

## Semiconductor MoO<sub>3</sub>–TiO<sub>2</sub> thin film gas sensors

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### Abstract

The O<sub>2</sub>, CO and NO<sub>2</sub> gas sensing properties of MoO<sub>3</sub>–TiO<sub>2</sub> thin films have been studied. The sol–gel process was employed to fabricate MoO<sub>3</sub>–TiO<sub>2</sub> thin films onto sapphire and alumina transducers for gas sensing measurements. It was found the MoO<sub>3</sub> dominated sensors have a lower optimal operating temperature of 370°C than the TiO<sub>2</sub> dominated sensors. The response of the sensors was stable and reproducible at operating temperatures below 400°C. However, once the films were exposed to temperatures higher than 400°C, repeatable gas sensing results could not be achieved. The low evaporation temperature of MoO<sub>3</sub> component of the mixed system is believed to be the cause of the sensors instability and irreversibility at high operating temperatures. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Molybdenum; Titanium; Gas sensing; Sol–gel process; Thin film

### 1. Introduction

Interest in mixed metal oxide compound materials for gas sensing applications has recently increased in popularity. The aim is to increase the current single metal oxide surface-to-volume ratio and to fabricate stable nano-sized grain morphologies for high performance gas sensing thin films. Both MoO<sub>3</sub> and TiO<sub>2</sub> are common single metal oxide compounds used in gas sensing. The empirical exploration of mixing MoO<sub>3</sub> and TiO<sub>2</sub> may lead to new gas sensing properties or may simply lead to a material composed of characteristics similar to MoO<sub>3</sub> and TiO<sub>2</sub>.

Gas sensing properties of mixed MoO<sub>3</sub> and TiO<sub>2</sub> was first reported by Ono et al. [1] and then by Arco et al. [2]. MoO<sub>3</sub> dispersed on TiO<sub>2</sub> catalysed the oxidation of hydrocarbons as well as the dehydrogenation of alcohols. Raju and Rao [3] investigated the sensing characteristics of MoO<sub>3</sub>–TiO<sub>2</sub> for ammonia. They concluded that 15 at.% MoO<sub>3</sub>–TiO<sub>2</sub> gives best results for NH<sub>3</sub>. The sensitivity is highest at 277–327°C range where the MoO<sub>3</sub>–TiO<sub>2</sub> is a stable sensing material. Pure MoO<sub>3</sub> sputtered thin films was also shown to be suitable ammonia sensors, operating at 400°C with a response time of less than 30 s as reported by Mutschall

et al. [4]. Azad et al. [5] reported on the developed pure thick film MoO<sub>3</sub> could be used for on/off type detectors for CO. Thin films based on two-phase mixture of ZrO<sub>2</sub>–MoO<sub>3</sub> (1:2 molar ratio) could be employed for measuring the concentration of CO gas. The sensitivity and response time of MoO<sub>3</sub>-based sensors was greatly improved by the addition of small amounts of Pd. Hamagami et al. [6] also investigated MoO<sub>3</sub> and Pd. He fabricated a double-layered thin film consisting of a sputtered MoO<sub>3</sub> layer covered with a thin Pd layer on a glass substrate used as a room temperature H<sub>2</sub> optical gas sensor. Barreca et al. [7] realized MoO<sub>3</sub>–Bi<sub>2</sub>O<sub>3</sub> thin films using chemical vapor deposition (CVD). Their preliminary measurements on Bi-doped MoO<sub>3</sub> films indicate that they could be used for the detection of reducing gases such as CH<sub>4</sub>. However, their results indicate the film has a long response time of 5 min to 500 ppm CH<sub>4</sub> and the films did not possess stable and repeatable characteristics. Chiorino et al. [8] used sol–gel technique to fabricate MoO<sub>x</sub>–SnO<sub>2</sub> thick film gas sensors. The molybdenum lowered the film conductance by two orders of magnitude in air. Furthermore, Mo lowered the response of tin oxide towards CO, however, it enhanced the film NO<sub>2</sub> sensing ability. The thermal pre-treatment parameters effect the Mo induced sensors response. Sol–gel prepared MoO<sub>3</sub>–In<sub>2</sub>O<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> films were found to be very sensitive to detecting low concentrations (100–200 ppb) of O<sub>3</sub> and NO<sub>2</sub>, investigated by Gurlo et al. [9]. Operating at 250°C, a response of 25 and 7–2 ppm

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of  $\text{NO}_2$  was achieved for  $\text{MoO}_3\text{-In}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  films, respectively.

