Lithuanian Journal of Physics, Vol. **55**, No. 4, pp. 319–329 (2015)

METAL OXIDE GAS SENSORS DECORATED WITH CARBON NANOTUBES

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Received 22 September 2015; revised 5 October 2015; accepted 15 December 2015

Gas sensors made from carbon nanotubes without their doping and functionalization have serious shortcomings. Analysis of physics and techniques of decoration (functionalization) of carbon nanotubes using organic polymers, doping with impurities, metallic nanoparticle/nanoclusters is carried out. The development of metal oxide nanocomposite sensors decorated with carbon nanotubes is very promising for realization of detectors of different important gases with dramatically improved response, better time characteristics and smaller consumed power.

Keywords: gas sensor, metal oxide, carbon nanotube, decoration, nanoparticle

PACS: 07.07.Df, 61.48.De, 68.43.-h,77.84.Bw

1. Introduction

Semiconductor metal oxide gas sensors proposed in 1962 [1] have been widely used for detection of different gases. Different gas, smoke and ion-selective sensors were investigated and developed at Yerevan State University. Gas sensors were made from Bi_2O_3, SnO_2, ZnO, TiO_2, In_2O_3, Ga_2O_3, Fe_2O_3, $NaBiTi_2O_6$, $LaAlO_3$-$CaTiO_3$, $Bi_2V_4O_{11}$ thin films and ceramic materials as well as porous silicon [2–7]. Our Bi_2O_3 smoke detectors are competitive with photoelectric (optical) and ionization detectors of smoke, which currently can be widely used in fire-alarm systems [8, 9]. Independent testing of our adsorptive type smoke detectors in the USA yielded fairly promising results.

There are several commercial products now, especially made of tin dioxide material (see, for example, www.figarosensor.com, www.honeywell.com, www.sinkera.com etc.). Sensors in the market are mainly based on a change of their resistivity R after gas exposure. Advantages of some semiconductor gas sensors are their rather high response (sensitivity), simple design, low cost. Nevertheless, these types of sensors continue to suffer from high temperature of the pre-heating of work body of the sensor (high consumption of energy) as well as lack of selectivity, which limits their applications. SnO_2 conventional sensors do not perform well when operated at room temperature. The range of their operating temperatures spans from 200 to 500 °C. For example, the sensor for O_3 gas appeared to be most effective at 350 °C [10, 11]. Many commercial SnO_2-based sensor devices have been realized to detect organic compounds and hazardous gases (e. g. CO and NO) [12]. These gas sensors often operate at high temperatures up to 400 °C in order to realize high gas sensitivity. Note also that the existing platinum wire sensors need the temperature of pre-heating of the work body above 400 °C and have very high cost.

The main problem today is to develop new semiconductor gas sensors working without the preheating of the work body. In addition, they should be small, cheap and easy to be inserted into microelectronic integral circuits. We will briefly report below the results of our investigations of metal oxide

carried out with the aim to decrease the temperature of their work body.

At the beginning of this review, we will report our results of the development of metal oxide hydrogen sensors. There are many types of H_2 sensors – see, for example, review papers [3–7, 15]. One of the main objectives for the research at YSU was to decrease the particle size of metal oxide which increases the effective surface area for gas adsorption. The existence of nanosized particles, porosity of films, and large surface/volume ratio ensure high sensitivity. Below a certain critical nanocrystalline size, when it becomes comparable with the double space-charge layer thickness, the sensitivity of the gas sensors increases sharply. For a nanocrystalline SnO_2 thin film or powder, the calculated value of the space-charge layer thickness is equal to ≈ 3 nm. There are different methods for manufacture of particles with required sizes. The sol–gel techniques are among these methods. The sol–gel process has many advantages with respect to other processes. These advantages include low processing temperatures and the possibility of chemically tailoring the starting solutions, resulting in new compositions and better control of the final microstructure as well as high specific area of the sensing layer. Another SnO_2 thin film processing technology is based on the reactive ion-plasma assisted sputtering in the presence of Ar/O_2 gas mixture and sol–gel deposition. It leads to an improvement of the sensitive films adhesion with the substrate and thus reliability. As a result, the superposition of technologies allowed obtaining both double layer structures of SnO_2 ensuring good adhesion with the substrate and highly gas sensitive SnO_2 one-dimensional nanostructures.

The results of our R&D works are presented in [15, 16]. We studied the response of sensors to detect the presence of H_2 in air at various temperatures (25–300 °C). As a result, the maximal response is registered in the 80–130 °C range of operating temperatures; however, rather high sensitivity to H_2 gas at room temperatures was observed.

