DOI 10.5162/IMCS2012/5.3.2

WO_3 sensor for ppb detection of ammonia

Aravind Reghu[1], Derya Deniz, Rahim Stennett, George Bernhardt, David Frankel, Robert Lad and John Vetelino,
Laboratory Of Surface Science and Technology, University Of Maine, Orono, Maine 04469, USA
vet@eece.maine.edu

Abstract

Two semiconducting metal oxide (SMO) sensors are proposed for ppb detection of ammonia (NH_3) in applications such as environmental monitoring and health related issues. One sensor uses a gold doped glancing angle deposition(GLAD) tungsten trioxide (WO_3) nanorod film and the other uses a standard flat gold (Au) doped film .The GLAD film sensor showed a faster response than the flat film sensor indicating that metal oxide films with nanorod structures have applicability for ppb gas sensing applications.

Key words: glancing angle deposition (GLAD)**,** nanorod, faster response, parts per billion (ppb) range.

Introduction

Since the early work of Bardeen in the late 1940s, it was known that the sorption of gas on a semiconductor can modify the carrier concentration, causing a change in the semiconductor's resistivity or conductivity [1]. Shortly after Bardeen's work, Heiland[2], Bielanski et al. [3] and Seiyama et al. [4] showed that semiconducting metal oxide (SMO) films could serve as the sensing element in gas sensors. The early work on SMO films was subsequently used by Taguchi in the development of a commercial SnO_2 gas sensor in 1971[5]. Since Taguchi's work, SnO_2 has been the most used SMO film since it is highly reactive to many gas species.

The lack of selectivity exhibited by SnO_2 however, has led researchers to investigate other metal oxides such as tungsten trioxide (WO_3). Sensing of gases such as NO_x, H_2S and NH_3 have been reported in the ppm range using flat WO_3 films [6-9]. In regard to NH_3 the research was motivated by ammonia's toxicity toward humans. To the authors knowledge, the only work done on ppb detection of NH_3 was done by Gouma et al [10] using a MoO_3 film deposited by the sol-gel method. Although this sensor responded to NH_3 in the ppb range, the data was noisy.

More recently a need for ppb levels of detection of NH_3 for environmental monitoring(climate change) and the health industry(medical breath analysis) has been identified [11,12,13]. Studies from remote ice core sites have found significant correlations between NH_4^+ concentration and temperature for Siberia and the Indian subcontinent for preindustrial time periods. In addition knowledge of ppb NH_3 concentration can be used to study climatic effects such as global warming [14,15]. In the area of health, changes in ppb levels of NH_3 in breath has been correlated to kidney disorders, ulcers etc.

In this paper two types of WO_3 sensors are proposed for detecting NH_3 in the ppb range. The first sensor uses an Au doped GLAD WO_3 nanorod film and the second uses a standard flat Au doped film. As reported by others, nanostructured GLAD WO_3 films have a high surface to volume ratio and may potentially enhance the film sensitivity [16,17].

Film Fabrication and Testing

Both GLAD and flat WO_3 films were fabricated in the Laboratory of Surface Science and Technology (LASST) at the University of Maine. The devices consisted of a WO_3 SMO thin film deposited over an interdigitated platinum electrode array on a single cystal sapphire substrate. The chemiresistive sensing platform is shown in Figure 1. The back of the platform contains a serpentine heater and resistive temperature device (RTD) [18]. The platform is calibrated by heating the device in an oven with a calibrated RTD against which the internal RTD is compared. Thus, the temperature of the platform can be precisely controlled.

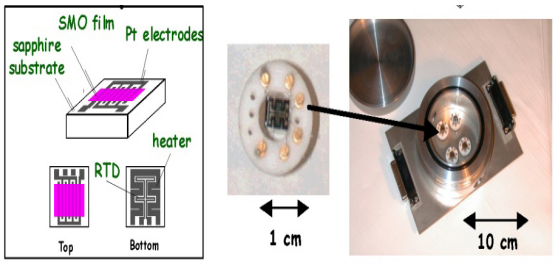

Fig. 1. SMO chemiresistive thin film sensor device comprised a SMO film deposited over a Pt electrode array. The reverse side of the device has a thin film heater and resistive temperature device (RTD). The sensor is wire-bonded into a TO-8 header that plugs into a gas-flow test cell [19].

The GLAD film was grown in a high vacuum system using reactive RF magnetron sputtering to a thickness of 1000 A^0. Surface diffusion limitations and flux shadowing effects during glancing angle deposition lead to nano-rod morphologies as shown in figure 2 [19]. After deposition, 15 A^0 of Au was deposited on top of the GLAD WO_3 film using electron beam evaporation.

