

# Investigation of the oxygen gas sensing performance of Ga<sub>2</sub>O<sub>3</sub> thin films with different dopants

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## Abstract

The oxygen gas sensing performance of Ga<sub>2</sub>O<sub>3</sub> semiconducting thin films doped with Ce, Sb, W and Zn have been investigated. These thin films have been prepared by the sol–gel process and were deposited on sapphire transducers with inter-digital electrodes and a platinum heater integrated. The sensors were exposed to various concentrations of oxygen gas in an ambient of nitrogen and the gas sensing performance has been examined. The responses of sensors doped with Ce, Sb, W and Zn were stable and reproducible at their respective operating temperatures. It was observed that Ga<sub>2</sub>O<sub>3</sub> films doped with Ce, Zn and W are promising for oxygen gas sensing applications.

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**Keywords:** Gas sensing; Gallium oxide; Zinc oxide; Cerium oxide; Sol–gel process

## 1. Introduction

The development of new and more efficient materials for gas sensing is a challenge of the near future, as the market for these devices continues to grow. Metal oxides, such as TiO<sub>2</sub>, WO<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub> have gained a great deal of interest in the scientific and technology communities. In particular, transition metal oxides are promising for electrochromic devices due to their reversible thermal coloration and for gas sensing as their optical and electrical properties change in presence of oxidizing or reducing gas species [1,2]. Metal oxide thin films have been traditionally used as gas sensing materials. They offer the possibility of “tailoring” the sensitivity and selectivity towards specific gas species. These samples can be obtained via the sol–gel technique, which represents a reliable, low-cost chemical route, widely used for the deposition of these materials.

Oxygen sensors have practical use in monitoring and controlling systems of combustion engines, waste gases and chemical processes, etc. with the current focus of research being novel materials for fast, stable, sensitive and selective gas sensing [3]. Ga<sub>2</sub>O<sub>3</sub> has emerged as a viable gas sensing material as a result of the pioneering work of Fleischer

et al. [4]. Pure Ga<sub>2</sub>O<sub>3</sub> thin films have strong sensitivity to oxygen gas at operating temperatures above 700 °C [5,6]. By doping these films, sensors with higher responses and lower operating temperatures may be obtained.

Gas measuring systems incorporating metal oxide semiconductor (MOS) thin films exploit the films change in resistance to the introduced gas. The resistance change depends on the semiconductor and gas type, whether it be reducing or oxidizing. These sensors operate on the principle that the surface conduction of the sensors varies in relation to the adsorption of the ambient gas. Such changes have been noted since the earliest studies of semiconducting materials [7,8]. Many reactions on the surface of metal oxides are possible which can be acceptable as the gas sensing mechanism. However, the most dominant reaction in semiconductor gas sensing is a reversible gas adsorption mechanism that occurs on the sensor’s surface. The adsorbed gas atoms inject electrons into or extract electrons from an n-type semiconducting material depending on whether they are reducing or oxidizing respectively [9].

Doping may dramatically change the electrical properties of metal oxide films, hence we present semiconducting Ga<sub>2</sub>O<sub>3</sub> thin films with Ce, Sb, W and Zn as dopants in this paper. The resistivity of the Ga<sub>2</sub>O<sub>3</sub> thin films can be tailored with different dopant and the concentrations. The sol–gel process was employed to prepare these films taking the advantages of atomic level mixing and low temperature

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synthesis. Their electrical response has been measured in the operating temperature range of 300–600 °C.

## 2. Experimental

### 2.1. Thin film preparation

The sol–gel process was employed to realize the semi-conducting metal oxide thin films. Precursor solutions of gallium isopropoxide, cerium isopropoxide, tungsten ethoxide, antimony butoxide, (Chemat Technology, Inc., USA), and zinc acetylacetonate hydrate ( $[\text{CH}_3\text{COCH}=\text{C}(\text{O}-\text{CH}_3)_2\text{Zn}\cdot x\text{H}_2\text{O}$ , Sigma–Aldrich, USA) were mixed to achieve solutions of the doped gallium oxide thin films. The precursor solutions with an analytic purity were used. Since the metal alkoxides are very sensitive to moisture, the preparation of all solutions was carried out in a dry nitrogen environmental bag.

Doped gallium oxide solutions of 0.15 M were prepared with the doping level at 3 mol%. The solutions were then sonicated for 1 h in an ultrasonic bath (Branson 1200) to achieve homogenous mixing of the components at the atomic scale. They were then left at room temperature to age and settle for 24 h, after which they were deposited using the spin coating technique on sapphire transducers (5 mm × 5 mm) with inter-digital electrodes on the top side and a Pt heater located on the backside. The solutions were spun at 3000 rpm for 30 s onto the sapphire transducers to achieve a homogenous distribution of the film. The thickness of the films was approximately 200 nm. Following the completion of the deposition, the films were left to gel for 24 h at room temperature and annealed in air for 1 h at 600 °C with a ramp rate of 2 °C/min.

### 2.2. Gas sensing characterization

Electrical measurements were carried out in a computerized multi-channel gas calibration system. It allows different concentration ratios of analyte gas to be exposed to the sensors. Certified  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{C}_3\text{H}_8$  gas bottles between balanced with dry  $\text{N}_2$  with a purity of 99.99% or better were used for the gas sensing measurements. The sensors were exposed to the gases at a flow rate of 0.2 l/min. The resistance variation as a function of time was measured with a picoammeter (Keithley 485) when a constant potential of 5 V was applied. A regulated DC power supply to the heater was employed to control the operating temperature of the sensors. The details of this system can be found elsewhere [10].