Our hydrogen leakage sensor is shown in Fig. 1. Most part of it contains batteries for realization of high temperature of the pre-heating of the work body. The data for the TGS 821 Figaro sensor, *Synkera Technologies Inc*. (Trace H_2 Sensor P/N 701), and our hydrogen sensor are given in the Table. The comparison of heater power consumption showed that, in particular, it is 5 and more times lower for our sensor, but the sensitivity to hydrogen is much higher.

Other reviews of hydrocarbon, NO_x and carbon monoxide gases metal oxide sensors were published in [3, 17–19].

Several studies [20–25] have been focused on doping the SnO_2 matrix to increase the sensitivity of the resulting sensors. Introduction of transitional metal cations into an oxide matrix leads to an increase in surface states, active sites and free carriers, which is important for gas sensor application. For example, the addition of Nb into TiO_2 enhanced the response to CO as it induces the formation of new electronic states, due to its donor-type behaviour. Tin dioxide doped with vanadium has a higher response towards SO_2 gas because of its redox activity for SO_2 oxidation to SO_3. Doping with CuO, MoO_3 and Fe_2O_3 leads to lowering of the pre-heating of the work body of a sensor and increase in gas response. Vanadium cations serve as reducible

Table. * YSU thin-film H_2 sensor; (1) ** commercial sensors by *Synkera Technologies Inc*. (Trace H_2 Sensor P/N 701) and (2) ** by *Figaro Inc*. (TGS 821 H_2 sensor).

Property	Symbol	YSU sensor*	Remarks	(1)**	Remarks	(2)**	Remarks
Heater power consumption	P_H	120 mW	At V_H = 3.5 V	~600 mW	At V_H = 5.4	660 mW	At V_H = 5.0 V
Heater voltage	V_H	3.5 V_{DC}	120 °C	5.4 V_{DC}	T_{sensor} ~240 °C	5.0 ± 0.2 V	AC or DC
Heater resistance	R_H	75 Ω	At room temp.	32 ± 2 Ω	At room temp.	38.0 ± 3.0 Ω	At room temp.
Sensing voltage	V_C	5.0	Recom.	5.0 V_{DC}	Recom.	Max 24 V	DC only
Sensitivity at 1000 ppm H_2	$S(R_S/R_G)$	~10^3	–	~10	–	$1.6 \cdot 10^2$	–
Response time at 100 ppm	τ_{res}	<7 s	(90% response)	15 s	(90% response)	–	–

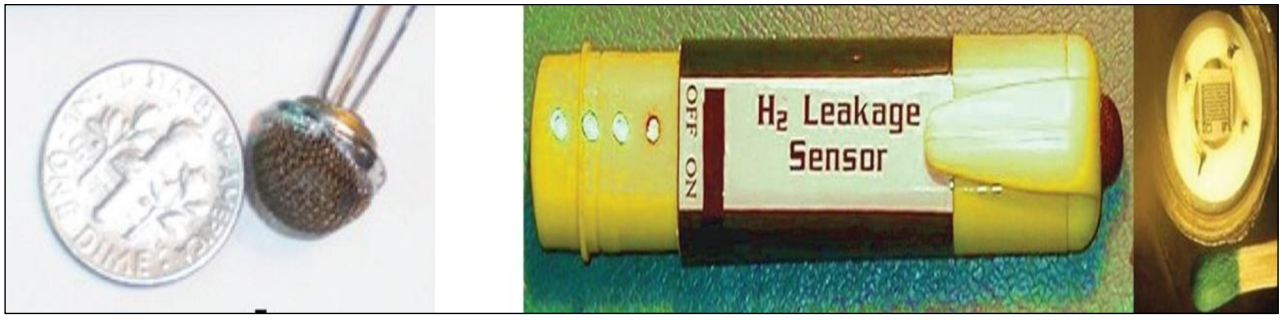

Fig. 1. Hydrogen leakage sensor.

catalytic centers to promote oxidation reactions and enhance O_2 consumption [24–26].

2. Carbon nanotube gas sensors

Carbon nanotubes (CNT) are extensively studied and have opened a new science and technology field on nanoscale materials [27–32]. CNTs are one-dimensional materials – quantum wires [30–32]. CNTs are graphene sheets of covalently bonded carbon molecules rolled into hollow cylinders. There are two main types of CNTs: single-walled nanotubes (SWCNTs), which have a single carbon layer, and multi-walled nanotubes (MWCNTs), which have multiple layers of carbon that are concentrically nested together.