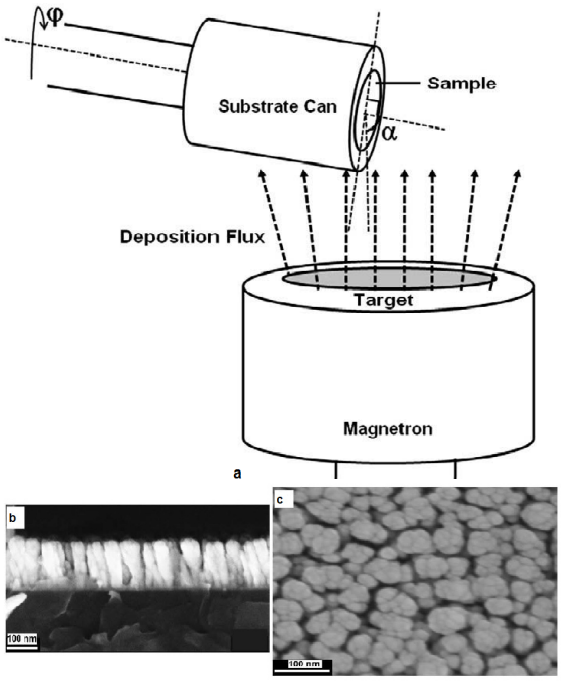

Fig. 2. (a) Glancing angle deposition (GLAD) geometry in which the flux from a magnetron sputter target is directed to the film substrate at very low angle. (b) Side view and (c) top view of WO_3 nano-rod structures.[19]

A 2500 A^0 thick Au doped WO_3 flat film was deposited using reactive RF magnetron sputtering. To incorporate Au into the film,the tungsten magnetron was shuttered at 500 A^0 intervals and a 15 A^0 Au interlayer deposited with a second magnetron. A final top layer of 15 A^0 of Au was also deposited.

The sensors were heated in the test cell to a temperature of 450^{0}C in 15% relative humidity air. The GLAD film is exposed to a cycle of 200, 500,100 and 600 ppb levels of NH_3 with each exposure lasting 45 minutes while the flat film was exposed to a cycle of 100,700,300 and 500 ppb levels of NH_3 with each exposure lasting for 1 hour. The cycle was repeated to determine the reproducibility of the results.

Results

Both the GLAD and flat gold doped WO_3 sensors responded to NH_3 gas. When the gas was introduced to the film, the film resistance decreased and remained at that value until the gas was turned off. This resistance change was due to an oxidation process where free electrons were released into the film upon exposure to NH_3 gas. The following reactions can take place when a gold doped WO_3 film interacts with NH_3 gas [20],

$$2NH_3 + 3O\text{-(ad)} \rightarrow N_2 + 3H_2O + 3e^- \quad (1)$$
$$2NH_3 + 5O^- \text{(ad)} \rightarrow 2NO + 3H_2O + 5e^- \quad (2)$$
$$4NO + 2NH_3 \rightarrow 2N_2 + N_2O + 3H_2O \quad (3)$$
$$NO + \tfrac{1}{2}\, O_2\,(g) \rightarrow NO_2 \quad (4)$$
$$NO_2 + e^- \rightarrow NO_2^-\,(ad) \quad (5)$$
$$NO_2 + \tfrac{1}{2}\, O_2\,(g) + e^- \rightarrow NO_3^-\,(ad). \quad (6)$$

O-(ad), NO_2-(ad) and NO_3-(ad) represent negatively charged chemisorbed species and e^- are the free electrons available for electrical conduction.

The dominant reactions are given by equations (1) and (2). The reaction of the adsorbed oxygen atoms and the NH_3 gas produces water molecules, free electrons and either nitrogen or nitrogen oxide. As the gas is removed from the environment, the number of free electrons decreases. This change brings the electrical conductivity/resistance back to its original value.

(a) Response of gold doped GLAD WO_3 film sensor to NH_3 gas

The GLAD film was annealed at 500^0 C for 18 hours and then wire bonded into a TO-8 header. The sensor was then plugged into the test cell, which can hold up to four sensors.The sensor was set to a temperature of 450^{0}C and allowed to stabilize for 2 hours with 150 standard cubic centimeters per minute (sccm) of air flowing through the test cell with 15% relative humidity. Once the baseline was established, the sensor was exposed 200, 500, 100, and 600 ppb levels of NH_3 in 15% humid air with each exposure lasting 45 minutes. Once the exposures were completed, the NH_3 was turned off and the sensor was left to recover in 150 sccm flow of air. The cycle was

repeated to ensure the reproducibility of the sensor response. Figure 3 shows the sensor response to ppb levels of NH_3. The response time, which is calculated as the time taken to reach 90% of the final value, varied for each exposure. The response times were in the range of 13-28 minutes for this film.

