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Sol–gel prepared MoO_3–WO_3 thin-films for O_2 gas sensing

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Abstract

Oxygen gas sensing properties of molybdenum trioxide and tungsten trioxide (MoO_3–WO_3) mixed metal oxide thin-films are investigated. Various MoO_3–WO_3 ratio thin-film samples are deposited onto silicon (1 0 0) and sapphire substrates via the sol–gel route. SEM analysis showed the presence of MoO_3 orthorhombic phase, abating as WO_3 dominated the mixed system. MoO_3–WO_3 sensors exhibited a linear response to O_2 concentrations varying from 10 to 10,000 ppm. The MoO_3–WO_3 film response was stable and reproducible operating at an optimal temperature of 420°C. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Molybdenum; Tungsten; Sol–gel; Gas sensors; Thin-film

1. Introduction

MoO_3 and WO_3 are well known metal oxide materials used in gas sensing, catalytic, photochromic, and electrochromic research fields. WO_3 has made itself popular with its promising NO_x and O_3 sensing capability [1–3]. MoO_3 has shown to be sensitive to NH_3, H_2, CO and NO_2 [4–8]. Both metal oxides have similar physical and chemical properties. Wang et al. [9] loaded WO_3 with 1 wt.% MoO_3 achieving a sensitivity of 5–40 ppm of NO and 10–30 ppm of NH_3 operating at 350°C. Xu et al. [10] fabricated MoO_3–WO_3 sensors for NH_3 detection. Increasing the MoO_3 (at.%) further increased the sensor response to NH_3. Khawaja et al. [11], reports on the optical properties of mixed oxides WO_3/MoO_3. It was found that the mixed oxide films were chemically inhomogeneous. This inhomogeneity may arise because of the differences in the vapour pressure of the MoO_3 and WO_3, at a given temperature. As a result, satisfactory optical results could not be obtained for films of the mixed oxides.

Metal oxide thin-films can be fabricated using various methods such as rf and dc sputtering, chemical vapour deposition (CVD), electron, thermal and ion cluster beams and several others. Each method provides various advantages and disadvantages. Recently, the sol–gel process has become a popular technique to prepare metal oxide thin-films for gas sensing. The low cost of production facilities, low fabrication temperature, easily accessible starting materials, and the potential to form large surface areas with the sol–gel technology have made it an attractive alternative for fabricating thin-films for gas sensing [9,10]. The process was first developed in the 1950s to assist with radioactive material fabrication. In the 1970s and 80s it made a resurgence in interest as the starting materials available where high quality, a strict requirement for successful material fabrication.

In this paper, our aim is to fabricate MoO_3–WO_3 thin-films onto sapphire transducers to test the films response when exposed to O_2. The sol–gel process was employed to realise the binary metal oxide compound of MoO_3–WO_3.

2. Experimental

2.1. Thin-film preparation

Metal alkoxide precursors (Chemat Technology Inc.) of molybdenum(V) isopropoxide ($Mo(OC_3H_7)_5$) and tungsten(VI) ethoxide ($W(OC_2H_5)_6$) were mixed in anhydrous butanol to achieve 0.1 M concentration. The mixed compounds realised are elaborated in Table 1.

The clear solutions were prepared in an environmental bag filled with dry nitrogen (<5% RH). The sols were placed in an ultrasonic bath for 1 h to achieve a homogeneous mixing of the components at the atomic scale and then left at room temperature to age and settle for 24 h. Using syringes with micropore filters, the solution was placed on both sapphire and silicon substrates and spun at 2500 rpm for

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Table 1
MoO_3–WO_3 thin-film sensors prepared with varying atomic percentages

Sensor reference	MoO_3 (at.%)	WO_3 (at.%)
MoO_3	100	0
A1	95	5
A2	75	25
A3	50	50
A4	25	75
A5	5	95
WO_3	0	100

25 s. The films were left to gel for 24 h at room temperature and then annealed at 450 and 500°C with a heating rate of 2°C/min. The sol–gel process and general procedure of the MoO_3–WO_3 film fabrication is illustrated in Fig. 1.

