

# Comparison of single and binary oxide MoO<sub>3</sub>, TiO<sub>2</sub> and WO<sub>3</sub> sol–gel gas sensors

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## Abstract

A systematic comparison of sol–gel prepared titanium dioxide (TiO<sub>2</sub>), WO<sub>3</sub>, and MoO<sub>3</sub> single metal oxide based gas sensors was conducted. Process variables such as solution concentration, deposition parameters, gelling time, annealing time and temperature, remained constant. Sensors based on binary compound MoO<sub>3</sub>–TiO<sub>2</sub> and MoO<sub>3</sub>–WO<sub>3</sub> were also investigated to determine if the performance is superior to their single oxide constituents. The sensors were systematically exposed to O<sub>2</sub>, O<sub>3</sub>, CO and NO<sub>2</sub> gases and ethanol vapor at concentration levels of particular interest. MoO<sub>3</sub> binary compound based sensors showed promising O<sub>3</sub>, CO and NO<sub>2</sub> gas response. Their use as a sensing film for gas is limited due to the materials low evaporating temperature, limiting its operating temperature below 350 °C. However, the binary oxide of MoO<sub>3</sub>–WO<sub>3</sub> showed a high response to ethanol vapor and a highly selective response to NO<sub>2</sub>. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Gas sensors; Titanium oxide; Tungsten oxide; Molybdenum oxide

## 1. Introduction

A variety of techniques are available for fabricating thin films of metal oxide semiconducting (MOS) materials. Popular techniques are sputtering, chemical vapor, thermal or electronic beam evaporation deposition. Sol–gel thin film fabrication is a simple and versatile method of realising metal oxide thin films. Many research efforts are progressively employing this technology to explore new and novel sensing materials for gas sensing applications, as it is a low cost alternative, financially beneficial as compared to maintaining physical vapor deposition or chemical vapor deposition (PVD–CVD) equipment and purchasing high-cost targets.

By standardizing many thin film fabrication variables in the sol–gel process, such as solution concentration, deposition parameters, gelling time, annealing time and temperature, operating temperature and transducers employed; a systematic comparison of single metal oxides of titanium dioxide (TiO<sub>2</sub>), WO<sub>3</sub> and MoO<sub>3</sub> has been undertaken.

## 2. Background

TiO<sub>2</sub>, WO<sub>3</sub> and MoO<sub>3</sub> single metal oxide compound materials have been extensively studied in the past decade. They show promising gas sensing properties as well as unique optical properties for various applications. However, as in most cases, practical and high performance MOS based gas sensors are seldom made up of pure single metal oxides. Catalysts are usually deposited to increase the chemisorption process and instigate fast response as well as high sensitivity and improved selectivity. Nevertheless, a complete understanding of any single metal oxide constituting within a material composition is required.

TiO<sub>2</sub> is commonly used in many devices such as solar cells, optical wave guides, interference filters, capacitors and as a popular material in the MOS gas sensor domain. In its rutile phase (tetragonal), stable at temperatures above 800 °C, it is employed as an oxygen gas sensor (bulk defect sensors) for automotive air:fuel ratio control (lambda sensors). Such sensors have been commercialized by NGK Spark Plug Co. Ltd. [1]. Compared to the traditional lambda sensors based on ZrO<sub>2</sub>, TiO<sub>2</sub> thick film sensors offer a faster response time [2]. TiO<sub>2</sub> gas sensors operating at temperatures below 600 °C, make use of the anatase phase that has a

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lower resistance and higher sensitivity to surface adsorbents than that of the rutile phase [3]. In this case, the sensing mechanism is dominated by chemisorption where oxygen captures electrons from the oxide, producing a depletion region (space-charge layer) near the surface. With respect to gas sensing, anatase  $\text{TiO}_2$  nanocrystalline thin films are preferred since they exhibit desirable gas sensing characteristics at operating temperature below  $400^\circ\text{C}$ .

Tungsten trioxide ( $\text{WO}_3$ ) films are reported to have promising electrical and optical properties for various applications like efficient photolysis, electrochromic devices, selective catalysts and gas sensors [4]. Amorphous and polycrystalline  $\text{WO}_3$  films are particularly attractive as gas sensors because they show a high catalytic behavior both in oxidation and reduction reactions [5]. Electrochromic devices which exploit  $\text{WO}_3$  are typically in an amorphous form, whereas electrical devices such as gas sensors, are in a crystalline form [6]. Tungsten also forms other oxides such as  $\text{WO}$ ,  $\text{W}_2\text{O}_3$ , and  $\text{W}_4\text{O}_{11}$ , however, in gas sensing the stable  $\text{WO}_3$  form is used.

