Electron Beam Evaporation of Tungsten Oxide Films for Gas Sensors

T. Tesfamichael
Queensland University of Technology
Faculty of Built Environment and Engineering, School of Engineering Systems
Brisbane, Australia
email: t.tesfamichael@qut.edu.au

***Abstract*—Pure and Iron incorporated nanostructured Tungsten Oxide (WO_3) thin films were investigated for gas sensing applications using noise spectroscopy. The WO_3 sensor was able to detect lower concentrations (1 ppm-10 ppm) of NH_3, CO, CH_4 and Acetaldehyde gases at operating temperatures between 100°C to 250°C. The iron doped Tungsten Oxide sensor (WO_3:Fe) showed some response to Acetaldehyde gas at relatively higher operating temperature (250°C) and gas concentration of 10 ppm. The sensitivity of the WO_3 sensor towards NH_3, CH_4 and Acetaldehyde at lower operating temperatures (50°C -100°C) was significant when the sensor was photo-activated using blue-light emitting diode (Blue-LED). From the results, photo-activated WO_3 thin film that operates at room temperature appeared to be a promising gas sensor. The overall results indicated that the WO_3 sensor exhibited reproducibility for the detection of various gasses and the WO_3:Fe indicated some response towards Acetaldehyde gas.**

***Index Terms*—Iron doping tungsten oxide, nanostructured thin films, gas sensor, noise spectroscopy**

I. Introduction

Gas sensors are of great importance for many applications including industrial production, environmental monitoring, medical diagnosis, domestic security, etc. There are several gasses known to be harmful to humans and the environment and to protect people and the environment from these harmful gases affordable gas sensors with higher detecting capacity and gas selectivity are needed.

The author acknowledges the Japanese Society for the Promotion of Science (JSPS) for the fellowship and financial assistance to this research.

Such devices are suitable to detect the presence of low concentration target gasses and can give warnings or send message for proper action when the designed threshold value is attained. For example health related problems may result from low indoor air quality due to various pollutants and immediate ventilation of these species is desirable when the limit is reached [1, 2]. Thin film sensors are widely compatible to microelectronic technology and can easily be integrated into different kinds of circuits. Most of research in gas sensing devices has been focused on metal oxide materials such as SnO_2, TiO_2, ZnO and WO_3 because of their simplicity and low cost [3-12]. The gas sensing properties of these oxides are determined by their intrinsic properties. The materials have band gap energies between 2.6 to 3.3eV at room temperature. The response behavior of various metal oxide films to a specific gas suggests that oxygen vacancy and charge transport mechanisms are dependent on film microstructure [12, 13]. A common sensing mechanism of the sensors involves the change in an electrical resistance caused by gas adsorption. These oxides behave like n-type semiconductor due to non-stoichiometry and they show good chemo-sensitivity towards oxidizing or reducing gas pollutants. Among these oxides SnO_2 is one of the most widely used sensors but recent research shows the other metal oxides are able to detect volatile organic compounds, pollutants and toxic gases such as methane, ammonia, carbon monoxide, hydrogen sulfide, nitrogen dioxide, etc.

The sensing properties of the metal oxides can be enhanced by optimizing various parameters including thickness of the oxide film, microstructure (e.g. particle size, distribution and orientation, surface morphology, porosity), by doping and mixing of various oxide films [8, 10, 14-17]. Thin films are usually compact and the active layer is limited to the surface whereas thick films are commonly porous and hence the whole layer can interact with the gas species. Through controlled porosity of a nanostructured thin film, the gas sensing properties can be enhanced significantly [18]. Optimum film