CNTs demonstrated a unique mix of electrical, optical, thermal and mechanical properties. The potential of applications of CNTs is shown in a wide range of science and technology: nanoelectronics, displays, hydrogen storage, batteries, etc. (see, for example, review-papers [33–37]). The development of CNT based gas sensors and sensor arrays has attracted an intensive research interest in the last years. Easy CNT configurations as chemiresistors and chemical field effect transistors are used as nanosensors. Here the electrical properties of nanostructures are dramatically changed when exposed to the target gas analytes. A rich π-electron conjugation is formed outside of the CNTs, making them electrochemically active, sensitive to charge transfer and chemical doping effects by various molecules [38]. When electron-withdrawing molecules (e. g. NO_2 or O_2) or electron-donating molecules (e. g. NH_3) interact with p-type semiconducting CNTs, they change the density of holes in the nanotube and its conductivity [39].

Pristine SWCNTs have low adsorption and affinity or long recovery time. Therefore, they cannot be used as basic material for a gas sensor. These shortcomings can be, at least in part, circumvented by a CNTs functionalizing (decoration).

There are the following approaches for the surface functionalization of CNTs: by organic materials, doping of CNTs, by a catalytic metal nanoparticle/nanocluster as well as metal oxides. Such approaches are discussed below.

Enhanced gas sensing by SWCNTs with organic polymers has been reported [36]. It was shown that non-covalent drop coating of polyethylene (PEI) and Nafion (a polymeric perfluorinated sulfuric acid monomer) onto SWNT ChemFETs resulted in gas sensors with improved sensitivity and selectivity for NO_2 and NH_3 [40]. SWCNTs were able to detect less than 1 ppb NO_2 while being insensitive toward NH_3. In contrast to PEI-coated sensors, Nafion coated SWNTs were insensitive to NO_2 while exhibiting a good sensitivity toward NH_3 [41]. PEI–polymer-coated SWCNT ChemFETs are used as CO_2 gas sensors. The SWCNT-ethyl cellulose and polymethylmethacrylate sensors are reported, chlorosulfonated polyethylene and hydroxypropyl cellulose are used for detection of Cl_2 and HCl [36]. A synergistic effect in the oxygen and NH_3 gas sensitivity of polypyrrole/SWCNT composites was demonstrated [42]. The modification in polypyrrole results in a synenergistic effect – nanocomposites are ten times more sensitive than sensors made of polypyrrole or SWCNT separately.

Single wall and multiwall CNTs decorated with different metals (Rh, Ni, Au, Pd etc.) were proposed for detecting H_2S, CH_4, H_2, CO, O_3, C_6H_6 and NH_3 [44]. Since the adsorption of a small quantity of chemical species results in a dramatic change of their conductivity, CNTs with comb electrodes can be used to detect gases at low concentrations (e. g. low ppb level) [41]. CNT-Al clusters showed sensitivity towards ammonia [45, 46]. Pd- or Co-modified CNT sensors to NO_2, NH_3, CO_2, CH_4, CO and C_2H_5OH worked at an operating temperature of 120 °C [46]. Note that in comparison with polymer-based sensors, metal-decorated sensors are mechanically and

chemically robust and stable as well as can operate at higher temperatures in harsher environments.

3. Gas sensors made from metal oxides decorated with CNTs

Combinations of metal oxides and CNTs have been recently used as a material for manufacture of semiconductor gas sensors, lithium-ion batteries and catalysts [47–54]. Gas sensors can be realized on the base of SnO_2/CNTs, TiO_2/CNTs, Fe_2O_3/CNT, WO_3/CNT and Co_3O_4/CNT composites. For example, gas sensors can be based on SnO_2-coated CNTs, SnO_2-filled CNTs and SnO_2-doped with CNTs. For example, the NH_3 gas sensors based only on CNTs [55, 56] and SnO_2 [57–61] have been extensively investigated. However, their gas-sensing performance has not yet been much improved in comparison to SnO_2 as well as CNTs-based sensors.

Using the mix of the SnO_2 nanoparticle with 1 wt.% MWCNTs (100:1) sensing materials, gas sensors were fabricated on micro-platforms made of a thick SiN_x membrane [62]. Such sensors were sensitive to NO_2, NH_3 and xylene gases at the temperature of pre-heating of the work body from 180 °C to 380 °C. It was found that 220 °C was the optimum temperature to have the best sensitivities. The selectivity of NO_2 was better than those of NH_3 and xylene gases.

We used an MWCNT membrane prepared at Yerevan State and/or Szeged (Hungary) universities for the manufacture of the nanocomposite SnO_2/MWCNT thin film gas sensors by the sol–gel method (see, for example, [28–29, 63]). Surface modification of the CNTs/metal-oxide hybrid gas sensors was carried out with noble metals (Pt, Pd, Au, Ru, and Rh). It leads to an improvement of the sensitivity and selectivity of gas sensors [63–64]. As usually, the response (sensitivity) to gases of the MWCNT/SnO_2/Pd sensors was determined as the ratio of the sensor resistance in the air (R_{air}) to the sensor resistance in the presence of the pollutant after reaching a steady state (R_{gas}). The increase in the electron concentration in the semiconductor conduction band results in the reduction of structure resistance in the case of reducing gases media.