As for  $\text{MoO}_3$ , it exhibits two problems for gas sensing. First, the material has a low evaporating temperature, permitting only low operating temperatures, however, such temperatures may not indeed be the optimal working temperature for particular gas species. The melting point of  $\text{MoO}_3$  is  $795^\circ\text{C}$ , relatively low compared to  $\text{SnO}_2$  at  $1127^\circ\text{C}$ . Second, the material has a very high resistivity, making it a difficult material to realize as a gas sensor and to integrate with electronics. Although, these two disadvantages have been identified,  $\text{MoO}_3$  possesses good gas response since it has been used in the field of catalysis for oxidation reactions of hydrocarbons [7].  $\text{MoO}_3$  has a bandgap of 3.2 eV and electrical resistivity at room temperature is of the order of  $10^{10}\ \Omega\ \text{cm}$ .

Multi-metal oxide compound materials for gas sensing applications has been an important focus recently in the MOS gas sensing field. Many oxide combinations can be tailored to achieve desired surface to volume ratios and morphologies as to attain various gas sensing performance. The addition of a second element may cause a decrease in the grain size, which in addition improves gas sensor response characteristics. Current research of binary-metal oxide films is extremely promising but still at an initial stage. By varying the composition of the binary-metal oxide material, the sensor performance can be modified, i.e. improve selectivity, reduce detection limit, fabricating n- or p-type material and modifying the material resistivity for ease of electronic interface. Recent studies focusing on Mo, W and Ti based mixed metal oxides report on their promising gas sensing potential [8–10].

### 3. Experimental

$\text{TiO}_2$ ,  $\text{WO}_3$ ,  $\text{MoO}_3$ ,  $\text{MoO}_3\text{-TiO}_2$  and  $\text{MoO}_3\text{-WO}_3$  were prepared by the sol-gel method. The precursors used to

Table 1  
Sol-gel precursors

| Component    | Chemicals                        | Formula                              |
|--------------|----------------------------------|--------------------------------------|
| Mo precursor | Molybdenum <i>iso</i> -propoxide | $\text{Mo}(\text{OC}_3\text{H}_7)_5$ |
| Ti precursor | Titanium butoxide                | $\text{Ti}(\text{OC}_4\text{H}_9)_4$ |
| W precursor  | Tungsten ethoxide                | $\text{W}(\text{OC}_2\text{H}_5)_6$  |

fabricate the solutions are shown in Table 1. The solutions were prepared as described in [8,9]. The solutions was spun onto alumina and sapphire conductometric structured substrates incorporating interdigital electrode fingers on the front side and an integrated heater on the backside. All the films were annealed at  $450^\circ\text{C}$  for 1 h.

## 4. Results and discussion

### 4.1. SEM analysis

It is well known that gas sensing properties of a metal oxide thin film strongly depends on its morphological features. A high surface area facilitates the chemisorption process by increasing the adsorption and desorption rates [11]. The grain, neck and grain boundary features also influences the gas sensing properties.

It has been shown that the smaller grain size increases gas sensitivity since the diameter is comparable with or less than the space-charge region of the grain [12]. Additionally, for high value of relative conductance change (high response) it is necessary to have a low density of bulk carriers,  $n_b$ , and a thin film thickness,  $d$ , [13]. The microstructure and the surface morphology of the films were examined using a scanning electron microscope (SEM, Philips XL-30). As shown from Fig. 1, the morphology of  $\text{TiO}_2$ ,  $\text{WO}_3$ , and  $\text{MoO}_3$  is dramatically different.  $\text{TiO}_2$  and  $\text{WO}_3$  are made up of spherical grain structures. However,  $\text{MoO}_3$  is made up of long needle like particles growing up from the film. Such film morphology clearly does not facilitate film electron flow. The binary oxides of  $\text{MoO}_3\text{-TiO}_2$  and  $\text{MoO}_3\text{-WO}_3$  are a composite of both their single metal oxide constituents. Fig. 1e shows that the segregated grown up  $\text{MoO}_3$  particles, as also detected by EDX analysis, disperses into a refined mixed multi oxide based structure as the W content of the film increases with respect to the Mo content.

The gas sensing properties of  $\text{TiO}_2$ ,  $\text{WO}_3$  and  $\text{MoO}_3$  single metal oxide compounds were examined when exposed to  $\text{O}_2$ ,  $\text{O}_3$ ,  $\text{CO}$ ,  $\text{NO}_2$  gases and ethanol vapor.