thickness also can have significant effect in improving sensor selectivity and sensitivity [19]. From a theoretical study elsewhere, gas detection capacity can be enhanced significantly if the grain size is smaller than 50 nm [20]. Gas detecting sensitivity also depends on the reactivity of film surface as sensors are strongly influenced by the presence of oxidizing or reducing gases on the surface. The adsorption of gas species can be enhanced due to impurities, defects and active species on the surface of the films. It has been shown that inclusion of different doping metals in the oxide films increased the sensitivity to specific gases [5, 14-16, 21-23]. Gas detection capacity can also be enhanced by mixing metal oxides since each material has its own response and the mixture can add sensitivity and selectivity to specific gas species and also often improves sensor quality and performance [10, 18, 24, 25]. An increase of response towards certain gasses has been reported elsewhere, when iron oxide was added into tungsten oxide film [26]. Recent research reports show that room temperature gas detection of metal oxide sensors can be enhanced based on photo-activation of the metal oxide film. In most of the work a UV-light had been used to activate and increase gas selectivity and sensitivity [27-30].

The main objective of this experiment is to investigate the gas detection capacity and sensitivity of an electron beam evaporated nanostructured tungsten oxide (WO_3) and iron-doped tungsten oxide (WO_3:Fe) thin film sensors operated at higher temperatures. In addition, low temperature gas detection of both sensors when photo-activated using blue-light emitting diode (Blue-LED) is presented.

II. GAS SENSING MEASUREMENTS

Preparations of tungsten oxide (WO_3) and iron doped (10at%) tungsten oxide (WO_3:Fe) thin films and sensor developments have been reported elsewhere [31]. In this paper noise spectroscopy has been used for evaluating the gas sensitivity of the sensors [32,33]. The sensors were annealed at 300^{o}C for 1 hour and the thickness of the films were 200 nm (WO_3) and 225 nm (WO_3:Fe), respectively. The gas sensing measurements were performed inside a 1 dm^3 volume stainless steel chamber connected to a low-noise current generator. The resistance and voltage fluctuation across the sensor were measured using digital multimeter and Stanford SR560 low-noise differential preamplifier, respectively. The later (voltage fluctuation) was sampled with a rate of 50 kHz by a PowerLab/4SP (AD Instruments) data acquisition unit to calculate a power density spectrum (PDS). The Power Density Spectrum (PDS) signal obtained from the noise spectroscopy measurements was used to determine the gas sensitive and selectivity of the sensors.

The sensing properties of each sensor as a function of operating temperature, type of gas and concentrations have been performed. Synthetic air was used as reference. Various types of gasses (NH_3, CO, CH_4 and Acetaldehyde) with different concentrations (1 ppm- 10 ppm) were tested at higher operating temperatures (100^{o}C-250^{o}C). In addition, the performances of the sensors at lower temperatures (50^{o}C-100^{o}C) were investigated by assisting the sensors with Blue-LED. A gas calibration system with mass flow controllers was used to allow continuous flow of known concentration gas into the chamber after a steady background reference signal in synthetic air was established. The total flow rate was kept constant at about 405 sccm. The PDS of a particular gas was then measured when the stochastic signal remained constant as a function of time. In most of the measurements, the time needed to reach a steady state signal of the target gas was in the range of about 10-15 minutes and the time taken to achieve the background signal (recovery time) of the synthetic air after cutting-off the target gas was about 5-10 minutes. It has been reported elsewhere that the change in stochastic signal when the film is exposed to a target gas, is due to resistance fluctuation of the film and not by other effects [34]. A common problem with a nanoparticle-based seniors is their long-term drift of the electrical resistance in which the noise spectroscopy method using PDS may become an alternative technique of gas detection measurements.

III. FILM CHARACTERISTICS

Figure 1 shows AFM images of WO_3 and WO3:Fe films annealed at 300^{o}C for 1 hour. The average particle diameter (film roughness) of these samples as estimated using the Nova and Image Analysis software were 9 nm (2.61 nm) and 12 nm (2.93 nm), respectively. In order to improve the gas-sensing characteristic of a film, optimizations of the grain size and porosity are important factors. The nanostructured films appeared to have particle size and porosity suitable for gas sensing applications.