Pure  $\text{MoO}_3$  exhibits fast response to  $\text{NO}_2$  and good sensitivity to  $\text{CO}$  in the temperature range of  $200\text{--}400^\circ\text{C}$  as reported by Ferroni et al. [10,11]. The optimum temperature for  $\text{NO}_2$  sensing was concluded to be  $300^\circ\text{C}$  with a response and recovery time of 1–2 and 6–7 min, respectively.

A systematic investigation of the  $\text{O}_2$ ,  $\text{CO}$  and  $\text{NO}_2$  gas sensing properties of  $\text{MoO}_3\text{-TiO}_2$  thin films derived by the sol–gel process is presented. The film's electrical resistance, operating temperature, sensor response time, stability and reversibility are focused throughout the investigation in the search for a promising gas sensor.

## 2. Experimental

### 2.1. Thin film preparation

The sol–gel process is a simple and versatile technique for realizing metal oxide thin films. Due to the nano-scale reacting mechanism a nano-composite material is produced, suitable for various applications particularly thin films for gas sensing.

Molybdenum (V) isopropoxide ( $\text{Mo}(\text{OC}_3\text{H}_7)_5$ ) (Chemat Technologies Inc.) and titanium butoxide ( $\text{Ti}(\text{OC}_4\text{H}_9)_4$ ) (Aldrich) were mixed and dissolved in anhydrous butanol (0.1 M). Various metal alkoxide atom ratios were mixed to gain specific molecular compounds as seen from Table 1.

The sol–gel films were deposited using the spin coating technique onto sapphire and alumina substrate transducers incorporating platinum (sapphire substrate) and gold (alumina substrate) IDT's and a heater on the backside. The

Table 1  
 $\text{MoO}_3\text{-TiO}_2$  thin films prepared with various atom percentages

Sensor reference	$\text{MoO}_3$ (at.%)	$\text{TiO}_2$ (at.%)
$\text{MoO}_3$	100	0
B1	95	5
B2	75	25
B3	50	50
B4	25	75
B5	5	95
$\text{TiO}_2$	0	100

solution was spun at 2500 rpm for 30 s onto sapphire and alumina transducers. The sol–gel prepared films were annealed at  $500^\circ\text{C}$  for 1 h with a temperature ramp of  $2^\circ\text{C}/\text{min}$ . This process is illustrated in Fig. 1.

### 2.2. Gas sensing characterization

The  $\text{MoO}_3\text{-TiO}_2$  film response to  $\text{O}_2$ ,  $\text{CO}$  and  $\text{NO}_2$  was tested. The sapphire transducers were employed to analyze the  $\text{MoO}_3\text{-TiO}_2$  films response to  $\text{O}_2$ . A computerized gas calibration system incorporating a multimeter to detect film conductance change was used as seen in Fig. 1. Certified oxygen gas bottles of 10, 100, 1000, and 10 000 ppm balanced with nitrogen was used at a  $\text{N}_2$  flow rate of 0.2 LPM. Regulated dc power was supplied to the transducers heater to operate the sensors at elevated temperatures.

