Deposition of tungsten oxide and silver decorated tungsten oxide for use in oxygen gas sensing

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***Abstract*—Tungsten oxide and silver-decorated tungsten oxide were investigated for the detection of oxygen in a humid environment. The sensor materials were deposited onto alumina sensor substrates *via* aerosol-assisted chemical vapour deposition. Results indicated that our sensors showed good sensitivity to oxygen, following an almost a linear relationship over a 0 to 20% concentration range. In comparison to WO_3, the Ag-decorated sensors showed a much higher sensitivity and better response (sensitivity of 0.22 per $\%O_2$ vs 0.80 per $\%O_2$ for Ag decorated), making Ag-WO_3 based sensors an interseting alternative to existing Pb-based sensors for quantitative oxygen sensing.**

Keywords—oxygen sensing, tungsten oxide, Ag-decoration, humid environment

I. INTRODUCTION

The detection of oxygen is one of the most important commercial gas sensor markets It is currently dominated by electrochemical techniques employing a Pb anode – a design which has been unchanged for over 20 years. However, "Restriction of Hazardous Substances Directive" (RoHS), also known as Directive 2002/95/EC, bans the use of lead in almost all electronic products. At the moment, gas sensors are exempt, but will be applied to gas sensors also by 2024 at the latest. Due to the importance of this market, modified electrochemical alternatives are being developed (and have made it to market) based on the use of zinc, iron or aluminium. However, these have problems in terms of sensitivity, life-span and cross-sensitivity. Furthermore, neither these new Pb-free or the existing sensors, attempt to bring the sensor technology into the 21st century, ignoring critical factors of form factor, cost, life-span and ease of integration with micro-electronics. Due to the importance of this market, researchers have developed alternatives. The most successful being zirconia based solid electrolyte sensors [1] for the automotive market. These sensors reside in the exhaust system and are used for engine management purposes – but are expensive (well in excess of current Pb sensors). In addition, they typically operate at 800°C, making them too high-power for alternative applications. Finally, there are optical methods [2] of detecting oxygen, either based on light absorbance or photo-quenching. Both work well, but require emitters, detectors, sensitivity is a function of path length and require a relatively high level of electronics to produce a reading. Together, these make such sensors bulky and expensive (more expensive than existing Pb based sensors) and therefore not an appropriate, viable replacement nor a technology well positioned for new consumer markets.

Our focus is the in development of a new generation of low-power, small, ultra-low cost oxygen gas sensors to fill the market need left by Pb-based sensors. Metal-oxides are one of the most commercially successful families of sensor technologies, with 20% of all gas analysis systems employing them. Their advantages include high sensitivity, simple resistive measurement, low-cost manufacturing and ability to operate in harsh/high-temperature environments. Moreover, the technology lends itself to ease of integration with smart electronic devices associated with the internet of things (IoT). Metal oxides have a conductivity that can be mediated by oxygen. At relatively low temperatures, typically < 600°C, the response of the materials is dominated by variations in the surface oxygen coverage, which is a function both of oxygen partial pressure and partial pressure of gases, which can interact with the surface oxygen. At these temperatures the oxygen response is relatively small (resistance $pO_2^{1/4}$) and the response is typically dominated by the presence of reducing gases. However, previous research by our group and others has shown that better performance can be achieved, specifically based on Pt/In_2O_3 [3] and $SrTiO_3$ [4]. These sensors considerable outperform the typical sensitivity of SnO_2 [5].

In this paper, we report on our latest work to develop a metal-oxide oxygen sensor, based on silver decorated tungsten oxide, with good oxygen concentration discrimination.

II. EXPERIMENTAL

A. Synthesis of WO3 films and Ag decorated WO3 films

Tungsten oxide was deposited on 2 mm x 2 mm alumina gas sensor substrates (with Au electrodes and Pt heater), by using aerosol-assisted chemical vapour deposition (AACVD) [6]. Silver nitrate [AgNO3] (≥99.0%) and tungsten hexcarbonyl [$(W(CO)_6)$] (≥97.0%) were purchased from Scientific Laboratory Supplies and Sigma-Aldrich, respectively and used as precursors without any purification.