2.2. Microstructure and gas sensing characterisation

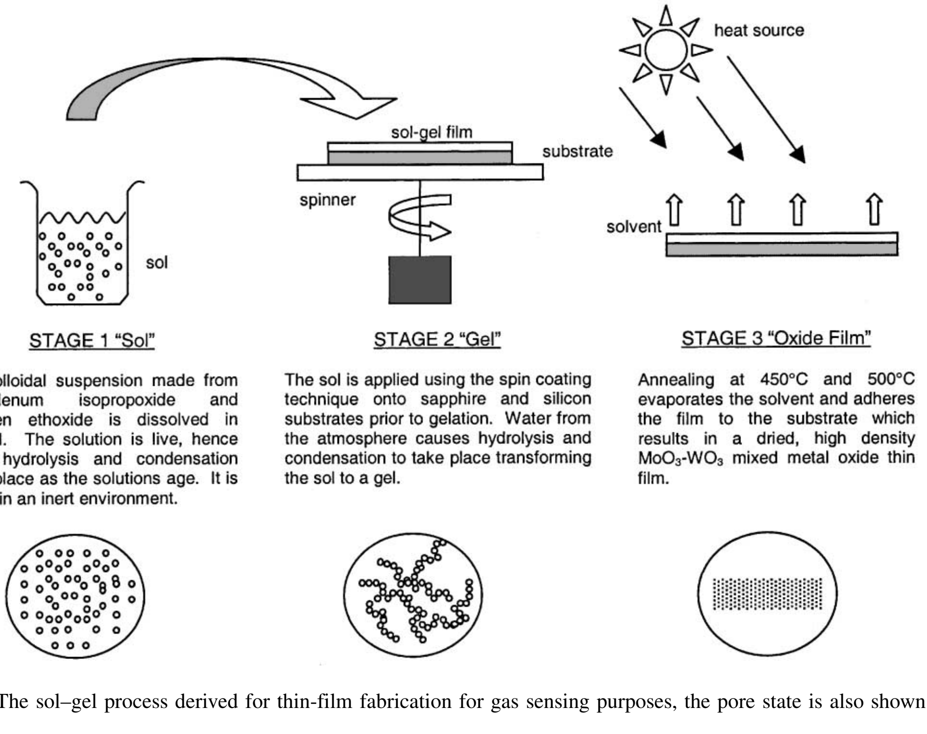
The microstructure and the surface morphology of the films were examined using a scanning electron microscope (SEM, Philips XL-30) operating at 30 kV. The gas sensing properties of the MoO_3–WO_3 thin-films to O_2 were measured using a computerised multimeter system (34401A Hewlett-Packard) and a gas calibration system incorporating mass flow controllers set at 0.2 LPM. The measurements were carried out at different operating temperatures in the range of 220–420°C. The ambient temperature was 20°C and RH 30%. The electrical response S of the sensor is defined as $S = R_{gas}/R_{10\,ppm}$ for O_2. Certified O_2 gas bottles of 10, 100, 1000, and 10,000 ppm balanced with dry N_2 were used for gas sensing. The films optimal operating temperature, resistance, response ($\tau_{res} = 0.9$) and recovery times ($\tau_{rec} = 0.3$) were also analysed. All results presented are referenced to samples annealed at 500°C unless otherwise stated.

3. Results and discussion

3.1. Microstructure characterisation (SEM)

Fig. 2(a–h) shows SEM micrographs of the mixed metal oxide thin-films annealed at 500°C. It is well known that the single metal oxide of MoO_3 has a layered structure with orthorhombic symmetry, similar to a plate-like structure [11,12]. Such a structure is seen in Fig. 1(a) and (h), dominated by MoO_3, the particles vary from 100 nm to 2 μm in diameter. These particles have also been identified to be MoO_3 using the selected area function of energy dispersive X-ray microanalysis (EDX). The presence of the MoO_3 orthorhombic phase reduces as WO_3 dominates the film composition as seen in Fig. 1(c) and (d). The film transforms to a uniform, nanosized homogeneous structure being porous and made up of nanosized grains and pores. Fig. 1(g) shows a crack in the film due to the silicon wafers curved edge structure, the thickness of the film is about 100–250 nm.