Alumina transducers were used to test the  $\text{CO}$  and  $\text{NO}_2$  response of the  $\text{MoO}_3\text{-TiO}_2$  films. The conductance change of the alumina based sensors were recorded using the volt amperometric technique. A constant potential of 1 V was applied, while a picoammeter measured the resistance

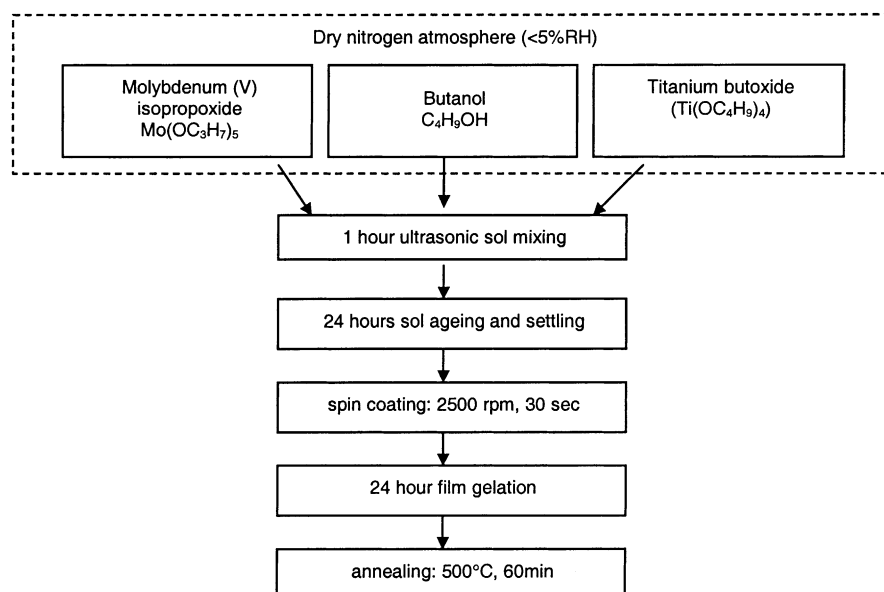


Fig. 1. A flowchart of  $\text{MoO}_3\text{-TiO}_2$  thin film preparation via the sol–gel process.

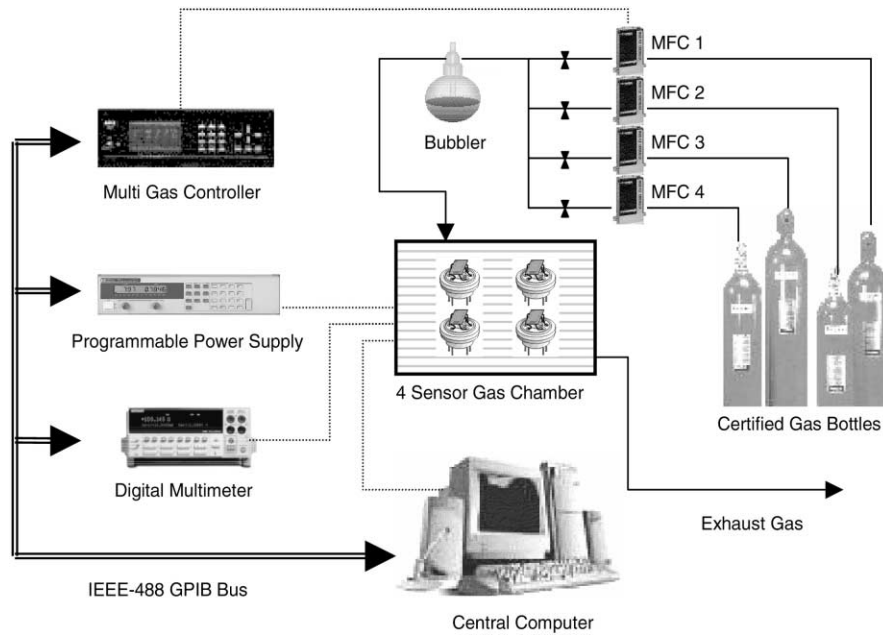


Fig. 2. Four-channel gas sensor measurement set-up.

variation as a function of time. A constant flux of synthetic air of 0.3 LPM was used as the gas carrier and the desired concentrations of CO and NO<sub>2</sub> were mixed in from certified gas bottles. The measurements were conducted under a controlled humidity environment (RH 30%) and the temperature of the sensor gas chamber was set at 20°C. Gas sensor measurement set-up is illustrated in Fig. 2.