It is known that Ru allows enhancing the sensor response and selectivity to hydrocarbons. Ruthenium stimulates an increase in the rate of oxidation and other surface reactions. Adsorption of oxygen from the air on the structure surface causes an increase in the depletion layer of the semiconductor near-surface region and provides the enhancement of response. High response appears only after sensibilization of the MWCNT/SnO_2 tablets in a 0.01 and 0.03 $Ru(OH)Cl_3$ water solution. For example, sensors made from the MWCNT/SnO_2/Pd tablets sensitized with the 0.03 M $Ru(OH)Cl_3$ solution during 20 min showed high response to hydrogen and isobutane (i-butane) already at 120 °C (Fig. 2). Resistivity of the sensor decreased 10 times in ~10 and ~30 s after the injection of isobutane and hydrogen, respectively. Sensors recovered slowly at this temperature – the recovery time was equal to ~30 and 15 min after the switch-off of flow of isobutane and hydrogen at 120 °C, respectively.

Gas i-butane is widely used for domestic purposes, in the cooling plant, and as a fuel, being a part of liquefied petroleum gas (LPG). Vapours of this gas are hazardous to the human health. Therefore, the detection of i-butane vapours in the environment is an important problem. Note that i-butane is not detected by sensors made of pure SnO_2 and pure CNTs. But the response and selectivity of sensors made of a nanocomposite including both CNT and SnO_2, ZnO or another metal oxide are dramatically

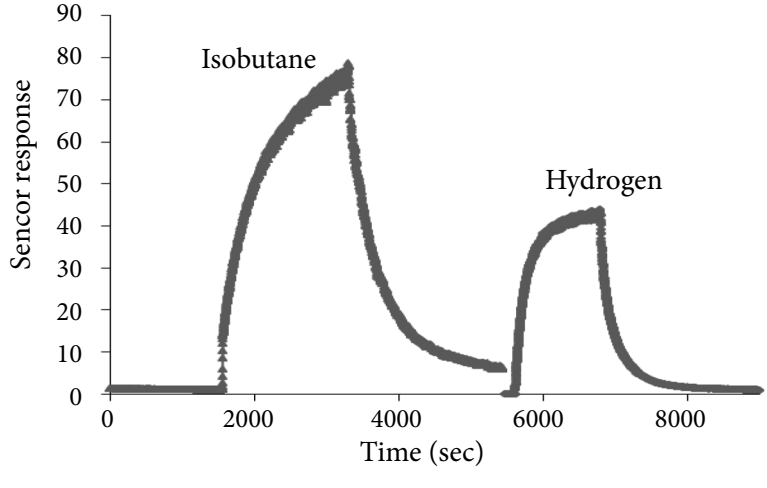

Fig. 2. Sensor response to the 5000 ppm hydrogen and isobutane for the sensor made of the nanocomposite MWCNT/SnO_2/Pd sensitized with the 0.03 M $Ru(OH)Cl_3$ solution at 120 °C.

increased. So, we realized some synenergistic results in such hybrid sensors. The measurements of the sensor response to i-butane at higher temperatures have shown more stable characteristics. The sensor reaches the equilibrium state faster, the recovery time decreases down to ~10 min. The sensor response increases with the increase in temperature. It was mentioned above that the sensitization of the MWCNT/SnO_2 nanocomposite was carried out in the 0.01 and 0.03 M Ru $(OH)Cl_3$ solutions. Note that the sensors made of the MWCNT/SnO_2 nanocomposite and sensitized with the 0.03 M $Ru(OH)Cl_3$ solution were the most sensitive ones. It is important that the response time was nevertheless lower for the samples sensitized in the 0.01 M $Ru(OH)Cl_3$ solution, for it was equal to ~30–40 s, while the response time for the samples sensitized in the 0.03 M $Ru(OH)Cl_3$ solution was equal to ~2–3 min. The sensors made of the nanocomposite MWCNT/SnO_2/Pd and sensitized with the 0.03 M $Ru(OH)Cl_3$ solution during 20 min had faster sensor recovery (the recovery time decreased down to 2–3 min). In order to improve the characteristics, the second annealing after a sensitization with ruthenium at higher temperatures (650 °C and 850 °C) was recommended.

The dependence of the response on the concentration of i-butane is almost linear for the MWCNT/SnO_2/Pd sensors (Fig. 3). For them, almost the same times of response and recovery, ~30–40 s, were reported. They are equal at low concentrations of the gas. Note that parameters of these structures remained stable at long-term testing of sensors.