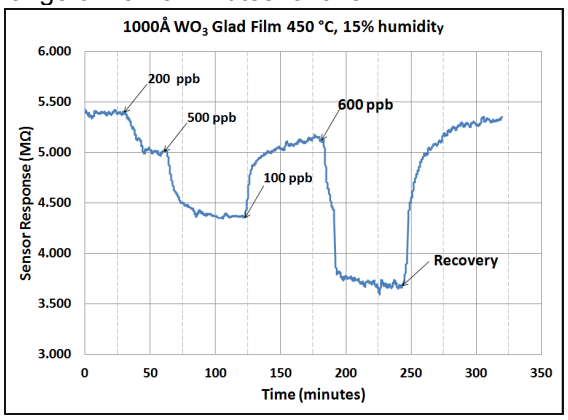

Fig. 3. *Sensor response from a Au doped WO_3 GLAD film as a function of time.*

Sensitivity is given by dR/R where dR is the change in resistance and R is the baseline resistance. Sensitivity is measured against the change in concentration which means that when switching from 200 ppb to 500 ppb of NH_3, sensitivity of the film is calculated for the 300 ppb change in concentration. Figure 4 shows the sensitivity versus concentration for the gold doped GLAD WO_3 film. The curve is quite linear in this range as well as reproducible.

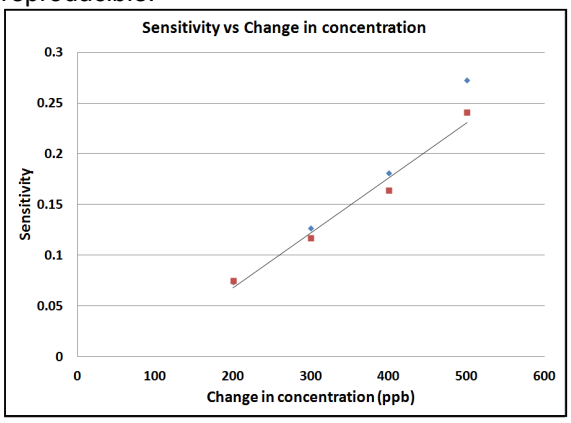

Fig. 4: *Sensitivity of the Au doped WO_3 GLAD film as a function of NH_3 concentration.*

(b) ***Response of the gold doped flat WO_3 film sensor to NH_3 Gas***

The Au doped flat WO_3 film sensors were annealed at 500^0 C and loaded into the test cell in the same manner as the GLAD film. After stabilization the films were exposed to 100, 700, 300 and 500 ppb levels of NH_3 gas with each exposure lasting for one hour. The gas was turned off at the end of the exposure and the sensors were allowed to recover in the air flow. As in the case of the GLAD films, the test was repeated to ensure reproducibility of the sensors. Figure 5 shows the sensor response to NH_3 gas. For the first exposure (100 ppb), there is no sharp change in resistance. Instead it slowly drifts towards a lower value. There is a noticeable change in resistance for the next three exposures. The response times for this film were in the range of 14-52 minutes.

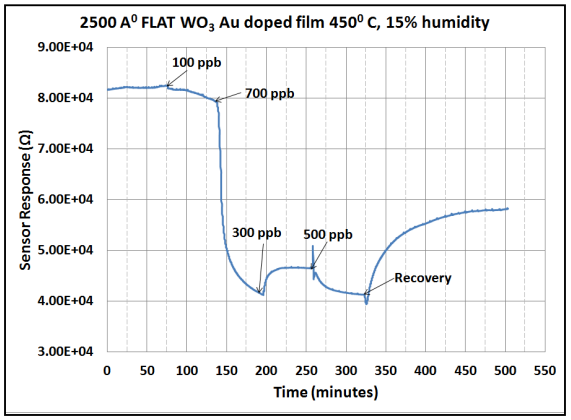

Fig. 5. *Sensor response from a Au doped WO_3 FLAT film as a function of time.*

The sensitivity versus concentration plot for the flat WO3 film sensor is shown in figure 6.

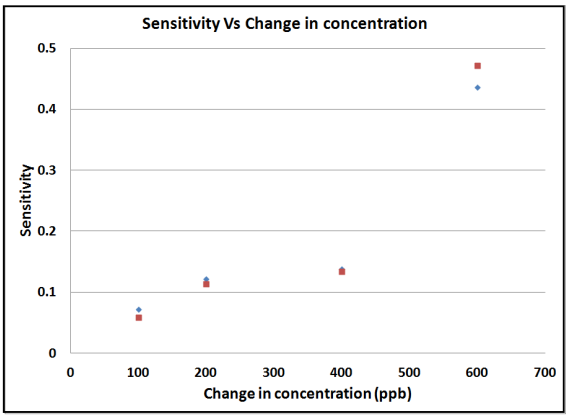

Fig. 6: *Sensitivity of the Au doped WO_3 FLAT film as a function of NH_3 concentration.*

Discussion

Many scientific papers have been written concerning gas sensors for different sensing applications. Most of the work involving SMO sensors for detecting NH_3 gas have focused on ppm levels. However, for many applications sensors are needed to detect NH_3 gas in the ppb region [21]. This paper has focused on two different types of SMO sensors. The first one is

a gold doped GLAD WO_3 film which has nano-rod structures and offers a larger surface area for detecting trace concentrations of NH_3 gas.The second one is a Au doped flat WO_3 film which has more reaction centers throughout the bulk of the film than flat films in which Au has been post-sputtered.