Other SEM micrographs taken with samples deposited onto quartz show similar MoO_3 phase features. Due to the MoO_3–WO_3 films morphological similarities on different substrates, it could be concluded, therefore that the film



The colloidal suspension made from molybdenum isopropoxide and tungsten ethoxide is dissolved in butanol. The solution is live, hence some hydrolysis and condensation takes place as the solutions age. It is stored in an inert environment.

The sol is applied using the spin coating technique onto sapphire and silicon substrates prior to gelation. Water from the atmosphere causes hydrolysis and condensation to take place transforming the sol to a gel.

Annealing at 450°C and 500°C evaporates the solvent and adheres the film to the substrate which results in a dried, high density MoO_3-WO_3 mixed metal oxide thin film.

Fig. 1. The sol–gel process derived for thin-film fabrication for gas sensing purposes, the pore state is also shown.

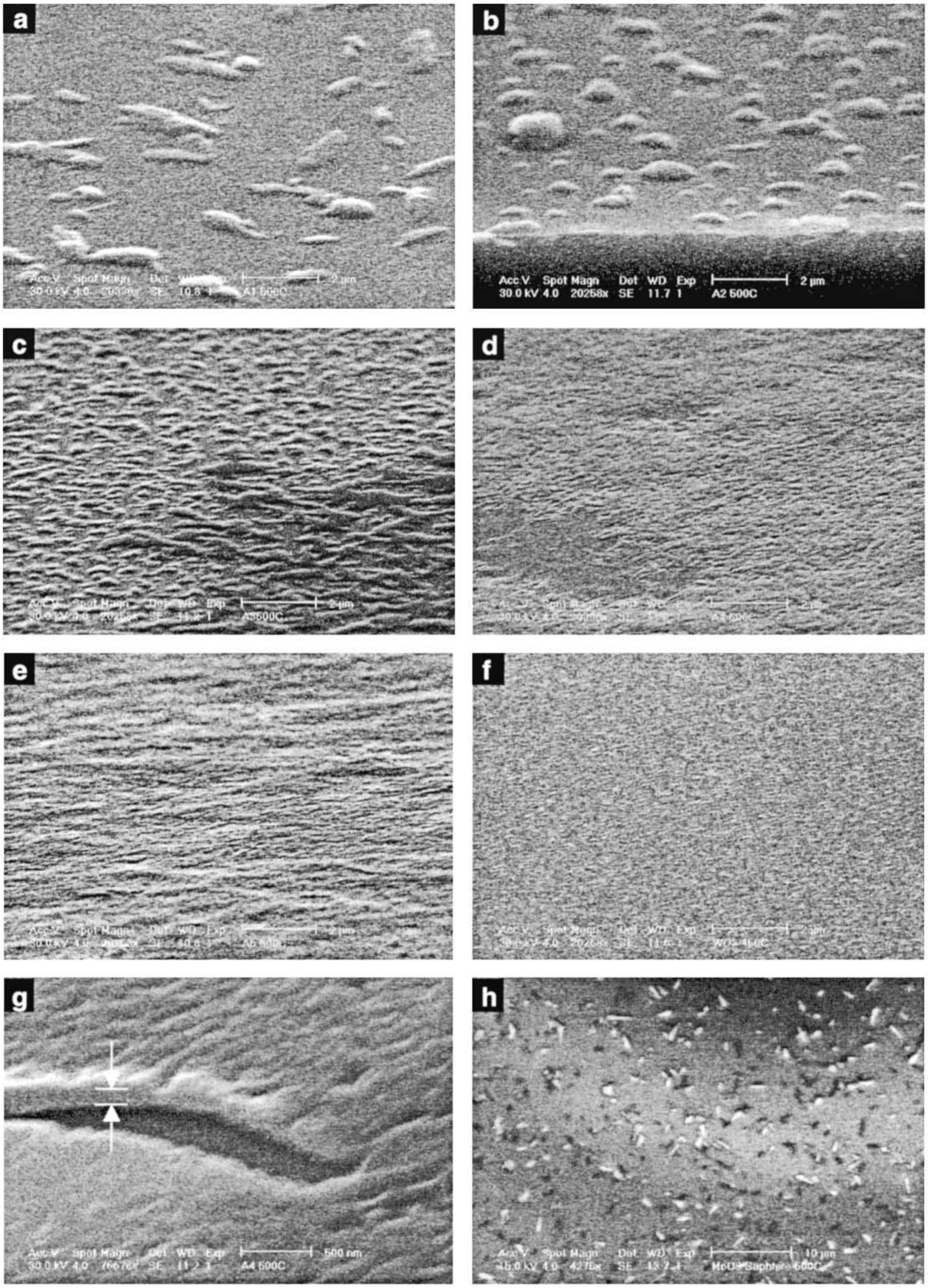


Fig. 2. SEM micrographs of MoO_3–WO_3 samples annealed at 500°C on silicon substrates: (a) Al, (b) A2, (c) A3, (d) A4, (e) A5, (f) 100% WO_3, (g) sample A4 illustsrating the layer thickness, (h) sample 100% MoO_3 on sappire substrate.