WO_3 films: tungsten hexcarbonyl [$(W(CO)_6)$] (0.06 g, 0.17 mmol) previously dissolved in a mixed solution of acetone and methanol (15 ml, 2:1, Sigma-Aldrich, ≥99.6%) was transferred to a glass flask after sonicating for 5 min. Aerosol droplets were generated from the precursor solution using Johnson Matthey Liquifog ultrasonic atomizer and then transported to an alumina sensor substrate, pre-heated at 375°C, *via* a nitrogen carrier with flowrate of 300 sccm. The obtained coated substrates were

annealed in an oven at 500°C for 2 hours (ramp rate at 10°C/min) and then cooled down to room temperature.

Ag-WO_3 films: silver decorated WO_3 thin films were fabricated via AACVD in two steps. Firstly, an identical procedure was used to make WO_3 thin films. Secondly, the Ag precursor solution, consisting of [$AgNO_3$] (0.06g, 0.35 mmol) and a mixed solution of acetone and methanol (15 ml, 2:1), were aerosolized and deposited onto previously deposited and annealed WO_3 films (preheated at 375°C) at 250°C. The Ag-WO_3 samples were not subsequently annealed after deposition.

B. Electrical and oxygen sensing tests

A dedicated gas handling test rig has been constructed at the School of Engineering, University of Warwick to carry out sensor testing. The gas rig is capable of supplying a predefined concentration of oxygen by diluting 99.999% nitrogen (Leman Instrument, France) with zero air (~20% O_2) over a range of flow rates. Sensing tests were carried out at different concentration of oxygen in the range of 0 - 20% by using a computer controlled programme. The gas line from the gas apparatus is passed through water bubblers and connected to an air-tight chamber where the sensors were mounted. The chamber was connected to AS-330 Sensor Management System (SMS) (Atmospheric Sensor Ltd, UK) where the experimental settings can be adjusted. Using this SMS unit, sensing tests were carried out in the temperature range 150 – 400°C and the resistance values were stored in the PC linked to the SMS unit.

III. RESULTS AND DISCUSSION

A. Characterisation of thin films

XRD analysis (Fig. 1.) showed the presence of peaks associated with tungsten oxide (γ-WO3 structure, P21/n, a = 7.30084(7), b = 7.53889(7), c = 7.68962(7) Å, β = 90.892(1)°) with strong preferred orientation in the (002) direction as seen previously [7], and peaks associated with the alumina substrate. No peaks associated with silver (~ 38 and 44^0 2θ) were observed in the silver decorated sample likely due to low silver incorporation.

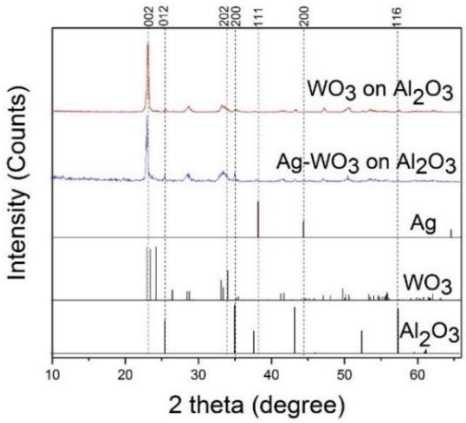

Fig. 1. XRD patterns of WO_3 and Ag-decorated WO_3 films on alumina substrates

X-ray photoelectron spectroscopy (XPS), illustrated in Fig. 2., was used to study the oxidation states and impurity levels for an annealed WO_3 sample. Analysis of the W 4f environment showed no measurable presence of W^{5+} states, and solely the W^{6+} environment, with binding energies similar to reference values [8]. Analysis of a silver decorated sample showed the presence of peaks attributable to silver, although the binding energy is more consistent with the presence of silver oxide than silver metal.

