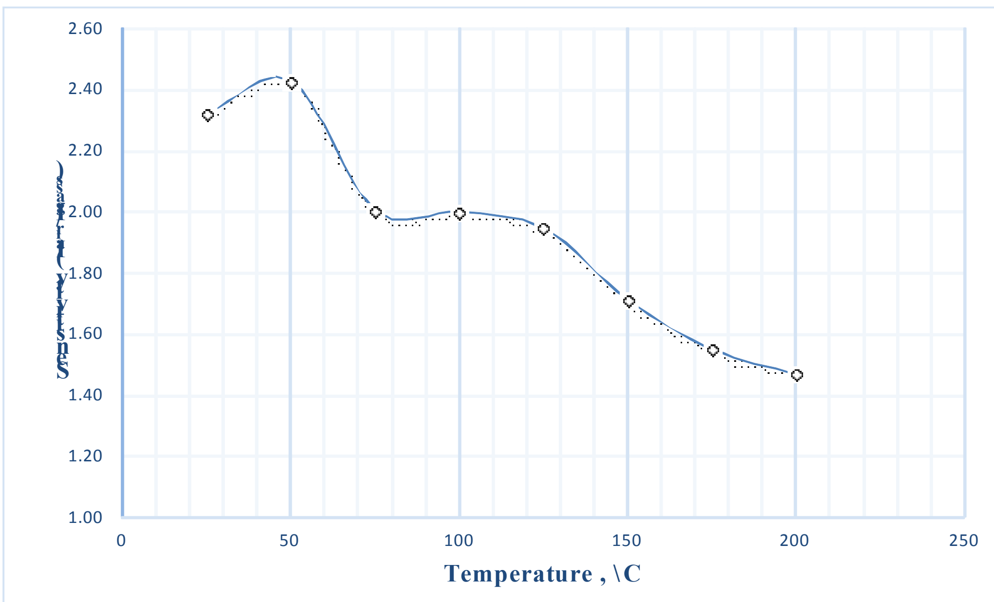

Fig. 4. The dependence of ZnO doped with 2 at.% La sensor sensitivity to 105 ppm of H_2O_2 vapors on the operating temperature.

The dependence of the ZnO doped with $2at.\%La$ sensor sensitivity to $105\,ppm$ of hydrogen peroxide vapors on the work body temperature is presented in Fig. 4. When the operating temperature of the sensor increases the sensitivity also increases and starting at 50^0C is falling. The maximum sensitivity is observed at 50^0C. The reason for this is that the rate of desorption processes on the semiconductor surface exceeds that of adsorption processes starting this temperature. It is near to room temperature and it will result in low energy consumption of hydrogen peroxide vapor detector.

There were also measured the I-V characteristic curves of ZnO doped with $2at.\%La$ sensor in the air and at the presence of $210\,ppm\ H_2O_2$ vapors at 50^0C operating temperature (see Fig. 5).

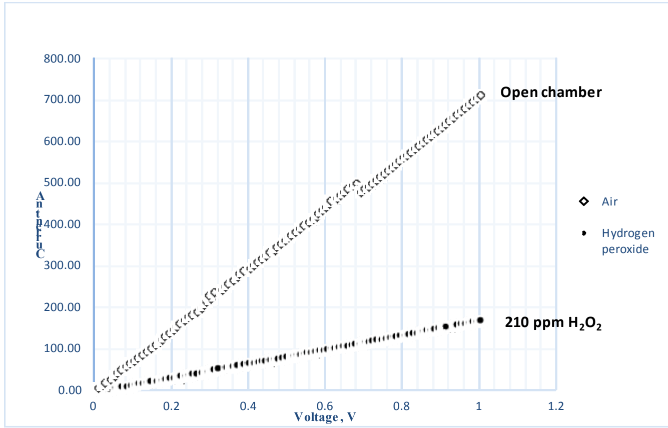

Fig. 5. I-V characteristics of ZnO doped with 2 at.% La sensor in the air and at the presence of 210 ppm H_2O_2 vapors at 50 ^{0}C operating temperature.

When the concentration has increased twice, the sensitivity has grown more than twice. At the higher concentration of H_2O_2 vapors, the sensitivity increases, which is typical for this type of sensor.

4.Conclusions

Thus, we have synthesized the ZnO doped with $2at.\%La$ ceramic target by solid-phase reaction method. The simple technology for the manufacturing of semiconductor gas sensor based on ZnO doped with $2at.\%La$ was developed. We obtained semiconductor $ZnO<La>$ thin film onto the Multi-Sensor-Platforms using the high-frequency magnetron sputtering method and Pd catalytic particles on the active surface of the sensor by ion-beam sputtering method. The sensitivity measurement results showed that the sensor had high sensitivity to hydrogen peroxide vapors. The $ZnO<La>$ sensor shows excellent results compared to the other fabricated sensor and it is excellent candidate for the fabrication of H_2O_2 vapor detector in near future.

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