### 4.2. Oxygen ( $\text{O}_2$ ) gas sensing

Table 2 summarizes the  $\text{O}_2$  response results.  $\text{TiO}_2$ , and  $\text{MoO}_3$  exhibit high oxygen responses compared to  $\text{WO}_3$ . As was expected, the sol-gel  $\text{TiO}_2$  sensor exhibited a superior  $\text{O}_2$  response, relatively fast and consistently returning to its baseline as seen from Fig. 1.

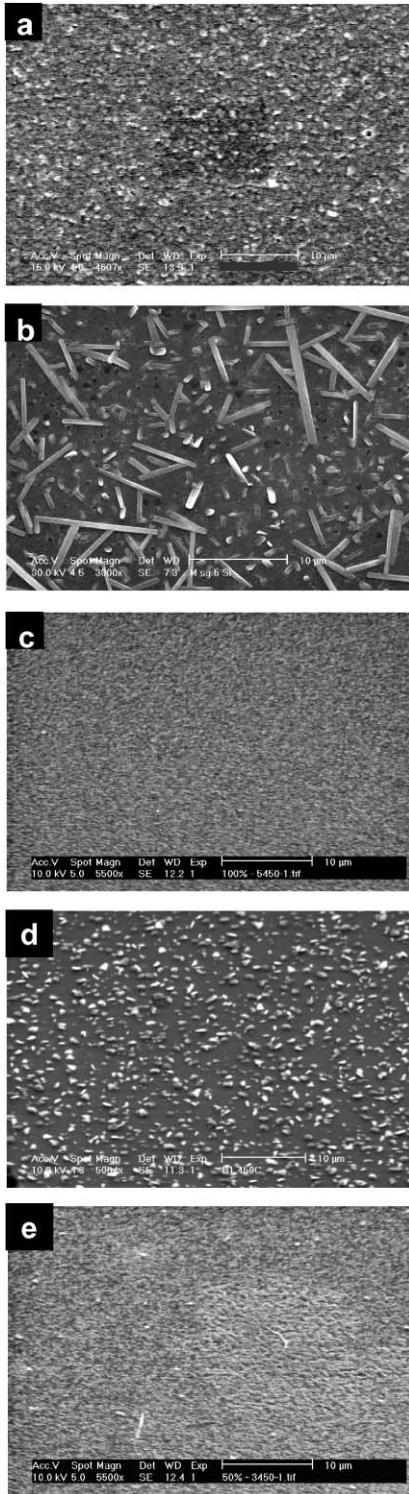


Fig. 1. Morphological difference of (a) TiO<sub>2</sub>; (b) MoO<sub>3</sub>; (c) WO<sub>3</sub>; (d) MoO<sub>3</sub>-TiO<sub>2</sub>; (e) MoO<sub>3</sub>-WO<sub>3</sub> on Si substrates annealed at 450 °C.

4.3. Ozone (O<sub>3</sub>) gas sensing

It is well known that both In<sub>2</sub>O<sub>3</sub> [14] and WO<sub>3</sub> [15] are highly sensitive to O<sub>3</sub>. Sol-gel based WO<sub>3</sub> has a response of 35–80 ppb of O<sub>3</sub> [15]. Sol-gel based MoO<sub>3</sub>-WO<sub>3</sub> was

Table 2  
Response to 1000 ppm of O<sub>2</sub>

| Sensor           | ( $\tau_{res} = 0.9$ ) | ( $\tau_{rec} = 0.3$ ) | Response | Temperature (°C) |
|------------------|------------------------|------------------------|----------|------------------|
| MoO <sub>3</sub> | 1                      | 5                      | 39       | 370              |
| WO <sub>3</sub>  | 4                      | 4                      | 7.5      | 420              |
| TiO <sub>2</sub> | 2                      | 1.5                    | 28       | 420              |

compared to commercially available In<sub>2</sub>O<sub>3</sub> based sensors (New Cosmos Electric Co. Ltd.). TiO<sub>2</sub> did not show a measurable response to ozone gas. MoO<sub>3</sub> response to O<sub>3</sub> could not be measured due to a high resistance. Therefore, to measure the MoO<sub>3</sub> ozone response, MoO<sub>3</sub>-TiO<sub>2</sub> and MoO<sub>3</sub>-WO<sub>3</sub> were fabricated which reduced the films resistivity. Most interesting was MoO<sub>3</sub>-TiO<sub>2</sub> with a response time less than 20 s to 100 ppb of O<sub>3</sub> and a response of 1.7. The response is also very stable for ozone, while the recovery time is sluggish at about 2 min. MoO<sub>3</sub>-WO<sub>3</sub> exhibits promising results to O<sub>3</sub> as shown in Figs. 2 and 3. Hence, MoO<sub>3</sub> based sensors could be considered as promising candidates for O<sub>3</sub> gas sensing.