The chemical nature of the films was determined using Raman spectroscopy. Raman peaks of the annealed sample were found at peak positions about 957 cm^{-1} and 779 cm^{-1}, respectively (Fig. 2). From the Raman characteristics band, the short range order of the annealed films may be assigned to the tetragonal-phase as reported

elsewhere [35]. The addition of Fe to WO_3 seems to prompt the crystallization of the WO_3 film, as seen from the Raman intensity.

IV. GAS SENSING CHARACTERISTICS

Fig. 3 is an example of WO_3 sensor exposed to 10 ppm NH_3 gas at 200^{o}C for different times between 3 to 15 minutes where saturation occurred after 10 minutes. The PDS spectra obtained at higher temperatures tend to bend in the lower frequency range and the reason for this was not known which may need further understanding of the spectroscopy signal.

A. *NH_3 Gas Detection of WO_3 Sensor*

In the present time, study of ammonia (NH_3) gas sensor has greatly increased as it is one of the industrial gasses with high toxicity [9, 36]. The American Conference of Government Industrial Hygienists has established threshold limit values, for an 8-h work day and 40-h work week for humans exposed to NH_3 gas as 25 ppm [18]. In this paper, temperature dependence of the WO_3 sensor exposed to 10 ppm of NH_3 are presented. As shown in Fig. 4, the gas detection capacity of the sensor was significant over a wide temperature range at higher operating temperatures (>100^{o}C). The detection of the sensor at lower temperature (100^{o}C) was appreciable (see Fig. 4c), when the sensor was photo-activated using blue-light emitting diode (Blue-LED). To the best of our knowledge this is the first to observe the enhancement of a low concentration (10 ppm) gas detection using photo-activation method at lower operating temperatures. The WO_3 film as reported elsewhere [31] has optical band-gap energy (E_g) of 3.12 eV (0.38 μm) and is within the UV/Vis wavelength of the solar spectrum.

B. *CO Gas Detection of WO_3*

The toxic nature of CO necessitates the detection of this gas for household and environmental applications and for controlling emissions from combustion processes [19, 37]. Fig. 5 shows the response of WO_3 sensor to 1 ppm of CO gas measured at various operating temperatures between 100^{o}C to 250^{o}C. As shown in the figures, the WO_3 sensor exhibits low sensitivity for all the measured temperature range. This indicates that the WO_3 sensor is less sesntive to CO at lower concentrations. However, at higher concentration (10 ppm) and higher operating temperature (200^{o}C) some appreciable response towards CO was observed as show in Fig. 6. The stochastic signal increases with increasing gas concentration and the change in the signal is directly related to the concentration of the exposed gas. At lower operating temperature (50^{o}C), small amount of signal was detected for higher CO concentration (10 ppm) only after illumination the sensor using Blue-LED (Fig. 6d).

C. *CH_4 Gas Detection of WO_3 sensor*

Methane is one of the green house gases and hence requires environmental monitoring using gas sensors. The detection of the WO_3 sensor towards 1 ppm and 10 ppm CH_4 gas at 50^{o}C with and without blue light illumination are shown in Fig. 7. From the figures, a significant response can only be observed after the sensor was photo-activated with Blue-LED. The response increases with increasing the concentration of the gas from 1 ppm to 10 ppm (Fig. 7b). For comparison photo-activation of the sensor using UV-LED for detection of a 10 ppm CH_4 gas is shown in Fig. 7c. From the results, it can observe that the blue-LED is more efficient than the UV-LED while both LED have similar intensity.

D. *Acetaldehyde Gas Detection of WO_3 Sensor*

Acetaldehyde has received much attention as a hazardous and odorous substance in studies of air pollution as it is one of the 33 air pollutants indicated by the U.S. Environmental Protection Agency and considered being a probable carcinogen. Temperature dependence spectra of the WO_3 sensor exposed to 10 ppm of Acetaldehyde operated at 150^{o}C and 200^{o}C are shown in Fig. 8. The gas detection capacity of the sensor was found to be large over the measured temperature range.