From the results that have been shown, one can see that while the overall sensitivity is similar,the GLAD film has a faster response time and is better suited for low ppb detection of NH_3 gas than the flat WO_3 film. The flat film has response times in the range of 14-52 minutes. The 14 minute response for the third exposure can be due to the fact that the sensor might be responding to NH_3 gas from the previous exposure. If that response is neglected the response times for the flat film sensor varies from 30-52 minutes for the other exposures. The sensitivity of the GLAD film is quite linear in the ppb range while for the flat film the response shows certain anomalies. The flat film response (change in resistance dR) for the third and fourth exposure is almost the same.This might be due to the fact that there is NH_3 present in the test cell after the second exposure.

Conclusions

To our knowledge this is the first time nanorod technology has been used for the ppb detection of NH_3 gas. The response of the Au doped GLAD WO_3 sensor was observed to be better suited for ppb detection of NH_3 than the Au doped flat WO_3 sensor. In particular the GLAD film had a faster response time compared to the flat film in the ppb region. More work is being done on the GLAD film to further improve sensitivity and address selectivity.

Acknowledgements

We would like to thank the W.M. Keck foundation for the funding of this project. We would also like to thank Dr. Paul Mayewski and Dr. Brian Frederick for their valuable inputs. Rahim Stennett was supported by NSF-REU grant EED-0848014.

References

[1] J. Bardeen, Phys.Rev,71:717,1947

[2] G. Heiland, Z. Physik, Vol. 138, 1954, pp. 459–464.

[3] A. Bielanski, J. Derren and J.Haber, Nature, Vol. 179, 1957, pp. 668–669.

[4] T. Seiyama, A. Kato, K. Fujiishi and M. Nagatani, Anal. Chem., Vol. 34, 1962, pp. 1502–1503.

[5] N. Taguchi , U.S. Patent 3,631,436 (1971)

[6] X. Wang, N. Miura, N. Yamazoe, Sens.Actuators, B 66 (2000)74–76.

[7] C.N. Xu, N. Miura, Y. Ishida, K. Matuda, N. Yamazoe, Sens.Actuators, B 65 (2000) 163–165.

[8] E. Llobet, G. Molas, P. Molinàs J. Calderer, X. Vilanova, J. Brezmes, J. E. Sueiras, and X. Correig, *Journal of The Electrochemical Society,* **147** (2) 776-779 (2000)

[9] B. Marquis, J. Vetelino, Sens.Actuators, B 77 (2001) 100-110.

[10] P.Gouma, K.Kalyanasundaram, X.Yun, M.Stanac´evic´, and L.Wang, IEEE Sensors Journal, VOL. 10, NO. 1, JANUARY 2010.

[11] B.Timmer, W. Olthuis, A.Van Den Berg ,Sens.Actuators ,B, 107,PP. 666–677, 2005.

[12] S.A.Kharitonov and P.J.Barnes,Biomarkers,vol 7,no 1,PP. 1-32, 2002.

[13] K.Sawicka, P.Gouma and S.Simon, Sens.Actuators,B 108, PP. 585-588, 2005

[14] T. Kellerhals,S. Brütsch,M. Sigl,S. Knüsel,H. W. Gäggeler and M. Schwikowski, Journal Of Geophysical Research, VOL. 115, D16123, 2010.

[15] P.Mayewski and M.Legrand, Reviews Of Geophysics, VOL. 35, NO. 3, PP. 219-243, 1997.

[16] B. Deb, S. Desai, G.U. Sumanasekera, M.K. Sunkara, Nanotechnology 18 (2007) 1.

[17] D. Deniz, D.J. Frankel, R.J. Lad, Thin Solid Films 518 (2010) 4095–4099.

[18] *G*. *Bernhardt*, *C*. *Silvestre*, N. LeCursi, S.C. Moulzolf, D. J. *Frankel* and R. J. Lad, Sens.Actuators, B77,368-374(2001)

[19] D. Deniz, A.Reghu and R.J. Lad, 34th International Conference on Advanced Ceramics and Composites, Daytona Beach, FL, Jan 26, 2010.

[20] K.A. Snow, MS Thesis, University Of Maine, 1996.

[21] P.Warneck, International Geophysics, VOL. 71, 1999.