Armenian Journal of Physics, 2014, vol. 7, issue 1, pp. 28-37

# MWCNTs•Fe<sub>2</sub>O<sub>3</sub> GAS SENSORS WITH DIFFERENT STRUCTURE OF OHMIC CONTACTS

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Received 24 March 2014

**Abstract** - Thin film gas sensors made of the MWCNTs•Fe<sub>2</sub>O<sub>3</sub> (1:25) nanocomposite material with different structure of ohmic contacts were manufactured using the electron–beam spattering method. Investigations of the response of prepared sensors to such gases as methane, butane, hydrogen and ethanol vapors were carried out. It was established that sensors show significant response to hydrogen and ethanol vapors at relatively low temperatures of the working body. It was also established that the structure of ohmic contacts highly effects on sensors characteristics: sensors with different structure of ohmic contacts can be used as highly selective sensors for detection of small concentrations of ethanol vapors and hydrogen gas.

Keywords: MWCNT, sensor, response, selectivity.

# 1. Introduction

Nowadays hydrogen is considered as one of the best clean energy sources. The ignition product of hydrogen is water, which is free from contaminations. Hydrogen is also used in many industrial fields, for biomedical purposes, environmental protection, etc. However, hydrogen gas is easy inflammable and explosive, therefore quick and precise detection is required during its production, storage and use [1-3].

Because of the rapid progress in hydrogen economy and several shortcomings in traditional hydrogen detectors (large size, expensive cost, slow response and recovery times, etc.), researches on new types of hydrogen gas sensors, where sensing mechanisms are based on new physical principles so that their applications will allow achieving crucial improvement in sensors characteristics, took place. Among commercially available hydrogen sensors (electrochemical, semiconductor, thermoelectric, metallic, optical and acoustic ones, etc.) semiconductor sensors exhibit better performances (high response and fast recovery times, long-term stability, high specific surface area and potential for the integration in hydrogen sensing systems) [4–9]. Additionally,

semiconductor nanostructures decorated by different nanoparticles have also been broadly investigated for increasing of response and selectivity to hydrogen gas [10, 11].

Accurate detection of different types of alcohols is also required. Alcohol sensors are widely applied in numerous medical equipments, control of a variety of chemical processes and food quality, for determining the level of alcohol in wines and can also be fixed on vehicle steering wheels to monitor drunken driving [12]. Ethanol is one of the most widespread types of alcohols and has many useful and harmful properties [13-15]. Ethanol sensing mechanisms are widely demanded for a variety of purposes including its production, industrial chemical processing, fuel processing and use, physiological research on alcoholism, etc. Today's existing sensors are expensive and bulky, therefore, the use of carbon nanotube based devices for detection of ethanol vapor has received some attention for sensing in a smaller-size, inexpensive and portable way [16].

Here we reported about manufacture and investigation of resistive thin film gas sensors made of multiwall carbon nanotubes (MWCNT) modified by Fe<sub>2</sub>O<sub>3</sub> nanoparticles. Results of response measurements of sensors to hydrogen and ethanol vapors were analyzed.

### 2. Experimental

Two types of sensors with the similar structure of the working body were produced. We used a MWCNTs•Fe<sub>2</sub>O<sub>3</sub> (1:25) decorated (functionalized) nanocomposite powder, which was manufactured by researchers from the University of Szeged (Hungary).

For this purpose, a target with the composition of MWCNTs•Fe<sub>2</sub>O<sub>3</sub> (1:25) was made. Firstly, 3 weight % of polypropylene as binder was added to the MWCNT•Fe<sub>2</sub>O<sub>3</sub> (1:25) powder. Tablets with diameter of 3 mm and height 4 mm were pressed from the obtained mix at 160°C. The prepared tablets were used as a target for the electron beam evaporation of thin films on polycrystalline corundum (polycor) substrate.

For the manufacturing the first sensor ( $S_1$ ), optimum parameters of the evaporation were found: evaporation time - 30 min, substrate temperature - 200°C, target-substrate distance - 5 cm. In case of the second sensor ( $S_2$ ), the evaporation time was equal to 45 minutes. Thus, thin films made of nanocomposite MWCNTs•Fe<sub>2</sub>O<sub>3</sub> (1:25) were deposited on a polycor substrate. After, obtained structures were exposed to prior annealing in the air, at 500°C for 5 minutes for the  $S_1$  sensor and at 250°C for 2 hours for  $S_2$ . Further, for manufacturing of sensors, palladium catalytic nanoparticles and gold (inter-digital only for  $S_1$ ) ohmic contacts were created on the surface of all prepared structures using the ion-plasma sputtering method. Duration of palladium deposition process was equal to 2 seconds for  $S_1$  and 4 seconds for  $S_2$ . Gold was deposited within 50 minutes (inter-digital for first sensor, and common for second one). The subsequent annealing of obtained samples in the air was carried out at 350°C during 2 hours for improving the adhesion of contacts, releasing any possible mechanical stress and stabilization of the sensors parameters. Images of two sensors are presented in Fig. 1.



