STUDY OF MWCNTs/SnO_2 NANOCOMPOSITE FORMALDEHYDE GAS SENSOR

Z.N. Adamyan, A.G. Sayunts, E.A. Khachaturyan, V.M. Aroutiounian

Center of Semiconductor Devices and Nanotechnologies at Yerevan State University, Yerevan, Armenia, E-mail:zad@ysu.am

Introduction

Formaldehyde (FA) is a colorless, water-soluble gas with a pungent odor which used in making building materials and many household products such as particleboard, plywood and fiberboard, glues and adhesives, textiles, paper and their product coatings. It is also used to make other chemicals. Formaldehyde is also used extensively as an intermediate in the manufacture of industrial chemicals. It can also be used as a preservative in some foods and in products, such as antiseptics, medicines, and cosmetics [1]. FA impacts on human organs when it exists in the air at levels higher than 0.1 ppm. For example, it can cause burning sensations of the eyes, nose, and throat, coughing, wheezing, nausea, skin irritation. Besides, exposure to relatively high amounts of formaldehyde can increase the risk of leukemia and even cause to some types of cancer in humans. But the effect of exposure to small amounts is less clear [2]. Hence, formaldehyde gas sensors have a huge application for detecting and continuous monitoring this gas, in the spheres where it is used. There are many formaldehyde gas sensors. For instance, FA gas sensors based on graphene or polymers which are working at room temperature [3,4]. On the other hand, FA gas sensors based on metal-oxide materials have advantages such as small sizes, low power consumption and price, repeatability and long reliability [5]. However pure metal-oxide structures react on FA at higher operating temperatures (300-400^{o}C) [6,7] or at room temperature with the assistance of UV LED [8,9]. Nanomaterial such as carbon nanotubes (CNTs) are widely used in gas sensing for their excellent responsive characteristics, mature preparation technology, and low cost of mass production. Due to the covering of CNTs walls with metal-oxide nanoparticles, specific surface area of such gas-sensitive nanocomposites increases more. Moreover, nanochannels in the form of hollows of CNTs promote penetration of gas molecules deeper down in the nanocomposite sensitive layer. Hence, it can be expected that application in gas sensors technology of nanocomposite structures composed of metal oxide functionalized with CNTs should lowering the gas sensor operating temperature [10].

The choice of tin oxide as a component of tin oxide multiwall (SnO_2/MWCNTs) nanocomposite structure is conditioned by the fact that SnO_2 is well known and studied basic material for metal-oxide gas sensors. We expected that coating of functionalized MWCNTs with SnO_2 nanoparticles with admissible, sizes should provide the improved performance of the gas sensor and lowered the temperature of its operating [5]. Here, we present the characteristics of the FA vapor sensors based on ruthenated thick-films MWCNT/SnO_2 nanocomposite structures.

Material and Samples Preparation

MWCNTs membranes, kindly provided to us by our colleagues from the University of Szeged, Hungary, were used for preparation of nanocrystalline MWCNTs/SnO_2 powder. MWCNTs were prepared by the decomposition of acetylene (CVD method) using Fe, Co/$CaCO_3$ catalyst [11,12]. This growth procedure using $CaCO_3$ catalyst enables a highly efficient selective formation of clean MWCNTs, suitable for effective bonding between CNT and metal-oxide, particularly, SnO_2 precursors.

For a functionalization of nanotube walls with oxygen-containing hydroxyl (OH), carbonyl (C=O), and carboxylic (COOH) functional groups, MWCNTs from the membranes were transferred to slurry in HNO_3/H_2SO_4 acids mixture during 1 h. Such a functionalization of the CNTs is very important and necessary for the following synthesis of SnO_2 nanoparticles on the MWCNTs walls since these oxygen-containing groups act as sites for the nucleation of nanoparticles. After rinsing with distilled water and drying at 80^{o}C, MWCNTs were poured and treated in deionized water in

the ultrasonic bath for 5 min. The preparation of SnO_2/MWCNT nanocomposite materials was carried out by a hydrothermal method. The purified MWCNTs is well dispersed in water via sonication. As a precursor solution, calculated amount of $SnCl_2 \cdot 2H_2O$ dissolved in water is used. The chose of water as a solvent, instead of e.g. ethanol, was preferably for us in the view of expected improvement in gas sensing characteristics, taking in account the fact that cover the overwhelming parts of CNTs with SnO_2 nanoparticles is ensured at that [13]. The target final mass ratio of the MWCNT/SnO_2 nanocomposite components for this study was chosen 1:200, respectively. This hydrothermal process described elsewhere in [14-16], in detail. SEM and TEM images of the sensors surface revealed that the average size of SnO_2 nanoparticles covered the nanotubes walls is about 14 nm. The thick films were obtained on the base of MWCNTs/SnO_2 nanocomposite powder. The paste for the thick film deposition made by mixing powders with α-terpineol ("Sigma Aldrich") and methanol was printed on chemically treated surface of the alumina substrate over the ready-made Pt interdigitated electrodes. The thin-film Pt heater was formed on the back side of the substrate. Obtained nanocomposite structures were cut into 3×3 mm pieces. After annealing and cooling processes, the MWCNTs/SnO_2 thick films were surface ruthenated by dipping its into the 0.01 M $RuOHCl_3$ aqueous solution for 20 min whereupon dried at 80°C for 30 min and then annealing treatment was carried out again at the same regime. The choice of the ruthenium as a catalyst was defined by its some advantages [14].

