Comparison of Single and Binary Oxide MoO_3, TiO_2 and WO_3 Sol-gel Gas Sensors

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SUMMARY

A systematic comparison of sol-gel prepared TiO_2, WO_3, and MoO_3 single metal oxide based gas sensors was conducted. Sensors based on binary compound MoO_3-TiO_2 and MoO_3-WO_3 were also compared where the performance is superior to their single oxide constituents. The sensors were systematically exposed to O_2, O_3, CO, NO_2 gases and ethanol vapor. MoO_3 binary compound based sensors showed promising O_3, CO, NO_2 gas response while MoO_3-WO_3 showed a high response to ethanol vapor and a highly selective response to NO_2.

Keywords: gas sensors, titanium oxide, tungsten oxide, molybdenum oxide.

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 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 TiO_2, WO_3 and MoO_3 has been undertaken.

BACKGROUND

TiO_2, WO_3 and MoO_3 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.

Titanium dioxide (TiO_2) 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 commercialised by NGK Spark Plug Co. Ltd [1]. Compared to the traditional lambda sensors based on ZrO_2, TiO_2 thick film sensors offer a faster response time [2]. TiO_2 gas sensors operating at temperatures below 600°C make use of the anatase phase that has a 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 TiO_2 nanocrystalline thin films are preferred since they exhibit desirable gas sensing characteristics at operating temperature below 400°C.

Tungsten trioxide (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 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 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 WO, W_2O_3, and W_4O_3, however, in gas sensing the stable WO_3 form is used.

As for 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 MoO_3 is 795°C, relatively low compared to SnO_2 at 1127°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, MoO_3 possesses good gas response since it has been used in the field of catalysis for oxidation reactions of hydrocarbons [7]. MoO_3 has a bandgap of 3.2 eV and electrical resistivity at room temperature is of the order of 10^{10} Ω cm.

EXPERIMENTAL

TiO_2, WO_3, MoO_3, MoO_3-TiO_2 and MoO_3-WO_3 were prepared by the sol-gel method. The precursors used to fabricate the solutions are shown in Table 1. The solutions where prepared at a concentration of 0.1M in butanol.

Table 1: *Sol-gel precursors.*

Component	Chemicals	Formula
Mo precursor	Mo isopropoxide	$Mo(OC_3H_7)_5$
Ti precursor	Ti Butoxide	$Ti(OC_4H_9)_4$
W precursor	W Ethoxide	$W(OC_2H_5)_6$

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°C for 1 hour.

RESULTS AND DISCUSSION

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 [8]. The grain, neck and grain boundary features also influences the gas sensing properties.

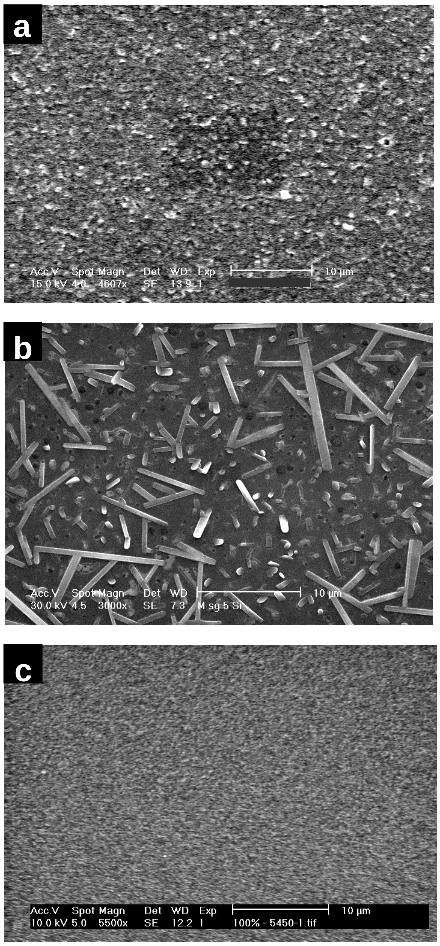

Fig.1: *Morphological difference of a) TiO_2, b) MoO_3 and c) WO_3 on Si substrates annealed at 450 ℃.*

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 [9]. 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, [10]. As shown from Fig. 1. the morphology of TiO_2, WO_3, and MoO_3 is dramatically different. TiO_2 and WO_3 are made up of spherical grain structures. However, 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 gas sensing properties of TiO_2, WO_3 and MoO_3 single metal oxide compounds were examined when exposed to O_2, O_3, CO, NO_2 gases and ethanol vapor.

Oxygen (O_2) Gas Sensing

Table 1 summarizes the O_2 response results. TiO_2, and MoO_3 exhibit high oxygen responses compared to WO_3.

Table 1: *Response to 1000 ppm of O_2.*

Sensor	($\tau_{res=0.9}$)	($\tau_{rec=0.3}$)	Response	Temp (°C)
MoO_3	1	5	39	370
WO_3	4	4	7.5	420
TiO_2	2	1.5	28	420

As was expected, the sol-gel TiO_2 sensor exhibited a superior O_2 response, relatively fast and consistently returning to its baseline as seen from Fig. 1.