E. *Gas Detection of WO_3 :Fe Sensor*

The sensing characteristics of iron-doped tungsten oxide sensor (WO_3:Fe) to various gasses (NH_3, CO, CH_4 or Acetaldehyde) was performed. From the measurements, there was no response of the sensor towards NH_3, CO and CH_4 gases in the concentration range of 1 ppm to 10 ppm and at operating temperature between 100^{o}C to 250^{o}C. Fig. 9a shows PDS of the WO_3:Fe sensor exposed to 1 ppm CO at operating temperature of 200^{o}C. The highest response observed was for 10 ppm Acetaldehyde gas at operating temperature of 250^{o}C (Fig. 9b). This may indicate to a certain degree the gas selectivity of the sensor. Thus, the response of tungsten oxide sensor toward NH_3, CO, CH_4 and Acetaldehyde gases has been diminished when 10at% of iron was added.

V. Conclusion

The gas sensing characteristics of nanostructured WO_3 and WO_3:Fe sensors have been studied to NH_3, CO, CH_4 and Acetaldehyde gases. Experimental results indicated that the pure WO_3 sensor has good sensitivity to these gases in the concentration range of 1-10 ppm and operating temperature between 100^{o}C to 250^{o}C s. The iron doped WO_3:Fe sensor showed some sensitivity to only Acetaldehyde gas. The sensitivity of the WO_3 sensor at lower temperatures (50^{o}C to 100^{o}C) was appreciable when the sensor was photo-activated with Blue-LED. From the results, it can be concluded that photo-activated WO_3 thin film that can be operated at room temperature appeared to be a promising gas sensing devices.

Acknowledgment

The author is indebt to Associate Prof Masashi Arita from the Graduate School of Information Science and Technology (Hokkaido University) and to the Solid State Physics group at the Angstrom Laboratory (Uppsala University) for their assistance when using their facilities and laboratories during this research.

References

[1] C. G. Granqvist, A. Azens, P. Heszler, L. B. Kish, and L. Osterlund, "Nanomaterials for benign indoor environments: Electrochromics for "smart windows", sensors for air quality, and photo-catalysts for air cleaning," *Solar Energy Materials and Solar Cells*, vol. 91, pp. 355-365, 2007.

[2] A. P. Jones, *Atmos. Environ.*, vol. 33, p. 4535, 1999.

[3] A. Dieguez, A. Romano-Rodriguez, J. R. Morante, U. Weimar, M. Schweizer-Berberich, and W. Gopel, "Morphological analysis of nanocrystalline SnO2 for gas sensor applications," *Sensors and Actuators B: Chemical*, vol. 31, pp. 1-8, 1996.

[4] X. He, J. Li, X. Gao, and L. Wang, "NO2 sensing characteristics of WO3 thin film microgas sensor," *Sensors and Actuators B: Chemical Proceedings of the Ninth International Meeting on Chemical Sensors*, vol. 93, pp. 463-467, 2003.

[5] V. Khatko, E. Llobet, X. Vilanova, J. Brezmes, J. Hubalek, K. Malysz, and X. Correig, "Gas sensing properties of nanoparticle indium-doped WO3 thick films," *Sens. Actuators, B*, vol. 111-112, pp. 45-51, 2005.

[6] T. Pagnier, M. Boulova, A. Galerie, A. Gaskov, and G. Lucazeau, "Reactivity of SnO2-CuO nanocrystalline materials with H2S: a coupled electrical and Raman spectroscopic study," *Sensors and Actuators B: Chemical*, vol. 71, pp. 134-139, 2000.

[7] B. Fruhberger, M. Grunze, and D. J. Dwyer, "Surface chemistry of H2S-sensitive tungsten oxide films," *Sensors and Actuators B: Chemical*, vol. 31, pp. 167-174, 1996.

[8] I. Jimenez, J. Arbiol, G. Dezanneau, A. Cornet, and J. R. Morante, "Crystalline structure, defects and gas sensor response to NO2 and H2S of tungsten trioxide nanopowders," *Sensors and Actuators B: Chemical Proceedings of the Ninth International Meeting on Chemical Sensors*, vol. 93, pp. 475-485, 2003.