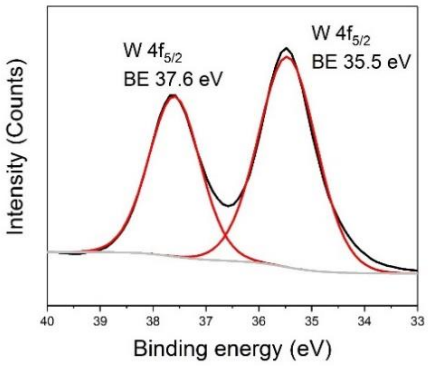

Fig. 2 High resolution XP spectra of W 4f core-level spectra of WO3 after annealing

The SEM micrographs in Fig. 3. show the microstructure of the Ag-WO_3 thin films. The sample exhibits nanorod morphology previously observed for tungsten oxide deposited under these conditions on ITO substrates [7], with no obvious particles observed on the bulk tungsten oxide morphology. The films showed a porous structure which is likely to facilitate the adsorption of O_2.

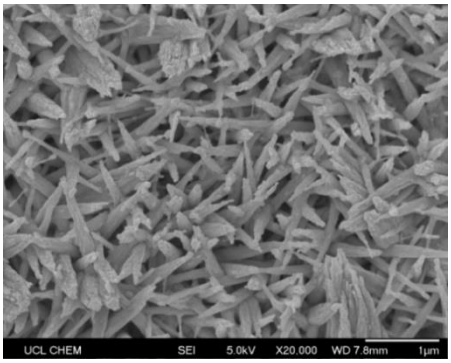

Fig. 3. Film morphologies observed by SEM images of Ag-WO3 on alumina substrate

B. Sensor response under high humidity environment

Measurements were carried out in humid environment (relative humidity of 80-85%) in the temperature range 150 – 400°C. The sensors were exposed to oxygen concentrations ranging from 0 to 20% volume in wet air. Different concentrations were obtained by varying the flow rate of nitrogen and air, keeping the total flow rate at 300 ml/min. Figure 4 illustrates WO_3 responses for comparison. The sensors exhibited no significant sensitivity toward oxygen at temperatures less than 250°C. From this temperature to 400°C, the maximum response, ($R_g/R_o - 1 = 7$ or 0.35 per $\%O_2$) of WO_3 sensors was obtained at 400°C. The addition of silver promotes the response toward oxygen in the whole temperature range. It also lowers the temperature of maximum response (R_g/R_o=16 or 0.80 per $\%O_2$ vs R_g/R_o= 4.4 or 0.22 per $\%O_2$) to 350°C. At this temperature, the base resistance was observed at 1.5 kOhm for

[1] Sensor response is expressed in Rg/Ro - 1 where Rg= resistance O_2 at certain concentration and Ro= resistance of N_2

Ag-WO_3 compared to 10kOhm for WO_3. Duplicate measurements carried out with the same sensors and/or sensors fabricated the same way shown similar results.