structure is not dependent on nor is influenced by the sample substrate, as also concluded by Ferroni et al. [13] depositing MoO_3 by rf sputtering. From SEM analysis, it was also found that the prepared samples annealed at 450°C had similar morphological features.

3.2. Electrical properties

Fig. 3. illustrates the log R versus $1000/T$ (K) curves for sensors MoO_3, A2, A4, and WO_3 to 100 ppm of O_2. The curves deviate from a straight line due to the oxygen-sensing

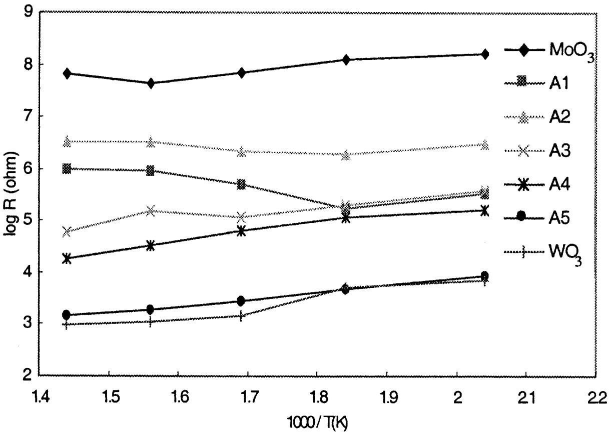


Fig. 3. MoO_3–WO_3 film log R vs. 1000/T (K) curves for sensors MoO_3, A2, A4 and WO_3 annealed at 500°C while exposed to 100 ppm of O_2 gas.

mechanism of Schottky barrier dominating at low temperatures while oxygen vacancy bulk effect dominating at high temperatures, hence during the transition a nonlinear effect results as explained by Xu et al. [14].

MoO_3 has a high resistivity making it somewhat impractical for gas sensing applications. Additional circuitry and transducer modification would be required to compensate for its intrinsic low conductivity properties. The dominating presence of WO_3 decreases the films resistivity. The high resistivity is due to the wide bandgap of MoO_3 at 3.2 eV and the electrical resistivity at room temperature is of the order of 10^{10} Ω cm measured on a sintered pellet [12].

