Available online at www.sciencedirect.com

ScienceDirect

Procedia Engineering 87 (2014) 1011 – 1014

Procedia Engineering

www.elsevier.com/locate/procedia

EUROSENSORS 2014, the XXVIII edition of the conference series

Effect of hexagonal WO_3 morphology on NH_3 sensing

M. Takács[a,b], Cs. Dücső[a] , Z. Lábadi[a] and A.E. Pap[a]*

[a]*Institute of Technical Physics and Materials Science – MFA, Research Centre for Natural Science, Hungarian Academy of Scineces, Konkoly-Thege Miklós út 29-33, H-1121 Budapest, Hungary*

[b]*Budapest University of Technology and Economics, Műegyetem rkp. 3, H-1111 Budapest , Hungary*

Abstract

Tungsten oxide nano-powders were prepared by acidic precipitation from sodium tungstate solution. The alternative processes of the applied hydrothermal method resulted in different structure and morphology of hexagonal WO_3nano-crystals. Micro-hotplates with gold electrodes on top to measure sensing layer conductivity were fabricated. WO_3 layers of the two morphologies were deposited using capillary dropping technique. Sensor responses were measured up to 220 °C operation temperature for NH_3 diluted in synthetic air in the 10-100 ppm range. Test results are compared in terms of conductivity, sensitivity and response time.

Peer-review under responsibility of the scientific committee of Eurosensors 2014

Keywords: hexagonal WO_3, gas sensor, micro-hotplate;

1. Introduction

Monitoring of dangerous gases in civil and industrial environment is crucial for safety, health and environmental applications. A large part of sensors must be operated in portable devices in order to provide flexibility and personal safety. Although MEMS based conductivity type gas sensors are ideal for these systems, there is still a huge effort ahead to elaborate appropriate sensors in terms of sensitivity, cross-sensitivity, response time and stability. As nano-structured metal-oxide layers in principle offer high sensitivity, the research activity was focused on the related processes and their characterization in the last decade [1]. In this work we investigate the morphology effect of nano-sized hexagonal [2, 3] WO_3 on gas sensing properties.

* Corresponding author. Tel.: +36-1-3922222; fax: +36-1-3922235.
E-mail address: pap.andrea@ttk.mta.hu

Peer-review under responsibility of the scientific committee of Eurosensors 2014
doi:10.1016/j.proeng.2014.11.331

2. Experimental

2.1. WO_3 powder prepared with sodium tungstate and oxalic acid - Sample A

WO_3 sol was prepared by dissolving 4,075 g sodium tungstate (Na_2WO_4) in 100 ml distilled water [2]. Then, the solution acidified to set the pH 1.2 by HCl solution (3 mol/l). The precipitate was generated by added oxalic acid ($H_2C_2O_4$) into the mixture and was stirred for 30 minutes at room temperature. A 50 ml volume of the obtained WO_3 sol was transferred to autoclave, and then Na_2SO_4 (3.33 g) was added to the solution, sealed and maintained at 180 °C for 24 h. Then the precipitates were filtered, carefully washed with water and ethanol to remove ions possibly remained in the final products. The material was finally dried at 60 °C.

2.2. WO_3 thin film prepared with sodium tungstate by Zocher method – Sample B

WO_3 powder was made by dissolving 4.69 g sodium tungstate (Na_2WO_4) in 62.14 ml distilled water and the solution was kept at 4 °C for 2 h [3]. Then 33.6 ml pre-cooled HCl (1 mol/l) was added to the solution. Before washing the gel, an overnight cooling of the precipitate was applied. The resulted gels were washed with distilled water and centrifuged 5 times. Suspensions of the gels were exposed to hydrothermal dehydrations in the autoclave at autogenous pressure at 125 °C for 24 h. The obtained $WO_3 \cdot 1/3\ H_2O$ suspension was dried in exicator and the anhydrous powder was annealed at 330 °C applying a ramp up profile of 5 °C/min. The samples were maintained at peak temperature for 1.5 h in order to form the targeted WO_3.

The two types of WO_3 powders prepared were dissolved in ethylene-glycol-water-ethanol solution. For deposition of gas sensing layers suspension drops were gently attached to the micro-hotplate and annealed at 200 °C for 10 minutes to remove the solvent.

3. Results

Morphology of *Sample A* and *B* was investigated by scanning electron microscope (Fig. 1) and characteristic geometry data of the nano-particles were also measured (Table 1).