Results and Discussions

Gas sensing properties of the MWCNTs/SnO_2 nanocomposite structures were measured by home-made developed and computer-controlled static gas sensor test system [17]. The sensors were reheated and studied at different operating temperatures. When the electrical resistance of all studied sensors was stable, the vital assigned amount of compound in the liquid state for sensors testing was injected by a microsyringe in measurement chamber. Moreover, the target matters were introduced into the chamber on the special hot plate designed for the quick conversion of the liquid substance to its gas phase. After its resistance reached a new constant value, the test chamber was opened to recover the sensors in air. The sensing characteristics were studied in the 20-300°C operating temperature range and the gas response of the sensors determines as R_a/R_g where R_a and R_g are the electrical resistances in the air and in target gas-air atmosphere, respectively. The response and recovery times are determined as the time required for reaching the 90% resistance changes from the corresponding steady-state value of each signal.

Firstly, we should determine the operating temperature of the sensors. As a result of measurements of the sensor resistance in air and air/gas environment, the maximal response to 1160 ppm of FA vapor was revealed at 200°C operating temperature (Fig. 1). Dependence of the response and recovery times of MWCNTs/SnO_2 FA vapor sensor on operating temperature is shown in Fig.2.

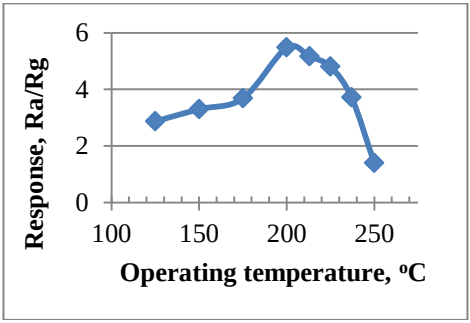

Fig. 1. Response of MWCNTs/SnO_2 thick-film FA sensors vs operating temperature.

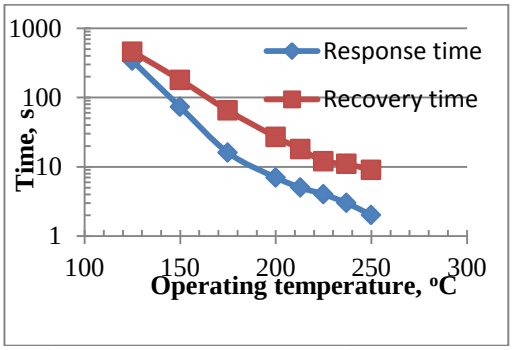

Fig. 2. Dependence of the response and recovery times of MWCNTs/SnO_2 FA vapor sensor on operating temperature.

Dependence of the resistance and response of MWCNTs/SnO_2 sensor on FA vapor concentration is shown in Fig. 3 and Fig. 4 respectively. As it is obvious from the figures, the sensor response occurs down to gas concentrations but the response approximately linearly depends on the gas concentration.

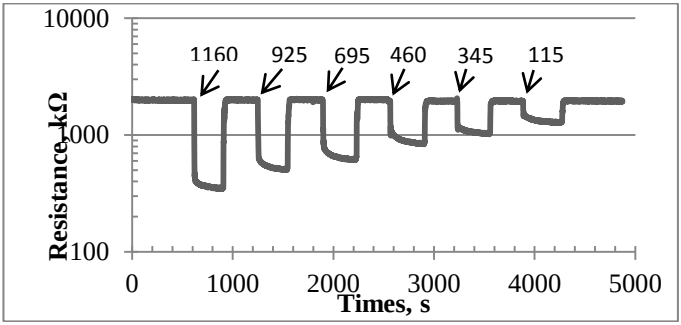

Fig. 3. The response/recovery curves observed at different FA gas concentrations (values of the ppm are mentioned within the picture) exposure measured at 200°C operating temperature.

