Int. J. Bio-Inorg. Hybr. Nanomater., 7(4): 315-319, Winter 2018

Enhanced methanol sensing performance of oblique deposited WO_3 thin films

E. Amani[1,], K. Khojier[2], S. Zoriasatain[3]*

[1,3] *Department of Physics, North Tehran Branch, Islamic Azad University, Tehran, Iran*
[2] *Department of Physics, Chalous Branch, Islamic Azad University, Chalous, Iran*

Received: 2 September 2018; Accepted: 6 November 2018

ABSTRACT: Methanol (CH_3OH) is a colorless liquid with a mild odor. The wide ranges of applications, toxicity and clinical implications of methanol have made necessary to develop reliable and high-performance methanol sensors. In this paper, WO_3 thin films were deposited on SiO_2/Si substrates by e-beam evaporation technique under normal and oblique angles and then post-annealed at 500 °C with a flow of oxygen for 4h to achieve a good crystallinity. The crystalline structure of the samples was confirmed by X-ray diffraction analysis while the physical adsorption isotherm was used to measure the porosity and effective surface area. These results reveal that the deposited sample under oblique angle shows more crystallinity, and porosity relative to the sample deposited at the normal angle. The response of the samples was tested with respect to methanol vapour with different concentrations in the temperature range of 140–260 °C. Reproducibility and stability of the samples were also investigated.

Keywords: *Methanol, Sensing properties, Thin film, WO_3.*

INTRODUCTION

Methanol (CH_3OH) or methyl alcohol is a colorless liquid with a mild odor, a boiling point of 65.15 °C, a melting point of -93.9 °C and a density of 0.7914 gr/cm^3 at 20 °C (Mirzaie, *et al.*, 2016). Methanol is a very useful organic solvent with widespread applications in automotive fuel and manufacturing of colors, dyes, drugs, perfumes, formaldehyde, etc. (Mirzaie, *et al.*, 2016, Patel, *et al.*, 2003, Patnaik, 2007). Methanol is highly toxic, causing acidosis and blindness. The symptoms of methanol poisoning include nausea, abdominal pain, headache, blurred vision, shortness of breath, and dizziness. Inhalation in humans may produce the headache, drowsiness and eye irritation. Prolonged skin contact may cause dermatitis and scaling. Eye contact can cause burns and damage vision (Mirzaie, *et al.*, 2016, Sahay and Nath, 2008). Therefore, there is the need of development of a reliable methanol sensor. According to the literature, metal oxide semiconductor (MOS) gas sensors such as α-Fe_2O_3 (Zolghadr, *et al.*, 2016, Yang, *et al.*, 2016), In_2O_3 (Han, *et al.*, 2015, Xu, *et al.*, 2015), WO_3 (Zou, *et al.*, 2012, Upadhyay, *et al.*, 2014), SnO_2 (Guo, *et al.*, 2013, Srivastava, *et al.*, 2011), CuO (Par-

(*) Corresponding Author - e-mail: e.amani.info@gmail.com

mar, 2011), and ZnO (Sahay, 2008, Teimoori, *et al.*, 2017) are able to detect the methanol vapour. Among different MOSs, WO_3 due to the chemical stability and high diffusion coefficient of oxygen vacancies may be a good candidate for this goal. It is well known that oblique deposition is a powerful technique to the growth of porous structures and the porous nano-materials possess large surface-to-volume ratios, well-defined and uniform pore structures, which can increase the adsorbent amount of analytic gas and accelerate the transmission speed so as to enhance the sensitivity (Li, *et al.*, 2011, Zhang and Zhang, 2012). This research also focuses on the methanol vapour sensing performance of the WO_3 thin films deposited by e-beam evaporation method under normal and oblique (60°) angles.

EXPERIMENTAL DETAILS

WO_3 thin films were deposited by e-beam evaporation technique on ultrasonically cleaned SiO_2/Si substrates under normal and oblique angles (60°). An Edwards coating plant (Edwards E19 A3) was employed to this goal. Film thickness and deposition rate were controlled using a quartz crystal deposition rate controller (Sigma Instruments, SQM-160, USA) positioned close to the substrate. A summary of the deposition parameters is presented in Table 1. Prior to deposition, a pair of Au interdigital electrodes with gaps of 50 μm and thickness of 50 nm was first formed on the SiO_2/Si (400) substrates. The device was then annealed at 500 °C for 90 min with a flow of (200 sccm) high purity argon gas in a tube furnace (Khojier, *et al.*, 2016). After deposition, in order to improve the nano-structure and crystalline properties, the WO_3 thin films were post-annealed in the tube furnace at the temperature of 500 °C with an oxygen flow of 200 standard cubic centimeters per minute (sccm) for 4 h.