We also manufactured thick films made of the MWCNT/SnO_2 powder nanocomposite using the sol–gel preparation technique (obtaining samples with MWCNTs/SnO_2 ratio 1:50). The hydrothermal synthesis allowed producing the samples with the MWCNTs/SnO_2 ratio 1:4 and 1:8. Such sensors have shown a sufficiently good response to i-butane at temperatures higher than 200 °C. The sensitization of films in the 0.01 M $Ru(OH)Cl_3$ solution led to better response. The higher response was observed at the temperature of pre-heating of the work body at 250 °C. The response and recovery times are equal to ~30 s. The prepared sensors were sensitive to i-butane already at its concentration of 200 ppm. The maximal response reached 50 at the 5000 ppm concentration.

The analysis of the results of testing of the set of samples made without any catalysts revealed a relatively high response to methanol and ethanol vapours. From the point of view of improvement of sensitivity and selectivity of these sensors to alcohol vapors, we sensitized the set of the MWCNT/SnO_2 nanocomposite with the Ru catalyst. Such sensitization leads to a sharp rise in response to methanol and ethanol vapour up to 10^3 and higher. At that, the cross-sensitivity to other gases decreases. The response to methanol and ethanol vapours appears at the operating temperature of 200 °C and decreases exponentially with a temperature rise up to 300 °C.

The surface-rutheniumated nanocomposite containing a large amount of nanocrystalline SnO_2 (1:50) shows high response both to methanol and ethanol vapours. Simultaneously, a relatively high response to i-butane is also observed. Approximately the same sensitivity to alcohols (about 10^3) remains at the 1:8 ratios of the nanocomposite components, but the response to i-butane sharply decreases. The responses to hydrogen and i-butane disappear completely with the following decreasing of the SnO_2 part in the nanocomposite (at 1:4 weight ratios of the components).

Thick-film volatile organic compounds (VOCs) sensors based on rutheniumated multi-wall carbon nanotubes coated with tin-dioxide nanoparticle nanocomposite structures (MWCNTs/SnO_2) were

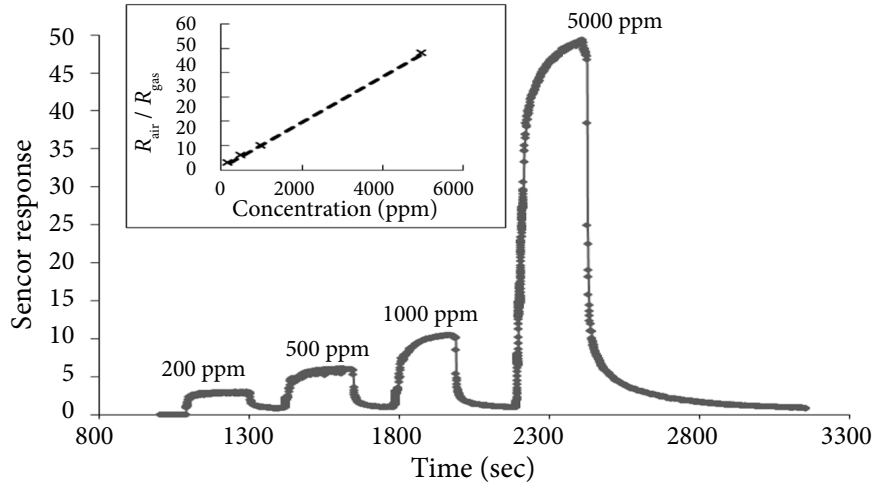

Fig. 3. Sensor response to different concentration of isobutane for the sensors made of the MWCNT/SnO_2/Pd nanostructure sensitized with the 0.01 M $Ru(OH)Cl_3$ solution. Linear dependence of the sensitivity of the sensor on the concentration of gas is shown in the inset.

reported in [65]. It was shown that the optimal conditions for applications as acetone, toluene, ethanol and methanol vapour sensors in view of high response and selectivity relative to each other depend on the choice of the material synthesis method, the mass ratio of the nanocomposite components and the selected operating temperature (see Fig. 4 [65]). MWCNTs/SnO_2 sensor structures having the mass ratio of the components 1:4 and 1:24 exhibit selective sensitivity to acetone and toluene vapours at 150 °C operating temperature, respectively. With an increase in the operating temperature, the response to acetone vapour raises up to 360.4 values, the selectivity remains sufficiently high. The largest response to acetone vapours (R_a/R_g = 555.62) in the steady-state regime was fixed for the set of samples with the 1:200 mass ratio of the components to the 1000 ppm acetone vapours exposure at 250 °C operating temperature (Fig. 4). Response and recovery times of these sensors are about 22 and 27 s, respectively.