3.3. Static response

The film resistance variation was measured in the range between 10 and 10,000 ppm of O_2 operating at 320°C as shown in Fig. 4. The observed linear dependence occurs at different concentration ranges depending on the MoO_3–WO_3 ratio. Samples A3 and A4 possess a much linear response versus concentration over the range of 10–10,000 ppm than that of both MoO_3 and WO_3 pure components. From the static response, it could also be noted that the resistance change for MoO_3 is high at low concentrations of O_2, on the contrary, WO_3 has a high response at relative high O_2 concentrations. Therefore, by adjusting the mixed oxide ratio, various resistance versus concentration profiles can be obtained. The 450°C annealed samples exhibit similar characteristics.

MoO_3 is extremely sensitive to O_2, exhibiting a response of 40–1000 ppm of O_2 operating at 370°C as shown in Fig. 5. Sample A2 also exhibits some promising response characteristics, linearly increasing in response with temperature similar to the other mixed oxide samples. However, WO_3 has a fairly consistent response throughout the temperature range tested. Such a sensor may be desirable, if the operating temperature fluctuates due to ambient temperature influences. Similarly, WO_3 dominated samples A3, A4 and A5 also exhibit little response variation to sensor operating temperature in the range of 320–420°C.

3.4. Dynamic response

MoO_3 exhibits good response characteristics, however, it also exhibits instable and irreversible properties, worsening as its operating temperature increases. The cause is hypothesised to be due to its low melting point of 795°C, hence at high temperatures ($T > 400$°C) the film changes. However, this effect abates as the MoO_3 content reduces as seen by the stable and reproducible results achieved for A2, A4, A5 samples, illustrated in Fig. 6.

The trade off between response magnitude and speed of response is well illustrated in Table 2. MoO_3 is seen to exhibit fast response and recovery times with also a large

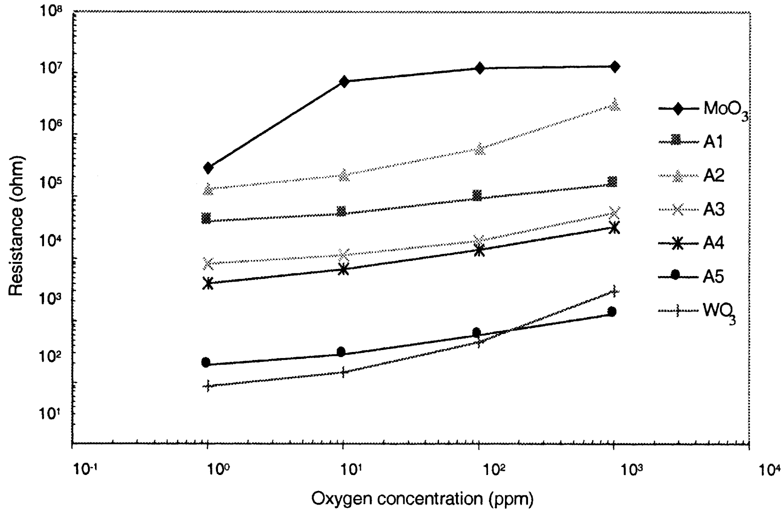


Fig. 4. Resistance vs. O_2 concentration for MoO_3–WO_3 samples at an operating temperature of 320°C.

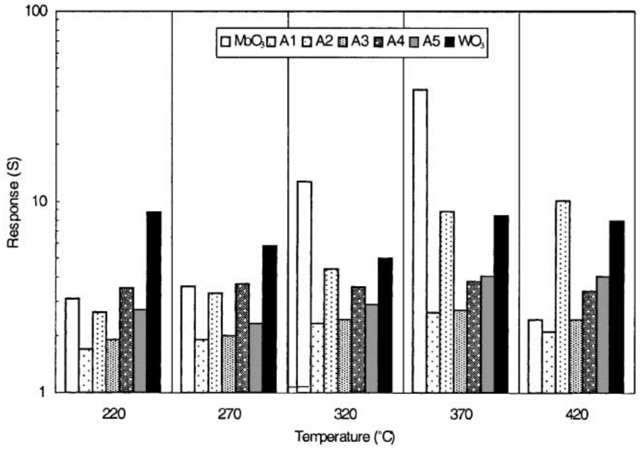


Fig. 5. Response vs. temperature bar graph of O_2 from 10 to 1000 ppm at an operating temperature of 320–420°C.