### 3. Results and discussion

#### 3.1. O<sub>2</sub> static response

The film resistance variation was measured from 10 to 10 000 ppm of O<sub>2</sub> operating at 320°C as shown in Fig. 3. The

TiO<sub>2</sub> dominated samples have a linear curve, unlike the MoO<sub>3</sub> dominated samples. Samples B2 and B3 exhibit relative low resistance compared to other samples. The TiO<sub>2</sub> dominated samples have similar static response characteristics. Fig. 4 shows the response versus temperature bar graph for all samples. The samples were exposed from 10 to 1000 ppm of O<sub>2</sub> and operating at a temperature of 370–420°C. The optimal operating temperature of MoO<sub>3</sub> at 370°C showed the highest response of 39–1000 ppm of O<sub>2</sub>. Similarly, all the MoO<sub>3</sub> dominated thin films followed this trend. TiO<sub>2</sub> and its dominated thin films operated best at higher temperatures, at around 400°C. Hence, by varying the composition of both MoO<sub>3</sub> and TiO<sub>2</sub> ratio, one can design a pre-determined optimal operating temperature MoO<sub>3</sub>–TiO<sub>2</sub> based sensor.

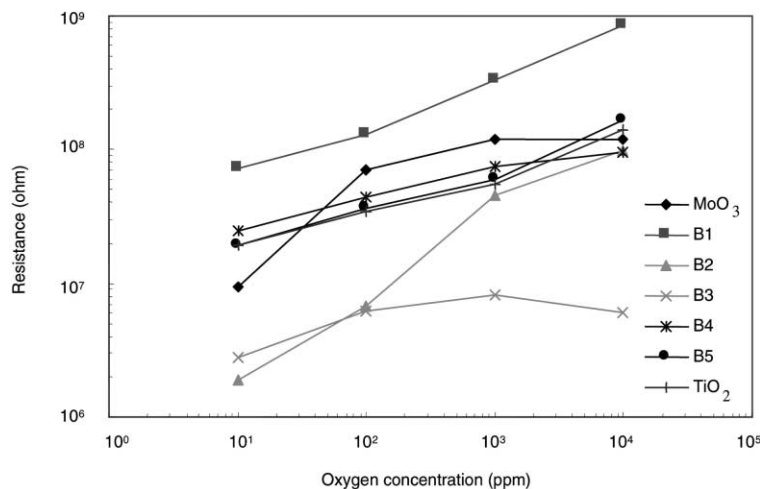


Fig. 3. Resistance versus O<sub>2</sub> concentration for MoO<sub>3</sub>–TiO<sub>2</sub> samples at an operating temperature of 320°C.

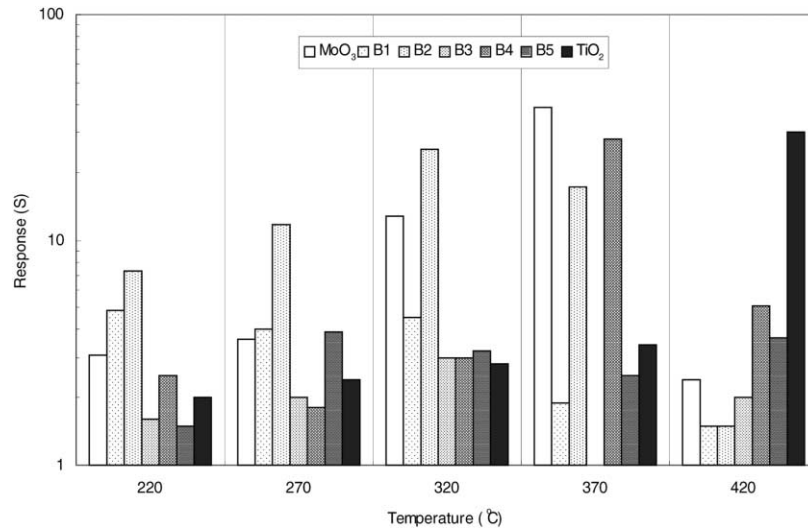


Fig. 4. Response versus temperature bar graph of  $O_2$  from 10 to 1000 ppm at an operating temperature of 370–420°C.