Table 1. The deposition parameters of the WO_3 thin films

Parameter	Value/Item
Substrate size	1×1 cm^2
Source target	WO_3 pellet (99.9% purity)
Source to substrate distance	30 cm
Film thickness	100 nm
Base pressure	2×10^{-7} mbar
Deposition rate	0.4 Å/S
Deposition angles	Normal (0°) and oblique (60°)

Structural analysis of the samples was carried out using a Philips XRD X'pert MPD Diffractometer (Cu Kα radiation) with a step size of 0.02° and a step time of 1 s. The pore size distribution and effective surface area of the films were determined by a Quantachrome AUTOSORB-1-MP at liquid nitrogen temperature. For pore size distribution measurement, isothermal adsorption–desorption of Ar gas was carried out. The effective surface area of WO_3 thin films was also determined by isothermal Kr gas physical adsorption measurements. In order to investigate the gas sensing of the samples, the electrical resistance of the samples were measured in the air and presence of methanol vapor (10 and 50 ppm) in the temperature range of 140-260 °C and relative humidity (RH) of 80%. The gas response is defined as follows (Upadhyay, *et al.*, 2014):

$$S(\%) = \frac{\left(R_{air} - R_{gas}\right)}{R_{air}} \times 100 \quad (1)$$

Where, R_{gas} and R_{air} are the electric resistances of a sensitive film in methanol vapor and in the air, respectively. The response time is the time interval over which response of the sensor materials attains a fixed percentage (usually 90%) of final value when the sensor is exposed to full-scale concentration of the gas, and the recovery time is also the time interval over which response reduces to 10% of the saturation value when target gas is switched off and the sensor is placed in synthetic air (Khojier, *et al.*, 2016). The calculating method of concentration and injection volume for methanol can be also found in (Luo, *et al.*, 2016).

RESULTS AND DISCUSSION

As mentioned in the previous section, the crystal phase of the sample was characterized by X-ray diffraction (XRD) analysis. It can be observed in Fig. 1 that both samples deposited at the normal and the oblique angles show three peaks belong to (200), (202) and (400) of WO_3 with monoclinic structure (with reference to JCPDS Card No. 83-0950, 2Θ: 24.3668°, 34.1673°,

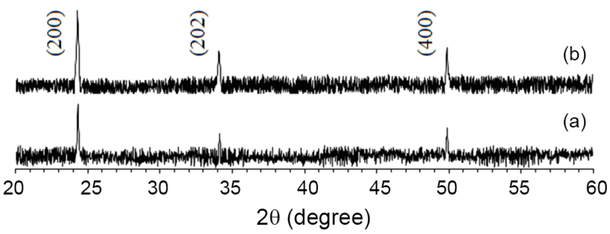

Fig. 1. XRD patterns of the WO_3 thin films deposited at (a) normal and (b) oblique angles.

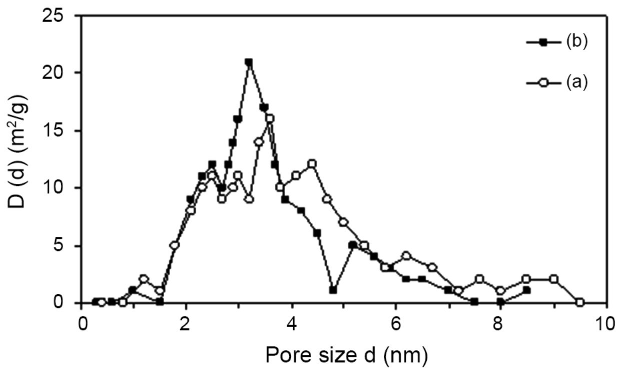

Fig. 2. Pore size distribution of the WO_3 thin films deposited at (a) normal and (b) oblique angles.

and 49.9325°). However, the diffraction lines become higher for the sample deposited at the oblique angle. Pore size distribution of the samples deposited at the normal and the oblique angles are depicted in Figs. 2. It can be seen that the samples deposited at the normal and the oblique angles have a pore size distribution peaked at about 3.6 nm and 3.2 nm, respectively. The effective surface area is obtained to be 4.8 m2/g and 5.4 m^2/g for the deposited sample at the normal and the oblique angles. From these results, it can be deduced that the sample deposited at the oblique angle

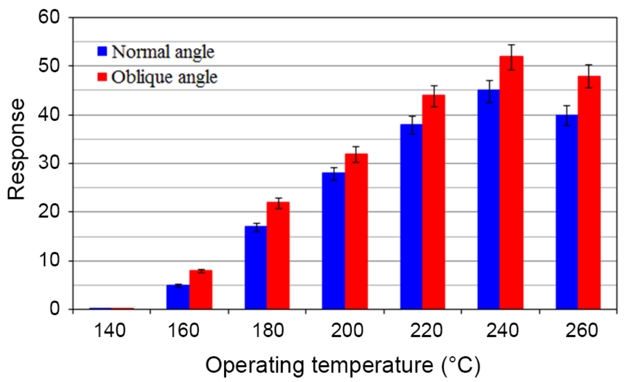

Fig. 3. Response value of the WO_3 thin films deposited at normal and oblique angles to methanol vapour (50 ppm) as function of temperature.