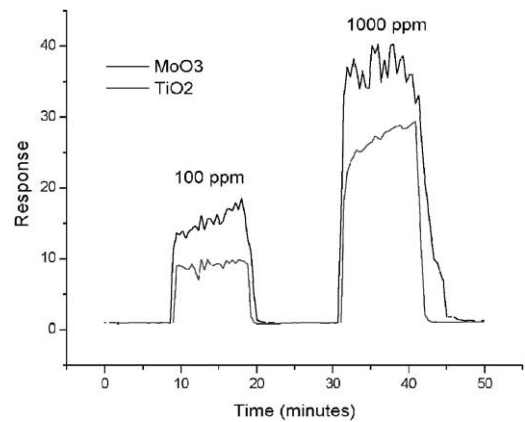


Fig. 2. Oxygen dynamic response of TiO<sub>2</sub> and MoO<sub>3</sub> sensors operating at 370 °C.

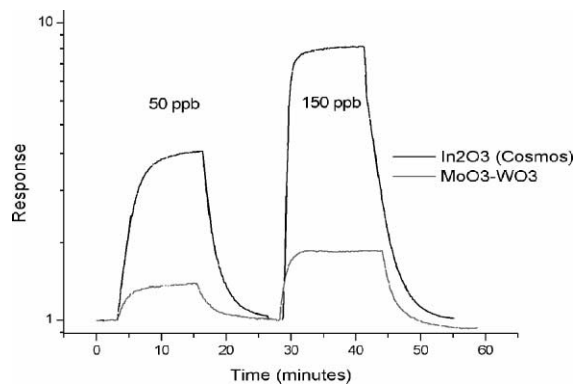


Fig. 3. Dynamic response MoO<sub>3</sub>-WO<sub>3</sub> ( $T = 150$  °C) compared to the superior In<sub>2</sub>O<sub>3</sub> (Cosmos) ozone sensor.

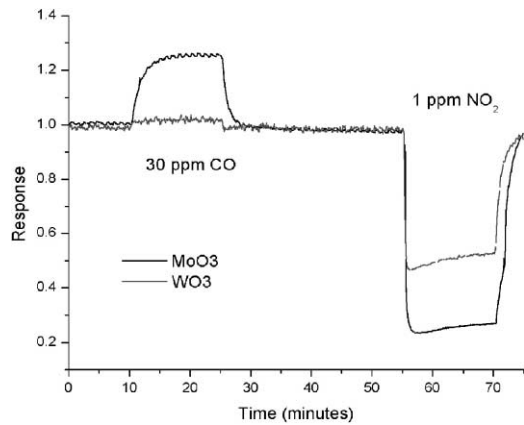


Fig. 4. CO and NO<sub>2</sub> response of Mo and W oxide sensors operating at 300 °C.

#### 4.4. Carbon monoxide (CO) and nitrogen dioxide (NO<sub>2</sub>) gas sensing

TiO<sub>2</sub> had a negligible response to CO compared with WO<sub>3</sub> and MoO<sub>3</sub>. MoO<sub>3</sub> and WO<sub>3</sub> showed promising CO and NO<sub>2</sub> results. MoO<sub>3</sub> exhibited a high response to both CO and NO<sub>2</sub> as shown in Fig. 4.

The binary system of MoO<sub>3</sub>–TiO<sub>2</sub> was fabricated so that the resistance of MoO<sub>3</sub> would decrease. The material attained its high response to CO, however, it was not as responsive to NO<sub>2</sub> as compared to pure MoO<sub>3</sub>. MoO<sub>3</sub>–WO<sub>3</sub> surprisingly did not respond to CO and was selective only to NO<sub>2</sub>, i.e. having a response of 2.3 and a time response of 60 s to 1 ppm of NO<sub>2</sub> as shown in Fig. 5.