### 3.2. $O_2$ dynamic response

Fig. 5 shows the dynamic response of samples  $MoO_3$ , B4, B5,  $TiO_2$  at an operating temperature of 370°C. The sensors were exposed to 10 ppm of  $O_2$ , used as baseline, and then to pulses of 100, 1000 and 10 000 ppm, each for a period of 15 min. The  $MoO_3$  dominated samples exhibited long response times at low operating temperatures less than 370°C, however, when operated at  $T \geq 400^\circ C$  the stability and reproducibility of the sensors disintegrated. The  $TiO_2$  dominated sensors, exhibited good stability and reproducibility throughout all operating temperatures tested. Impressive response times and recovery times were obtained at high operating temperature as illustrated in Table 2. The response

time of the  $MoO_3$ – $TiO_2$  sensors were consistent throughout all the samples tested averaging about 2 min for the response and 3 min for recovery. All the sensors responded very fast, less than 40 s to 100 ppm of  $O_2$ .

### 3.3. CO and $NO_2$ dynamic response

Sensors B2 and B4 were exposed to 25, 200 and 400 ppm of CO and to 0.5 and 2 ppm of  $NO_2$  gas. The operating temperature was varied between 300 and 500°C. Figs. 6 and 7 illustrate the dynamic response of the sensors operated at 300°C towards CO and  $NO_2$  pulses.  $NO_2$  had an oxidizing effect while CO had a reducing effect. For reducing gases the response is defined as the quotient of the resistance in pure

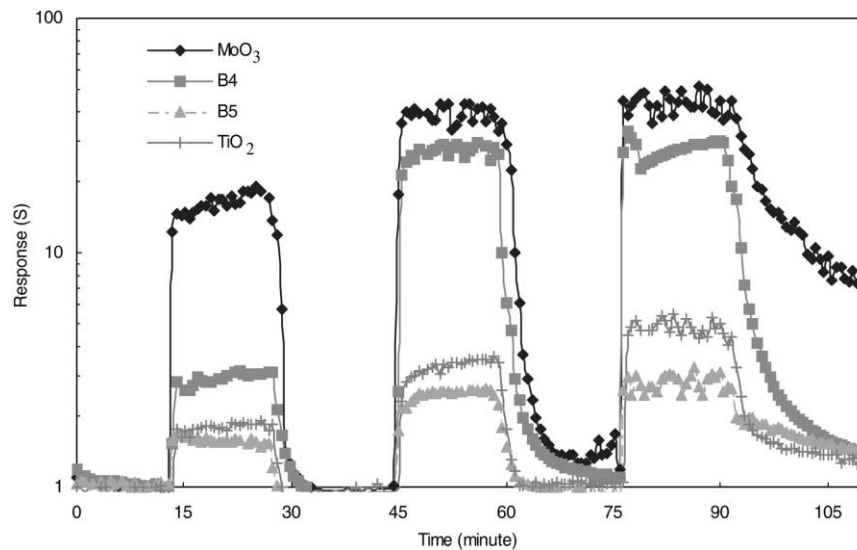


Fig. 5. Dynamic response of samples  $MoO_3$ , B4, B5,  $TiO_2$  at an operating temperature of 370°C exposed to 10 ppm as baseline, and then to pulses of 100, 1000 and 10 000 ppm each for a period of 15 min.

Table 2

The optimum response and recovery times with associated response magnitudes and operating temperatures during films exposure to 1000 ppm of O<sub>2</sub> for 15 min

Sensor reference	Response time (min) ( $\tau_{res} = 0.9$ )	Recovery time (min) ( $\tau_{rec} = 0.3$ )	Response ( $R_{gas}/R_{10\text{ ppm}}$ )	Optimal operating temperature (°C)
MoO <sub>3</sub>	1	5	39	370
B1	3.5	3	2	370
B2	1.2	3	16	370
B3	1.9	2.3	3	320
B4	1.1	2	30	370
B5	1	3	4	420
TiO <sub>2</sub>	2	1.5	28	420