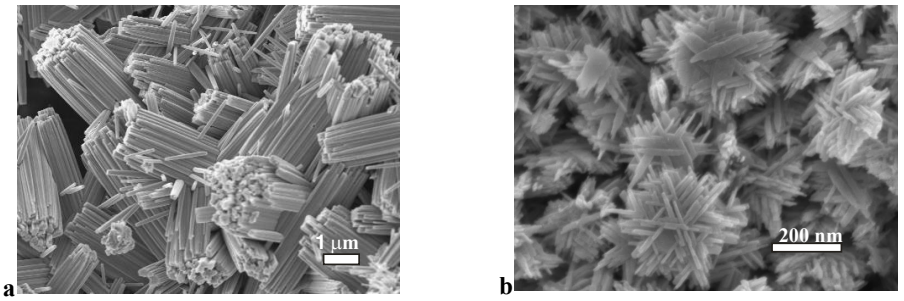

Fig. 1. (a) Sample A –prepared with oxalic acid; (b) Sample B – prepared by Zocher method. SEM views.

Table 1. Characteristic morphology data of the differently prepared samples

Sample	Oxalic acid	Additive	Morphology	Length (nm)	Diameter (nm)
Sample A	+	Na_2SO_4	nano-rods	400	150
Sample B	-	-	carnation	500	80

The SEM images reveal two significantly different morphologies. Application of oxalic acid and Na_2SO_4 in the preparation process led to nano-rod bundles (Fig. 1. a), and in case of the Zocher method a carnation-like structured (Fig. 1. b) WO_3 powder were formed, respectively.

Functional tests were carried out by depositing hexagonal WO_3 on MEMS based conductivity type sensor structures. Our device is a sandwich structured non-perforated membrane with embedded Pt heater and gold interdigital electrodes on top. The membrane was released by deep reactive ion etching of Si underneath. The Pt filament and the Au interdigital electrodes were positioned in the middle of the membrane (Fig. 2.).

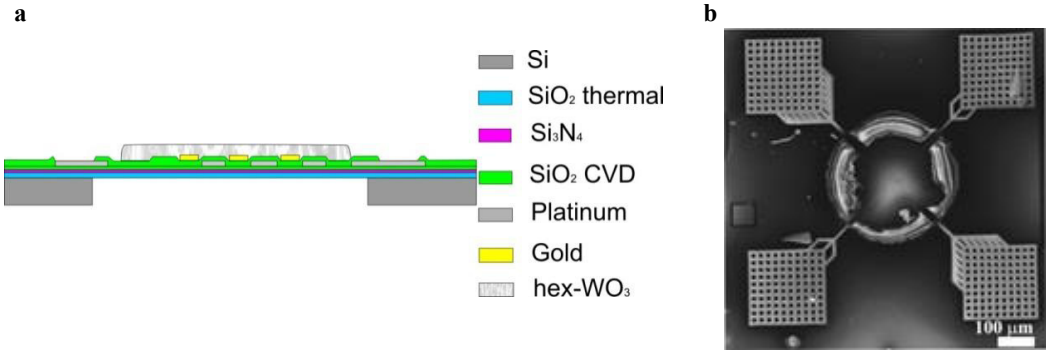

Fig. 2.(a) Schematic cross-section of the Taguchi sensor; (b) SEM image of the sensor with hexagonal WO_3 nano-powder (top view).

Sensors have been tested for NH_3 up to 100 ppm in synthetic air at 180 °C. The lowest detection limit is around 30 ppm in both cases, but there are a significant difference in sensitivity and response time: the carnation-like structured type *B* shows much better characteristics than the more compact bundles of type *A*.

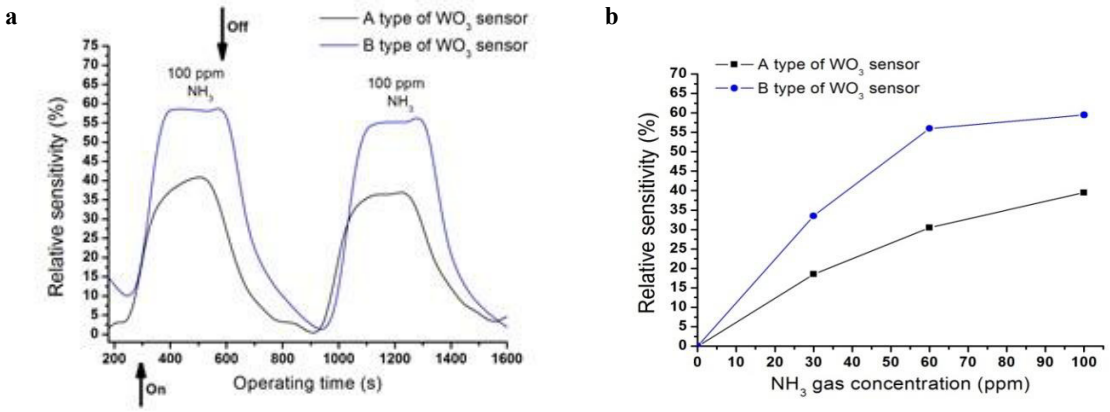

Fig. 3. (a) Response time difference between the two types of sensor in NH_3; type *A* 300s and type *B*50s.; (b) Relative sensitivity of the two types of WO_3 sensors as a function of gas concentration at 180°C operating temperature.

