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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 WO₃, the Ag-decorated sensors showed a much higher sensitivity and better response (sensitivity of 0.22 per %O₂ vs 0.80 per %O₂ for Ag decorated), making Ag-WO₃ based sensors an interesting 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/In₂O₃ [3] and SrTiO₃ [4]. These sensors considerable outperform the typical sensitivity of SnO₂ [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 hexacarbonyl [(W(CO)₆] (≥97.0%) were purchased from Scientific Laboratory Supplies and Sigma-Aldrich, respectively and used as precursors without any purification.

WO₃ films: tungsten hexacarbonyl [(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 at 375°C from the precursor solution using Johnson Matthey Liquifog ultrasonic atomizer and then transported to an alumina sensor substrate *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-WO₃ films: silver decorated WO₃ thin films were fabricated via AACVD in two steps. Firstly, an identical procedure was used to make WO₃ thin films at 350°C. Secondly, the Ag precursor solution, consisting of [AgNO₃] (0.06g, 0.35 mmol) and a mixed solution of acetone and methanol (15 ml, 2:1), were aerosolized and deposited at 250°C onto previously deposited and annealed WO₃ films. The Ag-WO₃ 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% O₂) 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 change in the lattice was observed due to silver decoration. No peaks associated with silver (\sim 38 and 44° 2 θ) were detected in the silver decorated sample likely due to low silver incorporation, but it was present in XPS analysis.

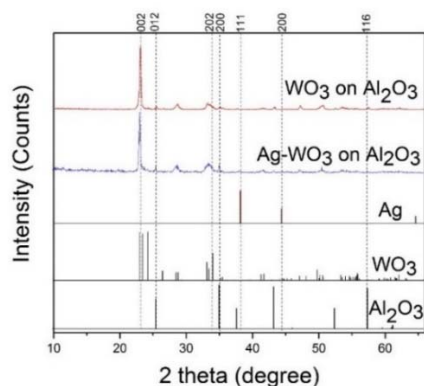


Fig. 1. XRD patterns of WO₃ and Ag-decorated WO₃ films on alumina substrates

X-ray photoelectron spectroscopy (XPS), illustrated in Fig. 2., was used to study the oxidation states and impurity levels for an annealed WO₃ sample. Analysis of the W 4f environment

showed no measurable presence of W⁵⁺ states, and solely the W⁶⁺ 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.

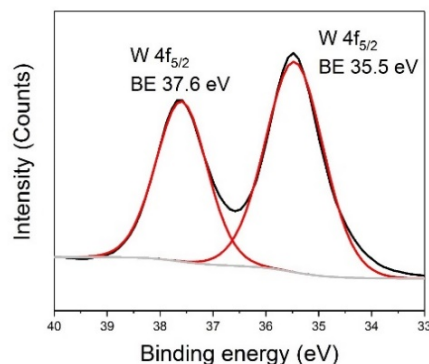


Fig. 2 High resolution XP spectra of W 4f core-level spectra of WO₃ after annealing

The SEM micrographs in Fig. 3. show the microstructure of the Ag-WO₃ 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 O₂.

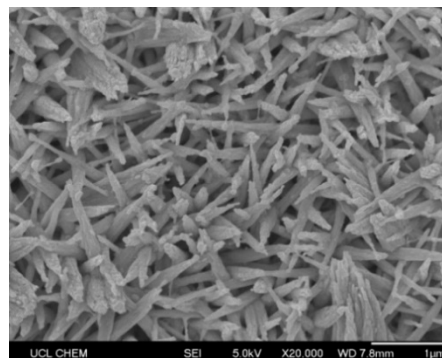


Fig. 3. Film morphologies observed by SEM images of Ag-WO₃ on alumina substrate

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 WO₃ 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 %O₂) of WO₃ 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 %O₂ vs $R_g/R_o= 4.4$ or 0.22 per %O₂) to 350°C. At this temperature, the base resistance was observed at 1.5 kOhm for

¹ Sensor response is expressed in $R_g/R_o - 1$ where R_g = resistance O₂ at certain concentration and R_o = resistance of N₂

Ag-WO₃ compared to 10kOhm for WO₃. Duplicate measurements carried out with the same sensors and/or sensors fabricated the same way shown similar results.