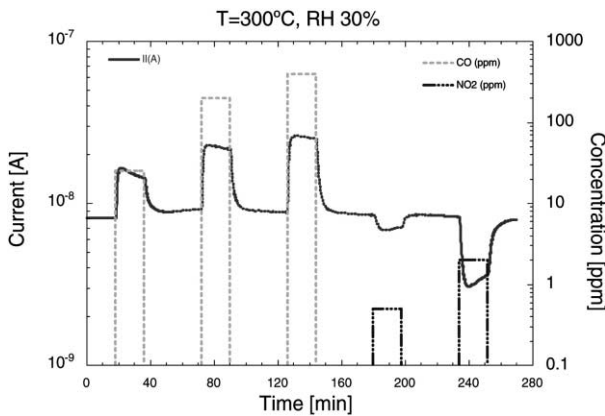


Fig. 6. B2 sensor response to CO and NO<sub>2</sub> at 300°C and 30% RH.

synthetic air and the resistance under gas  $S_{res} = R_o/R_{gas}$  and for oxidizing gases  $S_{ox} = R_{gas}/R_o$ . Table 3 illustrates the sensor response operating at the optimal temperature of 300°C.

The dynamic response ( $\tau_{res} = 0.9$ ) for all measurements is about 2 min, and the recovery time ( $\tau_{rec} = 0.3$ ) is about 3 min. B2 and B4 sensors are stable and reproducible when operated at 300°C. However, when the operating temperature increases, the sensors become unstable, and their response is time dependent. This unstable behavior of the

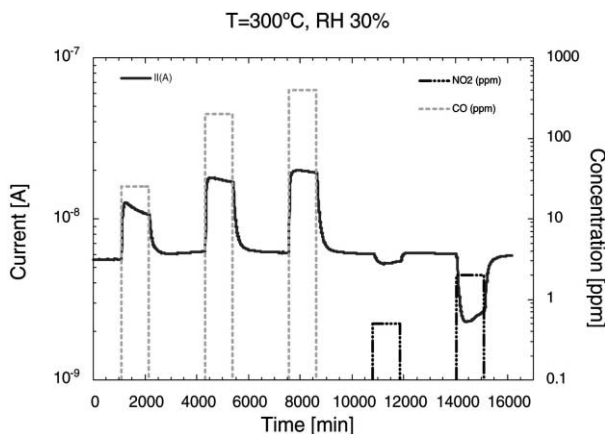


Fig. 7. B4 sensor response to CO and NO<sub>2</sub> at 300°C and 30% RH.

Table 3

B2 and B4 response magnitude to CO and NO<sub>2</sub> at an operating temperature of 300°C

Sensor reference	CO			NO <sub>2</sub>	
	25 ppm	200 ppm	400 ppm	0.5 ppm	2 ppm
B2	2	2.5	2.9	1.3	2.7
B4	1.8	2.4	2.9	1.1	2.3

MoO<sub>3</sub>–TiO<sub>2</sub> films is thought to be due to the low evaporation temperature of the MoO<sub>3</sub> component. Furthermore, when the sensor is operated at 400°C and then back again at 300°C reproducible results cannot be achieved, further indicating the film has been modified due to the exposure of high temperature. Furthermore, as the films surface changes caused by the possible MoO<sub>3</sub> evaporation, the films conductance decreases, increasing the total band gap energy of the mixed semiconductor system.

#### 4. Conclusions

The O<sub>2</sub>, CO and NO<sub>2</sub> gas sensing properties of MoO<sub>3</sub>–TiO<sub>2</sub> thin films have been analyzed. It was found that MoO<sub>3</sub> dominated sensors had a lower optimal operating temperature than the TiO<sub>2</sub> dominated sensors at 370°C as compared to 420°C. The response of the sensors were stable and reproducible, however, when the operating temperature increased beyond 400°C the sensors were unstable and did not possess the same gas sensing characteristics when again operated at low temperatures. The low evaporation temperature of the MoO<sub>3</sub> component of the mixed system is believed to be the cause of the sensors instability and irreversibility at high operating temperatures.

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