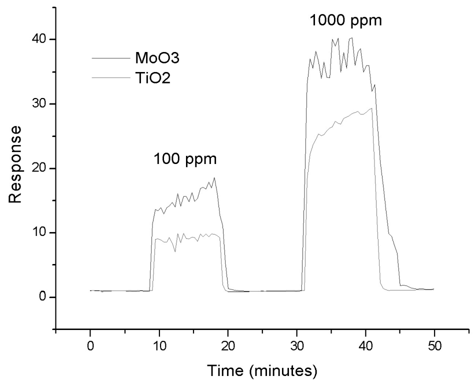

Fig.2: *Oxygen dynamic response of TiO_2 and MoO_3 sensors operating at 370℃.*

Ozone (O_3) Gas Sensing

It is well known that both In_2O_3 [11] and WO_3 [12] are highly sensitive to O_3. Sol-gel based WO_3 has a response of 35 to 80 ppb of O_3 [12]. Sol-gel based MoO_3-WO_3 was compared to commercially available In_2O_3 based sensors (New Cosmos Electric Co., Ltd.). TiO_2 did not show a measurable response to ozone gas. MoO_3 response to O_3 could not be measured due to a high resistance. Therefore, to measure the MoO_3 ozone response, MoO_3-TiO_2 and MoO_3-WO_3 were fabricated which reduced the films resistivity. Most interesting was MoO_3-TiO_2 with a response time less than 20 s to 100 ppb of O_3 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_3-WO_3 exhibits promising results to O_3 as shown in Fig. 3. Hence, MoO_3 based sensors could be considered as promising candidates for O_3 gas sensing.

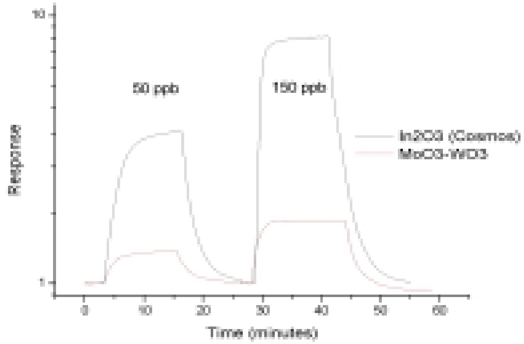

Fig.3: *Dynamic response MoO_3-WO_3 (T=150℃) compared to the superior In_2O_3 (Cosmos) ozone sensor.*

Carbon Monoxide (CO) and Nitrogen Dioxide (NO_2) Gas Sensing

TiO_2 had a negligible response to CO compared with WO_3 and MoO_3. MoO_3 and WO_3 showed promising CO and NO_2 results. MoO_3 exhibited a high response to both CO and NO_2 as shown in Fig.4.

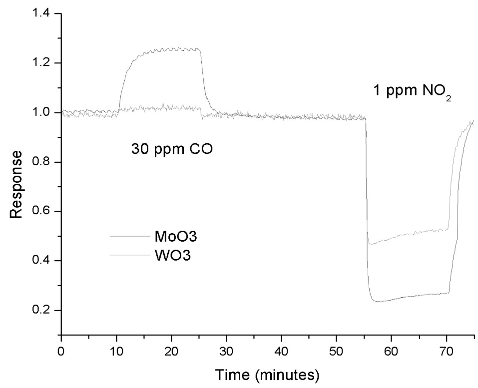

Fig. 4: *CO and NO_2 response of Mo and W oxide sensors operating at 300℃.*

The binary system of MoO_3-TiO_2 was fabricated so that the resistance of MoO_3 would decrease. The material attained its high response to CO, however, it was not as responsive to NO_2 as compared to pure MoO_3. MoO_3-WO_3 surprisingly did not respond to CO and was selective only to NO_2 i.e. having a response of 2.3 and a time response of 60 seconds to 1 ppm of NO_2.

Ethanol Vapour Sensing

All oxide compounds exhibited good gas sensing performance to ethanol. MoO_3 had the best response compared to the single metal oxides. Furthermore, the mixed oxide of MoO_3-WO_3 exhibited an exceptional response to ethanol trading off response time and stability as shown in Fig. 6. The MoO_3-WO_3 sensor had a response as high as 50 to 600 ppm ethanol as compared to commercialized alcohol sensors that have a response of 10 to 500 ppm of ethanol. The high sensitivity and selectivity of the fabricated sensors could be employed in commercial alcohol breath analyzers to combat drink driving.

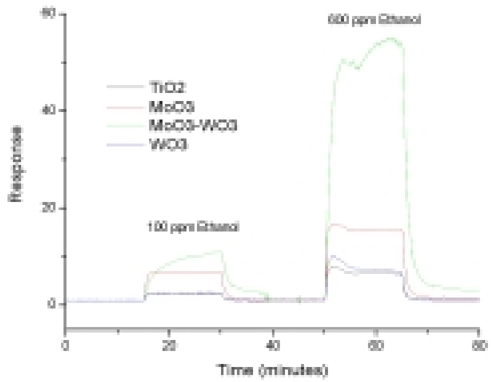

Fig. 5: *Response to 100 and 600 ppm of ethanol at an operational temperature of 300°C.*

CONCLUSIONS

MoO_3 based sensors showed promising O_3 gas sensing characteristics. MoO_3-TiO_2 showed a good response to CO, outperforming other single metal oxides tested. Interestingly, MoO_3-WO_3 exhibited a high selectivity to NO_2, i.e. having an undetectable response to 30 ppm of CO. The binary systems of MoO_3-WO_3 also showed a high response to ethanol vapor outperforming the single metal oxides. MoO_3 has to be highly oxidized and reduced. By mixing it with TiO_2 and WO_3 the resistivity is reduced and in cases of O_3, CO, NO_2 gas and ethanol vapor sensing, its performance is enhanced.

ACKNOWLEDGMENTS

The authors are grateful to Dr. Tadashi Takada from New Cosmos Electric Co., Ltd (Japan) for providing ozone sensors for comparative purposes. The work was partially supported by the Co-operative Research Center for Microtechnology, Australia, the project title "High performance gas sensing films".

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