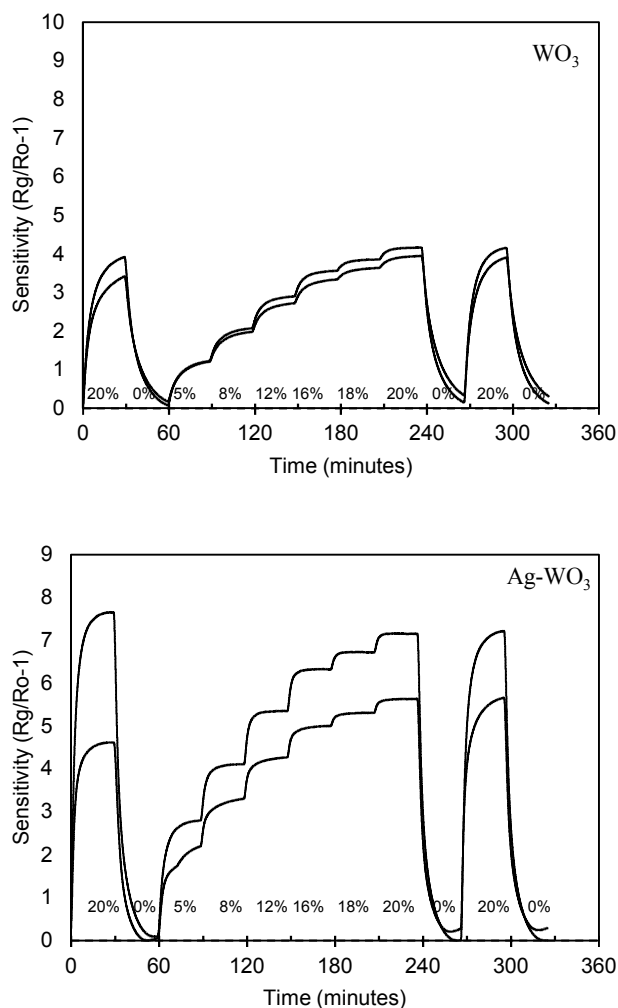


Fig. 3. Dynamic response of WO₃-based sensors to different O₂ concentrations at 300°C.: WO₃ (top) and Ag-WO₃ (down)

C. Sensitivity

Sensitivity ($R_g/R_o - 1$) and calculated in the temperature range 250 – 400°C. The Ag-WO₃ seemed to comply with traditional power law relationship, showing good response with an alpha value between 0.7 – 0.8. The WO₃ 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 O₂ concentrations at 300°C is illustrated in Fig. 4. Ag-WO₃ exhibits higher sensitivity than WO₃ in the whole range of temperature investigated.

The best sensitivity obtained at 350°C at different O₂ concentration also showed AgWO₃ performed better than WO₃ at 5 – 8 – 12 – 16 – 18 – 20% oxygen. Ag-WO₃ exhibited sensitivity at 5.3 – 9.0 – 12 – 14.2 – 15.2 - 16.1 respectively, in comparison with WO₃ 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.

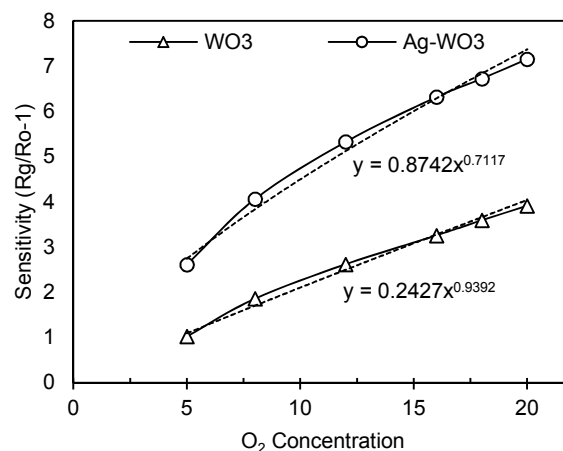


Fig. 4. WO₃ and Ag-WO₃ sensitivity as a function of O₂ concentration at 300°C

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 WO₃ has shown to promote sensor performance, making the sensors a good alternative to lead-free oxygen sensor technology.

ACKNOWLEDGMENT

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