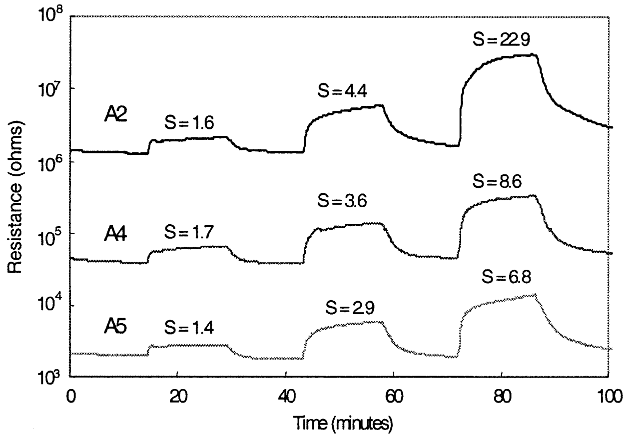


Fig. 6. Dynamic response of samples A2, A4 and A5 at an operating temperature of 320°C exposed to 10 ppm as baseline, and then to pulses of 100, 1000 and 10,000 ppm each for a period of 15 min.

response magnitude, however, the films possess poor reliability gas sensing properties. It is envisaged that MoO_3 could be used only as a low operating temperature sensor, or further as a dopant material. The optimal operating temperature for the sensors, excluding that of MoO_3 is at 420°C. Although, A3 has a relative fast response, its poor response magnitude debilitates the practical use of the sensor.

Table 2
The optimum response and recovery times with associated responses magnitudes and operating temperatures during films exposure to 1000 ppm of O_2 for 15 min

Sensor reference	Response time (s) ($\tau_{res} = 0.9$)	Recovery time (s) ($\tau_{rec} = 0.3$)	Response $R_{gas}/R_{10\ ppm}$	Optimal operating temperature (°C)
MoO_3	1.1	3.5	40.4	370
A1	–	–	–	–
A2	3.5	4	10.1	420
A3	1.5	2.5	1.9	420
A4	6	3	3.4	420
A5	5.4	6	4.4	420
WO_3	4	4	7.5	420

4. Conclusions

The systematic gas sensing analysis of MoO_3–WO_3 thin-films has been undertaken to overcome the instable gas sensing attributes of MoO_3. SEM revealed the presence of MoO_3 orthorhombic phase, reducing into a nanosized film morphology as the WO_3 component increased. It was found that the film resistance decreased as the MoO_3 component reduced. MoO_3–WO_3 samples exhibit linear response to a broad range of O_2 concentrations more so then both single component metal oxides. Furthermore, the O_2 response of MoO_3–WO_3 thin-films were stable and reproducible, however, did not possess a high response magnitude as compared to pure MoO_3. Future research will analyse MoO_3–WO_3 film response to CO, NO_x and O_3.

For further reading see [15,16].

Acknowledgements

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Biographies

K. Galatsis received his degree with honours in Computer Systems Engineering from the Royal Melbourne Institute of Technology University, Australia in 1998. His research efforts focus on MoO_3-based MOS gas sensors, gas analysers, vehicle cabin air quality, and smoke-dust IR backscatter detectors.

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W. Wlodarski has worked in the areas of sensor technology and instrumentation for over 30 years. He has published four books and monographs and over 200 papers and holds 26 patents. He is a professor at RMIT University, Melbourne, Australia and heads the Sensor Technology Laboratory located in the School of Electrical and Computer Systems Engineering.

K. Kalantar-zadeh received his BSc and MSc degrees in Communication Engineering from the Sharif University of Technology and Tehran University in 1993 and 1997, respectively. He has since worked for companies such as Benz in manufacturing and for various engineering research centres on underwater SONAR systems. Currently, his PhD research efforts are focused on Love mode surface acoustic wave transducers and sensors for the detection of bio-chemical components in the liquid media.