Thin film ethanol sensors made from α-Fe_2O_3 decorated with MWCNTs (25:1 weight ratios) were manufactured by the electron beam deposition method [66, 67]. The response of manufactured sensors was investigated at different temperatures of the sensor work body and concentration of gas vapours. A good response of the prepared sensors to ethanol vapours already at the work body temperature of 150 °C was shown (Fig. 5).

Cobalt oxide/MWCNT nanocomposites having a high selectivity for ammonia or CO were synthesized [68–70]. CuO/MWNT thin film based ethanol sensors were manufactured. The sensing response was the maximum at an operating temperature near 400 °C [71]. The MWCNT-doped WO_3 thin film exhibits high sensitivity and selectivity to hydrogen at reduced operating temperatures [72–73].

4. Room temperature sensors

An SnO_2/MWCNT composite-based NH_3 sensor working at room temperature was fabricated using the standard thin film microelectronic technology [74]. At room temperature, the optimal composite sensor exhibited much higher response and faster response and recovery (less than 5 min), the concentration of NH_3 gas ranging from 60 to 800 ppm. An increase in the sensor resistance can be understood taking into account that the composite sensing layer will stay a p-type semiconductor. Probably, the response of the composite sensor should be mainly contributed by the MWCNTs, which have been well known to behave as a p-type semiconductor [55–58]. Comparing with the CNTs-based NH_3 sensor [57, 59] and the SnO_2-based NH_3 sensor [59–61] reported previously, as-synthesized composite SnO_2/MWCNTs-based sensors have a higher response to NH_3 gas at room temperature.

Gas sensors made from doped-CNT/SnO_2 composites for NO_2 detection at room temperature were reported in [75]. The main reason for such response enhancement is a co-existence of two [75–76] different depletion layers and associated potential barriers [53, 76]: one at the surface of the metal oxide grains and the other one at the MWCNT/metal oxide interface. Nitrogen or boron doped CNTs were added into the SnO_2 matrix and enhanced the conductivity of the nanotube. Such a hybrid sensor was prepared to detect low ppb concentrations of NO_2 in air and showed at least 10 times higher response towards NO_2 at room temperature in comparison with the pristine SnO_2 and N or B-substituted CNT sensors [77]. Nitrogen doped MWNTs sensors exhibited response and recovery times of the order of a few seconds. It was recently established [78] that sensors

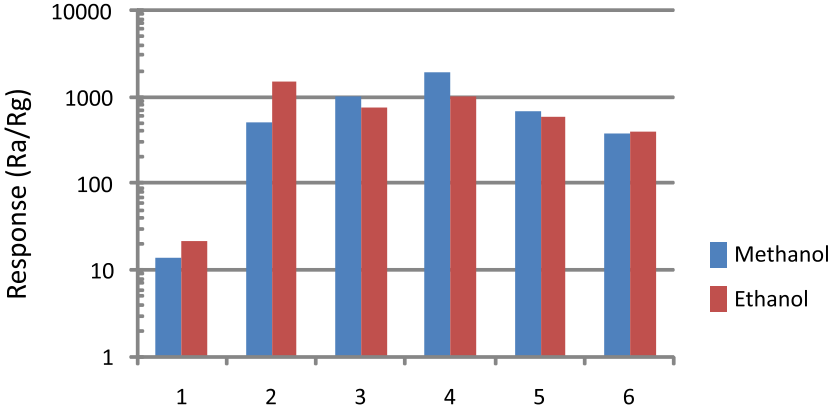

Fig. 4. Response to 1000 ppm methanol and ethanol vapours at operating temperature 200 °C.