#### 4.5. Ethanol vapor sensing

The sensors were exposed to 100–600 ppm of ethanol and to 10–30 ppm of CO to investigate the cross-sensitivity

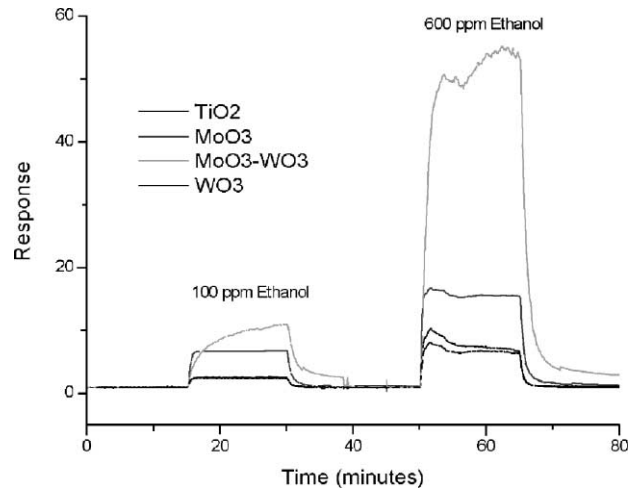


Fig. 6. Response to 100 and 600 ppm of ethanol at an operational temperature of 300 °C.

effects. CO is a typical nuisance gas commonly experienced by law enforcement bodies in the field of random breath testing as it is emitted from vehicle exhausts and cigarettes. All oxide compounds exhibited good gas sensing performance to ethanol.

MoO<sub>3</sub> had the best response compared to the single metal oxides. Furthermore, the mixed oxide of MoO<sub>3</sub>–WO<sub>3</sub> exhibited an exceptional response to ethanol trading off response time and stability as shown in Fig. 6.

Table 3 shows the response comparison of the three sensors tested, made up of different materials. The mixed metal oxide MoO<sub>3</sub>–WO<sub>3</sub> outperforms both single metal oxides in response, improving by 380 and 750% of pure MoO<sub>3</sub> and WO<sub>3</sub> based sensors, respectively. WO<sub>3</sub> has a negligible response to CO, which is desirable. Furthermore, commercialized alcohol sensors [16] have a response of 10–500 ppm (0.05%) of ethanol.

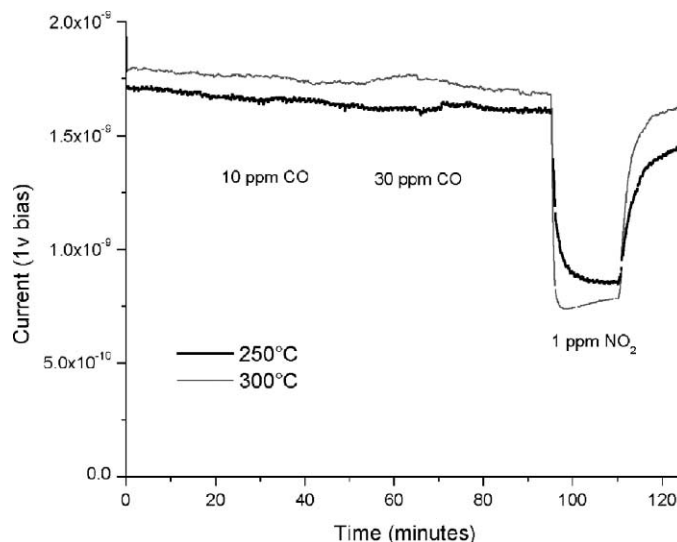


Fig. 5. The dynamic response of a MoO<sub>3</sub>–WO<sub>3</sub> film to CO and NO<sub>2</sub>.

Table 3  
Ethanol and CO response magnitude comparison

| Sensor                            | Ethanol<br>(100 ppm) | Ethanol<br>(600 ppm) | CO<br>(10 ppm) | CO<br>(30 ppm) |
|-----------------------------------|----------------------|----------------------|----------------|----------------|
| MoO <sub>3</sub>                  | 6.7                  | 14.0                 | 1.05           | 1.25           |
| MoO <sub>3</sub> –WO <sub>3</sub> | 10.0                 | 53.0                 | 1.0            | 1.0            |
| WO <sub>3</sub>                   | 2.5                  | 7.0                  | 1.0            | 1.0            |

## 5. Conclusions

MoO<sub>3</sub> based sensors showed promising O<sub>3</sub> gas sensing characteristics. MoO<sub>3</sub>–TiO<sub>2</sub> showed a good response to CO, outperforming other single metal oxides tested. Interestingly, MoO<sub>3</sub>–WO<sub>3</sub> exhibited a high selectivity to NO<sub>2</sub>, i.e. having an undetectable response to 30 ppm of CO. The binary systems of MoO<sub>3</sub>–WO<sub>3</sub> also showed a high response to ethanol vapor outperforming the single metal oxides. MoO<sub>3</sub> has to be highly oxidized and reduced. By mixing it with TiO<sub>2</sub> and WO<sub>3</sub>, the resistivity is reduced and in cases of O<sub>3</sub>, CO and NO<sub>2</sub> gas and ethanol vapor sensing, its performance is enhanced.

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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<sub>3</sub> based MOS gas sensors, gas analyzers, 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.