Fig. 1. Images of  $S_1(a)$  and  $S_2(b)$  sensors. The total surface areas of both sensors are equal.

A response of the prepared sensors to various gases (H<sub>2</sub>, CH<sub>4</sub>, and C<sub>4</sub>H<sub>10</sub>) and to alcohol vapors (C<sub>2</sub>H<sub>5</sub>OH) was investigated using a special measuring system [17]. Samples were placed in the hermetic chamber, where a certain gas concentration (from 100 to 10000 ppm) can be supplied. A certain quantity of liquid spirit is placed in the chamber for corresponding concentration of alcohol vapors supply. The heater allows raising temperature of the sensor working body up to  $350^{\circ}$ C. The dependences of sensor resistance on the working body temperature and influencing gas concentration were measured using of the special computer program. Management program is written by Dr. A. Adamyan in the Borland Delphi 6.0 environment. All measurements were carried out at applied voltage 1 V to sensor.

# 3. Results and Discussion

The realized investigations have shown that the prepared by us sensors both made of polycor/MWCNTs•Fe<sub>2</sub>O<sub>3</sub>(1:25)/Pdstructurewere sufficiently sensitive to hydrogen and alcohol vapors but their response to methane and butane was insignificant. Reduction of resistance of the sensor sensitive element under the gas influence is caused by chemical reactions taking place on the semiconductor surface with participation of molecules of influencing gas and oxygen ions that adsorbed on the semiconductor surface. For example, the following reaction will take place under hydrogen influence:

$$H_{2 \text{ (adsorbed)}} + O^{-}_{\text{ (adsorbed)}} \rightarrow H_2O + e^{-}.$$
 (1)

Ethanol detection on the MWCNTs•Fe<sub>2</sub>O<sub>3</sub> (1:25) surface is the result of two processes: interaction of alcohol vapors with both carbon nanotubes and semiconductor metal oxide surface. The transformation of the ethanol can take place by two ways on the metal oxide surface [18]:

Dehydrogenation: 
$$CH_3CH_2OH \rightarrow CH_3CHO + 2H_{ads}$$
, (2)

Dehydration:CH<sub>3</sub>CH<sub>2</sub>OH
$$\rightarrow$$
C<sub>2</sub>H<sub>4</sub>+H<sub>2</sub>O. (3)

Further, the interaction of the adsorbed on the oxide surface oxygen ions with originated from the dissociation components leads to a conductivity change. The following reactions, for example, may take place on the metal oxide surface:

$$CH_{3}CH_{2}OH + O^{2}_{ads} \rightarrow CH_{3}CHO + H_{2}O + 2e^{-}(\text{oxidizing dehydrogenation}),$$
(4)

$$CH_3CH_2OH + 6O_{ads} \rightarrow 2CO_2 + 3H_2O + 6e^{-}.$$
 (5)

Probably, decoration (functionalization) of MWCNT with  $Fe_2O_3$  nanoparticles provides existence of a depletion space charge layer owing to adsorption of oxygen from air. Thus, the metal oxide presence provides significant response of sensors made of carbon nanotubes.

The results of realized measurements are presented as the dependences of response on the temperature of sensor working body in Fig. 2. The response was determined as ratio  $R_{air}/R_{gas}$ , where  $R_{air}$  is the sensor resistance in air and  $R_{gas}$  is the sensor resistance in the presence of gas in air.



Fig.2. Dependences of response on the working body temperature for  $S_1$  (a) and  $S_2$  sensors (b). Concentration of influencing gas was 5000 ppm.

It was established that the sensors  $S_1$  appear notable response to hydrogen and alcohol vapors already when working body temperature was 150°C and 200°C, respectively (Fig. 2 (a)). The maximum response for these sensors is observed at 200°C for hydrogen gas, and at 250°C for ethanol vapors. Reduction of the sensors' response at temperatures of a working body above mentioned temperatures, possibly, can be explained to that the rate of desorption of influencing gas exceeds the rate of its adsorption at these temperatures. Response to hydrogen and alcohol vapors of sensors  $S_2$  begin to appear at heating of a working body up to 200°C and, in the case of hydrogen gas, the response monotonously increases with increase in sensors temperature (Fig. 2 (b)).

The comparison of responses of prepared by us sensors under influence of hydrogen and ethanol vapors are presented in Fig. 3.



Fig.3. Comparison of responses of  $S_1$  and  $S_2$  sensors under influence of hydrogen gas (a) and ethanol vapors (b). Concentration of influencing gas was 5000 ppm.