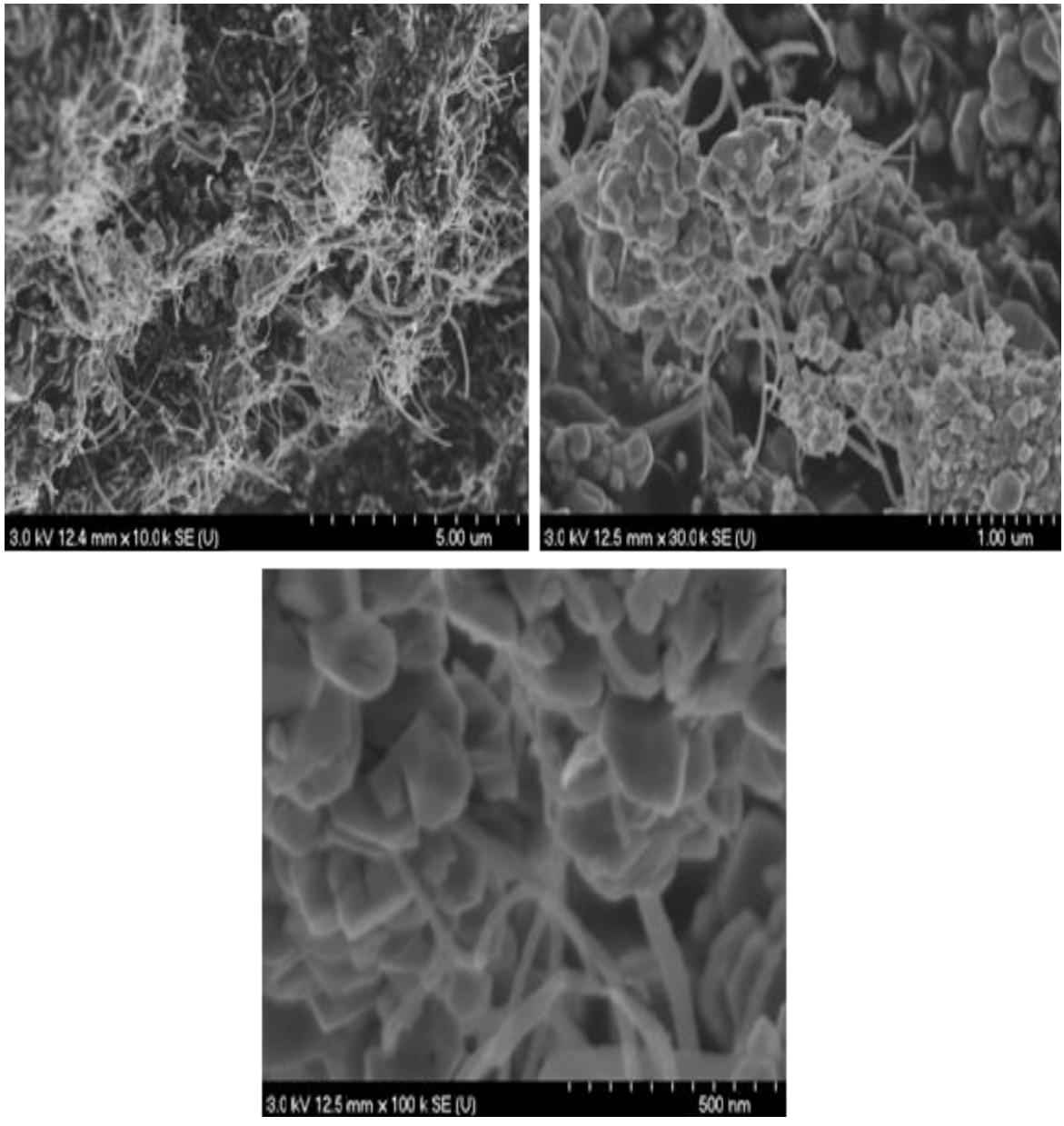

Fig. 5. Thin film ethanol sensors made from α-Fe_2O_3 decorated with MWCNTs by the electron beam deposition method. The morphology of decorated α-Fe_2O_3/MWCNTs (25:1) nanocomposite powder was investigated using the SEM and X-ray diffraction techniques.

made of SnO_2-decorated plasma treated CNTs are sensitive to NO_2 and CO_2 at room temperature. The response time to 1 ppm NO_2 was 4 and 3 min when sensors operated at room temperature and 150 °C, respectively. The response time was 5 min for 2 ppm of CO. Research teams [79–81] supposed that such behavior is the consequence of a decrease in the work function of SnO_2 in the presence of CO and decrease in the sensor resistivity.

The Co_3O_4–SnO_2 material was used in [82]. Its maximum sensor response to CO in the working temperature range from 25 to 100 °C was found at 25 °C. Doping of Co_3O_4–SnO_2 with 0.1% CNT enhanced the CO response of undoped Co_3O_4–SnO_2. The sensor response varied under CO concentrations ranging from 20 to 1000 ppm.

5. Mechanism of response of functionalized sensors to gases

It is obvious today that the doping of metal oxide with CNTs leads to better sensitivity and lower preheating of the work body of a hybrid sensor. Several processes take place in such nanocomposites.

The full picture of complicate phenomena is not possible to propose today, but we have to take into account the following:

MWCNTs have a huge specific surface area and a nanoscale structure, which exposes a large number of sites at which the gases can react. Detection of various gases can be provided at low temperatures of preheating of the work body of a sensor. The electric conductivity of CNTs is much higher in comparison with the conductivity of metal oxides. Therefore, CNTs reduce the resistance of the sensing metal oxide materials.