In order to improve device performance the roboust nano-rod boundles of WO_3 powder were exposed to ultrasonic agitation to separate the nano-rods and sensors were formed to investigate the effect. Gas sensing measurements were repeated in 100 ppm NH_3. The results clearly confirmed our expectations by the presented improvements both in sensitivity and response time (Fig. 4.).

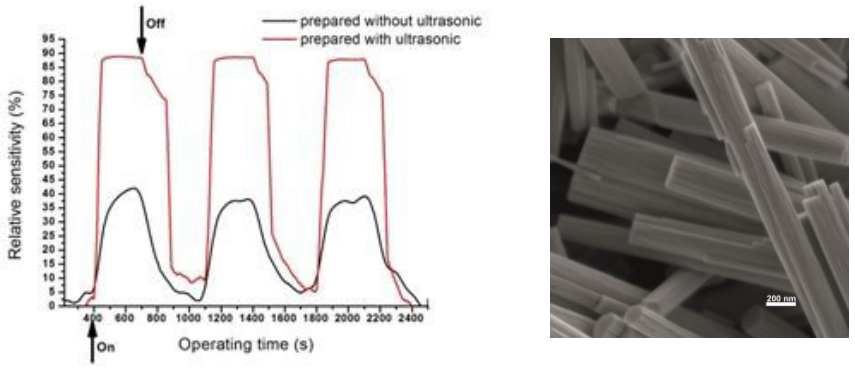

Fig. 4.Sensitivity of WO_3 nano-powder prepared with sodium tungstate and oxalic acid (Sample A) with and without ultrasonic manipulation (left); SEM image of the separated nano-rods (right).

Sensitivity of ultrasonically treated *Sample A* and non-modified *Sample B* was measured at 180 and 220 °C in the range of 10 – 100 ppm of NH_3 (Fig. 5.). The most effective working temperature was different; in case of carnation like structure we found it at 180 °C, while the rod type structure showed higher sensitivity and much better performance at 200 ^oC. Note, that the latter system is capable to detect NH_3 up to 30 ppm and its response saturates at higher concentrations.

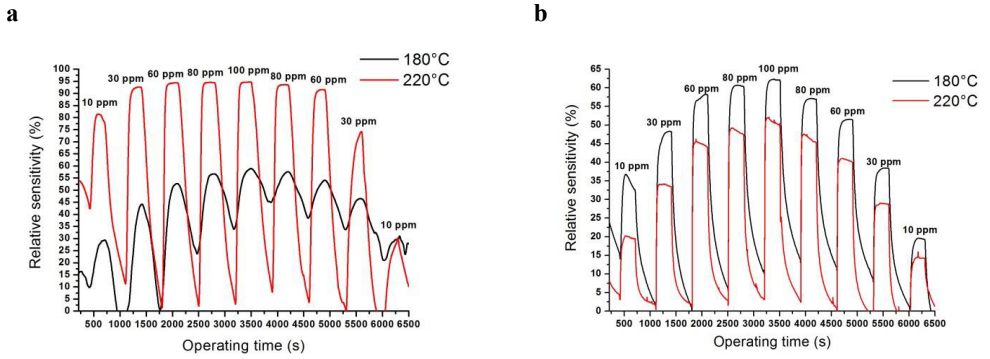

Fig 5. Sensor responses of WO_3 operated at different temperatures. (a) ultrasonically agitated A type (b), carnation-like B-type

4. Conclusion

Tungsten oxide nano-powders were prepared with different methods. All the alternative processes resulted in hexagonal WO_3 nano-crystals but different morphologies and characteristic sizes. NH_3 sensitivity measurements revealed the significance of morphology and crystallite size in device performance. Ongoing investigations of alternative processing routes may open the way towards fine tuning of sensor characteristics.

Acknowledgements

This work was supported by the Hungarian National Development Agency TÉT_10-1-2011-0305.

References

[1] E. Comini, Metal oxide nano-crystals for gas sensing, Analytica Chimica Acta 568 (2006) 28–40
[2] Zhanglian Xu, Teruo Hori at al, Preparation of platinium-loaded cubic tungsten oxide: A highly efficient visible light-driven photocatalyst, Materials Letters 65 (2011) 1252-1256
[3] Cs. Balázsi, L. Wang, E. O. Zayim at al, Nanosize hexagonal tungsten oxide for gas sensing applications, Journal of the European Ceramic Society 28 (2008) 913–917