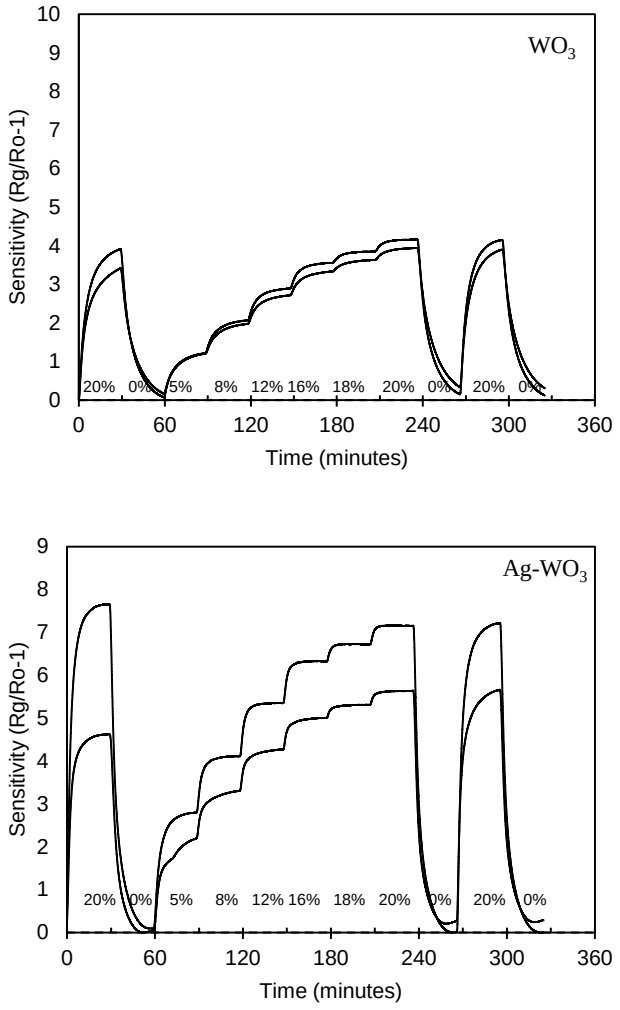

Fig. 3. Dynamic response of WO_3-based sensors to different O_2 concentrations at 300°C.: WO_3 (top) and Ag-WO_3 (down)

C. Sensitivity

Sensitivity (R_g/R_o - 1) and calculated in the temperature range 250 – 400°C. The Ag-WO_3 seemed to comply with traditional power law relationship, showing good response with an alpha value between 0.7 – 0.8. The WO_3 sensors, however, showed more linear fashion as seen in with alpha value in range 0.9 – 1.1. Sensitivity of sensors upon gas exposure at different O_2 concentrations at 300°C is illustrated in Fig. 4. Ag-WO3 exhibits higher sensitivity than WO_3 in the whole range of temperature investigated.

The best sensitivity obtained at 350°C at different O_2 concentration also showed $AgWO_3$ performed better than WO_3 at 5 – 8 – 12 – 16 – 18 – 20% oxygen. Ag-WO_3 exhibited sensitivity at 5.3 – 9.0 – 12 – 14.2 – 15.2 - 16.1 respectively, in comparison with WO_3 at 1.3 – 2.2 – 3.0 – 3.7 – 4.0 - 4.4 respectively. The silver decorated tungsten showed 4x higher sensitivity than tungsten oxide.

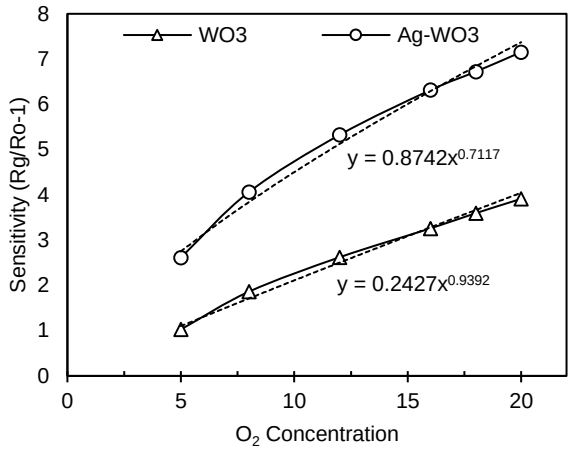

Fig. 4. WO_3 and Ag-WO_3 sensitivity as a function of O_2 concentration at 300°C

CONCLUSIONS

Tungsten oxide and silver decorated tungsten oxide have successfully been fabricated by AACVD and tested as oxygen sensors in wet air at temperature ranging from 150 – 400°C. The sensors showed good performance in terms of sensitivity and response. The addition of silver in WO_3 has shown to promote sensor performance, making the sensors a good alternative to lead-free oxygen sensor technology.

ACKNOWLEDGMENT

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