[9] G. Sarala Devi, V. Bala Subrahmanyam, S. C. Gadkari, and S. K. Gupta, "NH3 gas sensing properties of nanocrystalline ZnO based thick films," *Analytica Chimica Acta: Molecular Electronics and Analytical Chemistry*, vol. 568, pp. 41-46, 2006.

[10] K. Zakrzewska, "Gas sensing mechanism of TiO2-based thin films," *Vacuum Proceedings of the International Workshop on Surface Physics: Metals on Solid Surfaces*, vol. 74, pp. 335-338, 2004.

[11] N. Koshizaki and T. Oyama, "Sensing characteristics of ZnO-based NOx sensor," *Sensors and Actuators B: Chemical*, vol. 66, pp. 119-121, 2000.

[12] A. Rothschild and Y. Komem, "The effect of grain size on the sensitivity of nanocrystalline metal-oxide gas sensors," *J. App. Phys.*, vol. 95, pp. 6374-6380, 2004.

[13] S. C. Moulzolf, S.-a. Ding, and R. J. Lad, "Stoichiometry and microstructure effects on tungsten oxide chemiresistive films," *Sensors and Actuators B: Chemical*, vol. 77, pp. 375-382, 2001.

[14] L. J. LeGore, R. J. Lad, S. C. Moulzolf, J. F. Vetelino, B. G. Frederick, and E. A. Kenik, "Defects and morphology of tungsten trioxide thin films," *Thin Solid Films*, vol. 406, pp. 79-86, 2002.

[15] M. A. Ponce, C. M. Aldao, and M. S. Castro, "Influence of particle size on the conductance of SnO2 thick films," *J. Eur. Ceram. Soc.*, vol. 23, pp. 2105-2111, 2003.

[16] D. H. Yoon and G. M. Choi, "Microstructure and CO gas sensing properties of porous ZnO produced by starch addition," *Sens. Actuators, B*, vol. 45, pp. 251-257, 1997.

[17] C. Bittencourt, E. Llobet, M. A. P. Silva, R. Landers, L. Nieto, K. O. Vicaro, J. E. Sueiras, J. Calderer, and X. Correig, "Influence of the deposition method on the morphology and elemental composition of SnO2 films for gas sensing: atomic force and X-ray photoemission spectroscopy analysis," *Sensors and Actuators B: Chemical*, vol. 92, pp. 67-72, 2003.

[18] M. Stankova, X. Vilanova, J. Calderer, E. Llobet, J. Brezmes, I. Gràcia, C. Cané, and X. Correig, "Sensitivity and selectivity improvement of rf sputtered WO3 microhotplate gas sensors," *Sens. Actuators, B*, vol. 113, pp. 241-248, 2006.

[19] G. G. Mandayo, E. Castaño, F. J. Gracia, A. Cirera, A. Cornet, and J. R. Morante, "Strategies to enhance the carbon monoxide sensitivity of tin oxide thin films," *Sens. Actuators, B*, vol. 95, pp. 90-96, 2003.

[20] X. Wang, S. S. Yee, and W. P. Carey, "Transition between neck-controlled and grain-boundary-controlled sensitivity of metal-oxide gas sensors," *Sens. Actuators, B*, vol. 25, pp. 454-457, 1995.

[21] H. Kawasaki, T. Ueda, Y. Suda, and T. Ohshima, "Properties of metal doped tungsten oxide thin films for NOx gas sensors grown by PLD method combined with sputtering process," *Sens. Actuators, B*, vol. 100, pp. 266-269, 2004.

[22] J. Shieh, H. M. Feng, M. H. Hon, and H. Y. Juang, "WO3 and W---Ti---O thin-film gas sensors prepared by sol-gel dip-coating," *Sens. Actuators, B*, vol. 86, pp. 75-80, 2002.