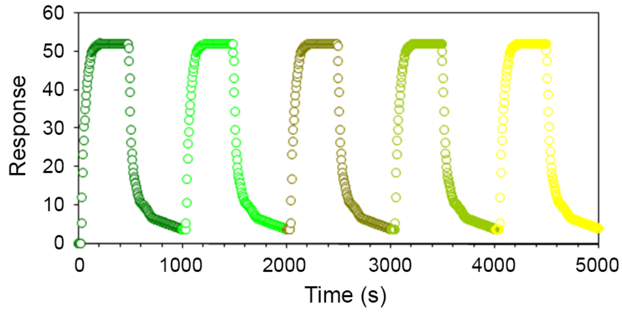

Fig. 4. Dynamic response of the WO_3 thin film deposited at oblique angle to 50 ppm methanol vapour at the operating temperature of 240 °C, a test for reproducibility.

presents more and smaller pores in the film structure which in turn results in more porosity and effective surface area.

It is well known that the response of MOS gas sensors is strongly affected by the operating temperature. In order to determine the optimum operating temperature of the samples based sensor the response of both samples was tested to 50 ppm methanol vapour as a function of operating temperature. The results are depicted in Fig. 3 that shows the best response for both samples is obtained at the operating temperature of 240 °C. In addition, it can be observed that the sample deposited at the oblique angle shows more response or sensitivity to methanol vapour. The enhanced sensitivity of the sample deposited at the oblique angle can be also due to the more porosity and effective surface area of the mentioned sample.

In order to investigate of the detection limit of the WO_3 thin film deposited at the oblique angle as the selected sample, the response of the sample was tested to various concentration of methanol vapour in the range of 10-50 ppm. The values of the response were obtained as following order; 7 for 10 ppm, 24 for 20 ppm, 37 for 30 ppm, 46 for 40 ppm, and 52 for

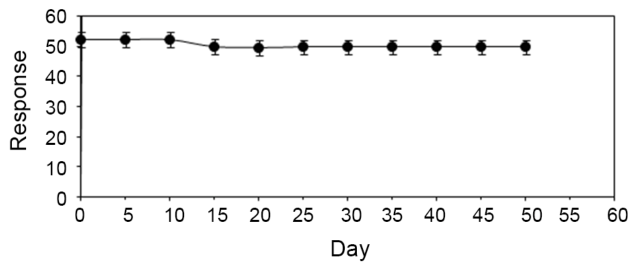

Fig. 5. Response value of the WO_3 thin films deposited at oblique angle to methanol vapour (50 ppm) at the operating temperature of 240 °C as function of day, a test for stability.

50 ppm. The sensor reliability is greatly dependent on the reproducibility and stability exhibited by the sensor material (Zolghadr, *et al.*, 2016). Fig. 4 depicts the dynamic response of the selected sample to 50 ppm methanol vapour at the operating temperature of 240 °C during five consecutive tests. As can be seen, the sample shows acceptable behaviour after five times of switching between 'ON' and 'OFF' states. In order to investigate the stability of the sample based sensor, the response of the selected sample was tested to 50 ppm methanol as a function of the day at the operating temperature 240 °C. The results are shown in Fig. 5 that indicates the good stability of the sample.

CONCLUSIONS

Methanol vapour sensing properties of the WO_3 thin films was studied. The WO_3 thin films were deposited by e-beam evaporation technique on SiO_2/Si substrates at the normal and the oblique (60°) angles, and then post-annealed at 500 °C for 4h with the flow of oxygen. The results showed that the sample deposited at the oblique angle was more sensitive to methanol vapour due to more porosity than that deposited at the normal angle. The WO_3 thin film based methanol sensor also showed a good reliability.

ACKNOWLEDGMENT

This work was carried out with the support of the Islamic Azad University, North Tehran branch. The authors are also grateful to Dr. Karim Shabani for partial support of this work.

REFERENCES

Mirzaie, A., Leonardi, S.G. and Neri, G., (2016). Detection of hazardous volatile organic compounds (VOCs) by metal oxide nanostructures-based gas sensors: A review. Ceram. Int., 42: 15119-15141.