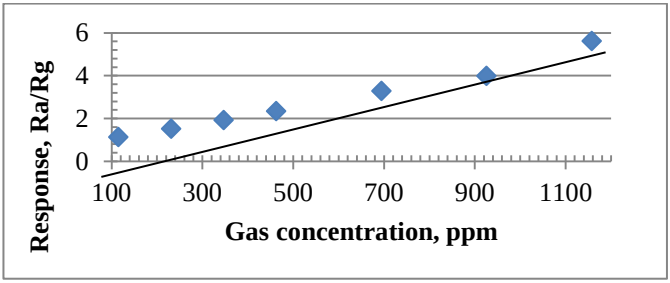

Fig.4. Dependence of the response of MWCNTs/SnO_2 FA vapor sensor on gas concentration measured at 200°C operating temperature.

FA gas sensing mechanism is not fully researched so far. It is proposed that the HCHO sensing process can be described by the commonly accepted gas sensing mechanism for n-type semiconducting metal oxides including SnO_2. Namely, as a result of adsorption-oxidation and desorption processes sensor surface is covered by chemisorbed oxygen ions, such as O^- and O^{2-}. When sensor exposed with FA gas HCHO molecules interact with the adsorbed oxygen according to the following reactions.

$$2O^- + HCHO \leftrightarrow H_2O + CO_2 + 2e^- ,$$
$$2O^{2-} + HCHO \leftrightarrow H_2O + CO_2 + 4e^- .$$

These reactions lead to enhance the free electron concentration which causes the decrease of the resistance of SnO_2. The role of carbon nanotubes in this case, apparently, is that the presence of nanotubes in the nanocomposite prevents the formation of SnO_2 agglomerates of nanoparticles, thereby providing a more developed and porous surface. In addition, hollow nanotubes facilitate the penetration of gas molecules into the interior of the nanostructured film and the yield of the products of the chemisorption reaction to the atmosphere. These facts lead to an increase in the sensitivity of the film to the acting gas, and to an improvement in the operation speed of the sensors (both the response and recovery times are on the order of seconds).

Conclusion

In this paper, we have carried out the investigation of obtaining ruthenated MWCNTs/SnO_2 thick-film nanocomposite sensors using hydrothermal synthesis and sol-gel technologies. The maximal response of FA vapor was revealed at 200^{o}C operating temperature. Response and recovery times of the sensors decrease with the increase in the operating temperature. The responses and short response and recovery times of the sensors (at the order of seconds) are observed under all gas concentrations influence at 200^{o}C operating temperature. The lowest FA gas concentration at which the perceptible signal ($R_a/R_g = 1.4$) is registered is 115 ppm.

Due to the linear dependence of the response on the concentration of FA gas, it is possible to easily measure the concentration of this gas in the atmosphere.

Acknowledgment: This work was supported by NATO EAP SFPP 984.597.

References

1. ***M.-A. Lefebvrea, W.J.A. Meulingb et al.*** Regulatory Toxicology and Pharmacology, **63**, 171, (2012)
2. ***L. Zhang, X. Tang, N. Rothman et al.***. Cancer Epidemiol Biomarkers Prev, **19**, 80, (2010)
3. ***W.-Y. Chuang, S.-Y. Yang, W.-J. Wu, C.-T. Lin.*** Sensors, **15**, 28842, (2015)
4. ***J. Flueckiger, F.K. Ko, K.C. Cheung.*** Sensors, **9**, 9196, (2009)
5. ***V.M. Aroutiounian.*** NATO Science for Peace and Security, Series B: Physics and Biophysics, Chapter 9, (2012)
6. ***K. Xu, D. Zeng, S. Tian, S. Zhang, C. Xie.*** Sensors and Actuators B, **190**, 585, (2014)
7. ***H.J. Park, N.-J. Choi et al***. Sensors and Actuators B, **203,** 282, (2014)
8. ***F.-C. Chung, R.-J. Wu, F.-C. Cheng.*** Sensors and Actuators B, **190,** 1, (2014)
9. ***X. Li, X. Li, J. Wang, S. Lin.*** Sensors and Actuators B, **219,** 158, (2015)
10. ***V.M. Aroutiounian.*** Journal of Contemporary Physics, **50**, 333, (2015)
11. ***E. Couteau, et al.*** Chem. Phys. Lett., **378**, 9, (2003).
12. ***A. Magrez, J.W. Seo, R. Smajda, M. Mionić, L. Forró.*** Materials, **3**, 4871, (2010)
13. ***Z. Nemeth, B. Reti, Z. Pallai et al.*** Phys. Status Solidi B, **251**, 1, (2014)
14. ***V.M. Aroutiounian, A.Z. Adamyan et al.*** Sensors and Actuators B, **177**, 308, (2013)
15. ***Z. Nemeth, Z. Pallai et al.*** J. of Coating Science and Technology, **1**, 137, (2014)
16. ***V. Aroutiounian et al.*** Int. J. of Emerging Trends in Science and Technology (IJETST), **01/08**, 1309, (2014)
17. ***A.Z. Adamyan.*** Izvestiya NAN RA and GIUA, Tekhnicheskie nauki, LIX, **1**, 155, (2006).