[23] A. Rothschild, F. Edelman, Y. Komem, and F. Cosandey, "Sensing behavior of TiO2 thin films exposed to air at low temperatures," *Sens. Actuators, B*, vol. 67, pp. 282-289, 2000.

[24] L. E. Depero, I. Natali Sora, C. Perego, L. Sangaletti, and G. Sberveglieri, "Kinetics of disorder-order transition of Ti---W oxide thin-film sensor," *Sens. Actuators, B*, vol. 31, pp. 19-24, 1996.

[25] G. Neri, A. Bonavita, G. Rizzo, S. Galvagno, N. Pinna, M. Niederberger, S. Capone, and P. Siciliano, "Towards enhanced performances in gas sensing: SnO2 based nanocrystalline oxides application," *Sens. Actuators, B*, vol. 122, pp. 564-571, 2007.

[26] E. Comini, L. Pandolfi, S. Kaciulis, G. Faglia, and G. Sberveglieri, "Correlation between atomic composition and gas sensing properties in tungsten-iron oxide thin films," *Sens. Actuators, B*, vol. 127, pp. 22-28, 2007.

[27] B. P. J. de Lacy Costello, R. J. Ewen, N. M. Ratcliffe, and M. Richards, "Highly sensitive room temperature sensors based on the UV-LED activation of zinc oxide nanoparticles," *Sensors and Actuators B: Chemical*, vol. 134, pp. 945-952, 2008.

[28] C. Ge, C. Xie, M. Hu, Y. Gui, Z. Bai, and D. Zeng, "Structural characteristics and UV-light enhanced gas sensitivity of La-doped ZnO nanoparticles," *Materials Science and Engineering: B*, vol. 141, pp. 43-48, 2007.

[29] J. Saura, "Gas-sensing properties of SnO2 pyrolytic films subjected to ultrviolet radiation," *Sensors and Actuators B: Chemical*, vol. 17, pp. 211-214, 1994.

[30] E. Comini, A. Cristalli, G. Faglia, and G. Sberveglieri, "Light enhanced gas sensing properties of indium oxide and tin dioxide sensors," *Sensors and Actuators B: Chemical*, vol. 65, pp. 260-263, 2000.

[31] T. Tesfamichael, M. Arita, T. Bostrom, and J. M. Bell, "Thin Film Deposition and Characterization of Pure and Iron-Doped Electron-Beam Evaporated Tungsten Oxide for Gas Sensors," *Thin Solid Films (* in Press); doi:10.1016/j.tsf.2010.01.037.

[32] V. Aroutiounian, Z. Mkhitaryan, A. Adamian, C.-G. Granqvist, L. Kish, *Fluctuation-enhanced gas sensing*, Procedia Chemistry, vol 1, pp. 216-219, 2009.

[33] V. M. Aroutiounian, Z. H. Mkhitaryan, A. A. Shatveryan, F. V. Gasparyan, M. Z. Ghulinyan, L. Pavesi, L. B. Kish, C.-G. Granqvist, Noise Spectroscopy of Gas Sensors, *IEEE Sensor Journal*, vol. 8, pp. 786-790, 2008.

[34] J. S. Bendat and A. G. Piersil, *Random Data Analysis and Measurment Procedures*. New York, USA: Wiley, 2000.

[35] M. Boulova and G. Lucazeau, "Crystallite Nanosize Effect on the Structural Transitions of WO3 Studied by Raman Spectroscopy," *Journal of Solid State Chemistry*, vol. 167, pp. 425-434, 2002.

[36] B. Karunagaran, P. Uthirakumar, S. J. Chung, S. Velumani, and E. K. Suh, "TiO2 thin film gas sensor for monitoring ammonia," *Materials Characterization*, vol. 58, pp. 680-684, 2007.

[37] M. F. Al-Kuhaili, S. M. A. Durrani, and I. A. Bakhtiari, "Carbon monoxide gas-sensing properties of CeO2-ZnO thin films," *Applied Surface Science*, vol. 255, pp. 3033-3039, 2008.