Patel, N.G., Patel, P.D. and Vaishnav, V.S., (2003). Indium tin oxide (ITO) thin film gas sensor for detection of methanol at room temperature. Sens. Actuators B, 96: 180-189.

Patnaik, P.A., (2007). Comprehensive Guide to the Hazardous Properties of Chemical Substances. John Wiley & Sons, New Jersey, US.

Sahay, P.P. and Nath, R.K., (2008). Al-doped ZnO thin films as methanol sensors. Sens. Actuators B, 134: 654-659.

Zolghadr, S., Khojier, K. and Kimiagar, S., (2016). Study of sensitivity and selectivity of α-Fe2O3 thin films for different toxic gases and alcohols. Mater. Sci. Semicond. Preocess, 54: 6-13.

Yang, H.M., Ma, S.Y., Yang, G.J., Jin, W.X., Wang, T.T., Jiang, X.H. and Li, W.Q., (2016). High sensitive and low concentration detection of methanol by a gas sensor based on one-step synthesis α-Fe2O3 hollow spheres. Mater. Lett., 169:73-76.

Han, D., Song, P., Zhang, S., Zhang, H., Xu, Q. and Wang, Q., (2015). Enhanced methanol gas-sensing performance of Ce-doped In_2O_3 porous nanospheres prepared by hydrothermal method. Sens. Actuators B, 216: 488-496.

Xu, X., Li, X., Zhang, H., Feng, C., Wang, C., Liu, F., Sun, Y., Sun, P. and Lu, G., (2015). Synthesis, characterization and gas sensing properties of porous flower-like indium oxide nanostructures. RSC Advances, 5 (38): 30297-30302.

Zou, X.X., Li, G.D., Wang, P.P., Su, J., Zhao, J., Zhou, L.J., Wang, Y.N. and Chen, J.S., (2012). A precursor route to single-crystalline WO_3 nanoplates with an uneven surface and enhanced sensing properties. Dalton Trans, 41: 9773-9780.

Upadhyay, S.B., Mishra, R.K. and Sahay, P.P., (2014). Structural and alcohol response characteristics of Sn-doped WO_3 nanosheets. Sens. Actuators B, 193: 19-27.

Guo, J., Zhang, J., Ju, D., Xu, H. and Cao, B., (2013). Three-dimensional SnO Microstructures Assembled by Porous Nanosheets and Their Superior Performance for Gas Sensing. Powder Technol., 250: 40-45.

Srivastava, P.P.J., Mishra, V.N. and Dwivedi, R., (2011). Structural and micro structural studies of PbO-doped SnO2 sensor for detection of methanol, propanol and acetone. J. Nat. Gas Chem., 20: 179-183.

Parmar, M. and Rajanna, K., (2011). Copper (II) oxide thin film for methanol and ethanol sensing. Int. J. Smart Sens. Intell. Syst., 4: 710-725.

Sahay, P.P. and Nath, R.K., (2008). Al-doped ZnO thin films as methanol sensors. Sens. Actuators B, 134: 654-659.

Teimoori, F., Khojier, K. and Dehnavi, N.Z., (2017). Investigation of sensitivity and selectivity of ZnO thin film to volatile organic compounds. J. Theor. Appl. Phys., 11: 157-163.

Li, Y.S., Xu, J., Chao, J.F., Chen, D., Ouyang, S.X., Ye, J.H., Shen, G.Z., (2011). High-aspect-ratio single-crystalline porous In_2O_3 nanobelts with enhanced gas sensing properties. J. Mater. Chem., 21: 12852-12857.

Zhang, W.H. and Zhang, W.D., (2012). Biomolecule-assisted synthesis and gas-sensing properties of porous nanosheet-based corundum In2O3 microflowers. J. Solid State Chem., 186: 29-35.

Khojier, K., Savaloni, H., Habashi, N. and Sadi, M.H., (2016). On the influence of temperature gradient of annealing process on the nano-structure and sensing properties of WO_3 thin films to NO_2 gas and relative humidity. Mater. Sci. Semicond. Process, 41: 177-183.

Luo, S., Shen, Y., Wu, Z., Cao, M., Gu, F. and Wang, L., (2016). Enhanced ethanol sensing performance of mesoporous Sn-doped ZnO. Mater. Sci. Semicond. Process, 41: 535-543.

AUTHOR (S) BIOSKETCHES

Eimira Amani, Department of Physics, North Tehran Branch, Islamic Azad University, Tehran, Iran, *Email: e.amani.info@gmail.com*

Kaykhosrow Khojier, Assistant Professor, Department of Physics, Chalous Branch, Islamic Azad University, Chalous, Iran

Susan Zoriasatain, Department of Physics, North Tehran Branch, Islamic Azad University, Tehran, Iran