Since a metal oxide film has mainly n-type semiconductor characteristics and MWCNTs have p-type semiconductor characteristics, there are two depletion layers in such hybrid films. Note that the first depletion region is located at the metal oxide surface and the second one is located in the interface between the metal oxide nanoparticle and the MWCNTs. Formation of nanochannels, p–n or heterojunctions lead to enhanced gas sensitivity of such hybridized gas sensors as the decrease in the work function (barrier height) or increase in the conductivity of the metal oxide sensitive layer lead to the improvement in the performance of the gas sensor at low operating temperature.

Apparently, the discussed possible mechanisms require further experimental and theoretical investigations.

6. Conclusions

1. There are commercial metal oxide gas sensors, especially made of tin dioxide material. Sensors in the market are mainly based on a change of their resistivity after gas exposure. These types of sensors continue to suffer from high pre-heating of the work body of a sensor (above 300 °C), i. e. high consumption of energy, lack of selectivity and long-term stability which limit their applications.

2. The main problem today is to develop new semiconductor gas sensors practically working without preheating of the work body. In addition, sensors should be small, cheap and easy to be inserted into microelectronic integral circuits. Investigations of metal oxide sensors, carried out with the aim to decrease the temperature of their work body, are necessary.

3. Development of metal oxide hydrogen sensors in Yerevan State University showed that a decrease in metal oxide particle sizes led to an increase in the effective surface area for gas adsorption, the porosity of the films and a large surface/volume ratio. Below a certain critical nano-crystalline size, the sensitivity of the gas sensor increases sharply. This occurs when the nanocrystalline size becomes comparable with the double space-charge layer thickness of the semiconductors under consideration. For a nanocrystalline SnO_2 thin film or powder, the calculated value of the space-charge thickness is equal to about 3 nm. There are different methods for getting a nanoparticle with required sizes. We used the sol–gel techniques and reactive ion-plasma assisted sputtering in the presence of Ar/O_2 gas mixture. It leads to an improvement of the sensitive films adhesion with the substrate and thus reliability and long-term stable operation of these gas sensors. As a result, the maximal response is registered in the 80–130 °C range of operating temperatures. High sensitivity to H_2 gas at room temperatures was observed.

4. The development of CNT based gas sensors and sensor arrays has attracted an intensive research interest in the last years. The use of pristine CNTs as sensors is not promising. The functionalization of CNTs can be made with organic materials as well as Pd, Rh, Au and Ni nanoparticles. It allowed detecting H_2S, CH_4, H_2, CO, O_3, C_6H_6, NH_3, NO_2, and C_2H_5OH down to their ppb level.

5. A special interest is displayed in investigations of the possibilities of manufacture of different metal oxide composites functionalized (decorated) with CNTs. We have shown that the sensibilisation of CNT- SnO_2 composites in water solutions of $Ru(OH)Cl_3$ ensured high response to hydrogen, the synenergistic effect during detection of isobutene as well as a lowering of the temperature of pre-heating of the work body of sensors (to 150–200 °C). Such sensors are also sensitive to vapours of VOC gases (acetone, toluene, ethanol and methanol) at the same temperature of pre-heating. Sensors of H_2, NO_x and CO were manufactured from Fe_2O_3, cobalt oxide, $Co_{1-x}N_xFe_2O_4$, CuO and WO_3 with CNTs.

6. Research and development of nanosensors working without the pre-heating of their work body arouse interest. The doping of metal oxides with CNTs leads to greater sensitivity to gases and a lowering of temperature of the pre-heating of the work body (to room temperature).

Different types of conductivity of CNTs and metal oxides, change in the work function (potential barrier), the modulation of formed heterojunctions should be taken into account during the analysis of complicate processes and phenomena in the gas sensitive structures reported above.

Acknowledgements

Many thanks to my colleagues-coauthors of joint works in Armenia, Hungary, the USA and Switzerland for many years of collaboration and helpful discussions.

This work was supported by NATO EAP.SFPP 984.587 and 13-1C075 (State Committee of Science at the Ministry of Education and Science of the Republic of Armenia) projects.

Many years of friendship with Juras, Rima, Elena, Karolis and Rasa Požela gave me possibilities to meet J. Viščakas, J. Vaitkus, A. Vėbra, E. Montrimas, A. Matulionis, V. Jucienė, S. Ašmontas, V. Dienys, R. Dagys, A. Sakalas, E. Starikov, S. Kalvėnas, Č. Mačiulaitis and other colleagues in Vilnius. Many thanks for everything.

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DUJŲ JUTIKLIAI IŠ METALO OKSIDŲ, DEKORUOTI ANGLIES NANOVAMZDELIAIS

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