We can assume from Fig. 3 (a) that the dramatic difference in the responses of  $S_1$  and  $S_2$  sensors to hydrogen is probably caused by the fact that the surface area of the sensitive material of  $S_1$  sensor is significantly larger than that of  $S_2$  sensor. However, we can also see from Fig. 3 (b) that the response of  $S_1$  and  $S_2$  sensors to ethanol vapors was nearly the same until 250°C temperature of the working body. This is probably caused by the circumstance that hydrogen is more active chemical element in comparison to ethanol. We can also conclude from figures that the responses for  $S_1$ sensor are going to saturate at relatively low temperatures of working body than for  $S_2$  sensors.

The results of response measurements of sensors under influence of different concentration of ethanol vapors and hydrogen are presented in Fig. 4 and Fig. 5, respectively.

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Fig.5. Dependence of the response of  $S_1$  sensor to different concentrations of  $H_2$ . Sensor working body temperature was  $150^{0}$ C.

We can see from Fig. 4 that the sensitivities of prepared sensors to ethanol vapors were nearly the same (even under the smaller than 5000 ppm concentrations of ethanol vapors). Both  $S_1$  and  $S_2$  sensors shows significant response to ethanol vapors at its concentration 500 ppm ( $S_1=5$ ,  $S_2=5.4$ ). We observe from Fig. 5 that prepared by us  $S_1$  sensor is also good for detection of small concentrations of  $H_2$ . The sensor shows significant response to hydrogen at its concentration 500 ppm.

The response and recovery time values of developed by us sensors are presented in Table 1.

Table 1. Response and recovery times of  $S_1$  and  $S_2$  sensors. In case of ethanol vapors sensors working body temperature was  $250^{\circ}$ C, and in case of hydrogen sensor working body temperature was  $150^{\circ}$ C.

Sensor	Concentration, ppm	Hydrogen		Ethanol vapors	
		Response	Recovery	Response	Recovery
		time, seconds	time, seconds	time, seconds	time, seconds
$\mathbf{S}_1$	5000	33	360	238	51
	3000	29	328	248	64
	1000	43	360	104	45
	500	192	289	196	42
$S_2$	5000	_	_	285	284
	3000	_	_	212	347
	1000	_	_	118	321
	500	_	_	112	327

We see from Table 1 that recovery time after being influenced by ethanol vapors for  $S_1$  sensor is significantly lower than for  $S_2$  sensor. High values for response time under influence of ethanol vapors are caused by the time required for liquid ethanol to evaporate and create corresponding concentration of gas in the chamber. Note also that any additional actions were not required for a complete recovery of the prepared sensors after switch-off gas supply.

Relatively higher response values to ethanol vapors of  $S_2$  sensor compared with response of  $S_1$  sensor are probably caused by the structure of the ohmic contacts. In case of  $S_2$  sensor, the golden layer of contacts is acting as barrier for ethanol molecules desorption, while in case of  $S_1$  sensor the surface area of sensitive material is much "free" and simultaneously with ethanol adsorption the

processes of active desorption are taking place. This assumption is also confirmed by significantly higher recovery time values for  $S_2$  sensor compared with those of  $S_1$ .

# 4. Conclusion

Resistive thin film gas sensors made of nanocomposite MWCNTs•Fe<sub>2</sub>O<sub>3</sub> (1:25) structure with inter-digital  $(S_1)$  and another with common ohmic contacts  $(S_2)$  were manufactured by electron beam evaporation methods. The investigations of developed gas sensors were carried out. The response of prepared sensor to influence of such gases as hydrogen, methane, butane, and ethanol vapors was investigated. Response measurements were carried out at different temperatures of the sensor working body and at different concentration of gas. Developed sensors show significant response to hydrogen and ethanol vapors and have rather good operation speed. It was established that  $S_1$  sensors show appreciable response to hydrogen and alcohol vapors already at temperature of the working body 150°C and 200°C, respectively. The appreciable response was observed at 200°C for S<sub>2</sub> sensors in case of ethanol vapors as influencing gas. The response of S<sub>2</sub> to hydrogen was insignificant, which makes it highly selective for ethanol vapors. All prepared sensors can be used for detection of low concentration of ethanol vapors (from their concentration 500 ppm), and S<sub>1</sub> sensor can also be used for accurate detection of small concentrations of hydrogen (from their concentration 50 ppm). Thus, by changing the geometrical structure of ohmic contacts of the sensors it is possible to afford sensors with selectivity to a certain gas. Particularly, in our case S<sub>1</sub> sensor can be used as excellent sensor for hydrogen, while  $S_2$  – for ethanol detection.

#### Acknowledgments

The author is grateful to Prof. K. Hernadi and Dr. Z. Nemeth from Department of Applied and Environmental Chemistry, University of Szeged, Hungary for providing the MWCNTs•Fe<sub>2</sub>O<sub>3</sub> (1:25) nanocomposite powder. Author thanks Dr. V. Arakelyan and Prof. V. Aroutiounian for the help and valuable discussions of results.

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