The gas sensitivity,  $S$ , is defined as:

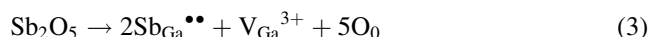
$$S = \frac{R_g}{R_b} \quad (1)$$

where  $R_g$  is the electrical resistance at different analyte gas partial pressures and  $R_b$  is the resistance of the baseline when

ultra high purity  $\text{N}_2$  gas was used. Measurements were carried out in the temperature range of 300–600 °C.

## 3. Results and discussion

The ionic size of  $\text{Ce}^{4+}$ ,  $\text{Sb}^{5+}$ ,  $\text{W}^{6+}$ ,  $\text{Zn}^{2+}$  and  $\text{Ga}^{3+}$  are very close to each other, i.e. 0.101, 0.062, 0.072, 0.074 and 0.062 nm, respectively (from Pauling's ionic radii data). Therefore,  $\text{Ce}^{4+}$ ,  $\text{Sb}^{5+}$ ,  $\text{W}^{6+}$  and  $\text{Zn}^{2+}$  can go into the lattice as substitutional metal dopants.  $\text{Zn}^{2+}$  may act as an acceptor, while  $\text{Ce}^{4+}$ ,  $\text{Sb}^{5+}$  and  $\text{W}^{6+}$  may act as donors. The incorporation of Zn and Sb in  $\text{Ga}_2\text{O}_3$  can be described by the following reactions:



An additional advantage of using donor dopants is that they lower the sensor resistivity. In the case of acceptor doping, high mobility of oxygen vacancies accounts for fast responses of the sensors [11].

The response of the doped  $\text{Ga}_2\text{O}_3$  gas sensors was investigated over several operating temperatures. Fig. 1(a) and (b) show the dynamic response of the  $\text{Ga}_2\text{O}_3$  thin films doped with Ce and Zn when exposed to a baseline of pure  $\text{N}_2$  and then to successive oxygen pulses of 100, 1000 and 10,000 ppm, each for a period of 15 min.

It is observed that films doped with Zn showed lower base resistance than those doped with Ce and their response is larger for every gas concentration examined. The Zn doped sensors were operational in the temperature range of 380–450 °C, with the largest response measured was at an operating temperature of 420 °C. It is observed from Fig. 1(b) that the Ce doped  $\text{Ga}_2\text{O}_3$  thin films exhibit a response of 1.2 compared to that of approximately 2 for the Zn doped sensor at an oxygen gas concentration of 100 ppm. Despite this lower value, the Ce doped sensors

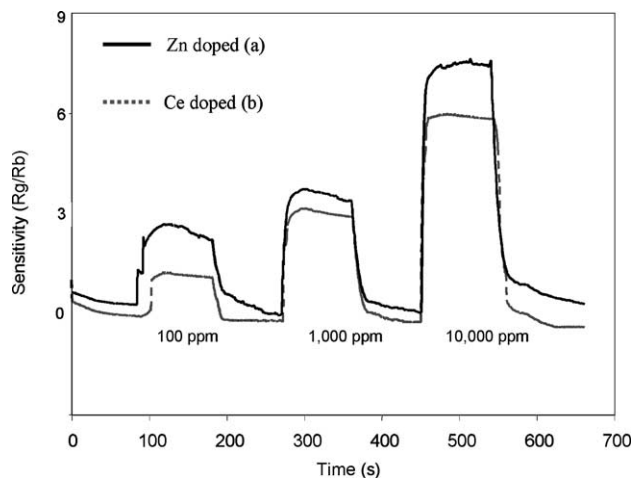


Fig. 1. Dynamic  $\text{O}_2$  responses of the Zn doped  $\text{Ga}_2\text{O}_3$  film (solid line (a), at 420 °C) and the Ce doped  $\text{Ga}_2\text{O}_3$  film (dot line (b), at 460 °C).

Table 1  
O<sub>2</sub> sensing properties of doped Ga<sub>2</sub>O<sub>3</sub> thin films

Dopant	Operating temperature (°C)	Resistance (10 <sup>6</sup> Ω)				Response time (s)	Recovery time (s)
		Baseline (N <sub>2</sub> )	100 ppm	1000 ppm	10000 ppm		
Ce	460	1.1	1.7	4.9	7.1	40	30
Sb	520	23.3	29.7	41.2	57.1	90	65
W	520	0.9	2.3	22.8	50.4	90	80
Zn	420	1.4	4.1	6.2	11.2	100	70

have faster response and recovery times, less than 40 s as compared to 100 s for those with Zn.

Table 1 is the optimum response and recovery times with associated response magnitudes and operating temperatures of doped Ga<sub>2</sub>O<sub>3</sub> thin films when exposed to oxygen gas for 15 min. It illustrates oxygen gas sensing performance of doped Ga<sub>2</sub>O<sub>3</sub> sensors. It is observed that both the Zn and Ce doped sensors show a response greater than 4.5 to 1% oxygen gas. At 460 °C, preferred sensing characteristics of the Ce doped films were obtained. Furthermore, from this data it is seen that the films doped with antimony had a base resistance, which is one order of magnitude higher than the other sensors. Furthermore, the response of the Sb doped sensor is lower than that of all the other sensors for every concentration tested. Both the W and Sb doped sensors showed preferred gas sensing at an operating temperature of 520 °C. The most interesting results in this table are for the tungsten doped sensors which showed a response of over 25 for 1000 ppm of O<sub>2</sub> and over 50 for 10,000 ppm. This sensor had a response and recovery between 80 and 100 s, yet by for the fastest response and recovery times were observed for the Ce doped sensors, which had a response and recovery time less than 40 s at low operating temperatures (<460 °C). It was also observed that the response and recovery times both decrease with higher oxygen concentrations for all the sensors tested.

Fig. 2 shows the dynamic response of the doped Ga<sub>2</sub>O<sub>3</sub> semiconducting thin films when exposed to a baseline of

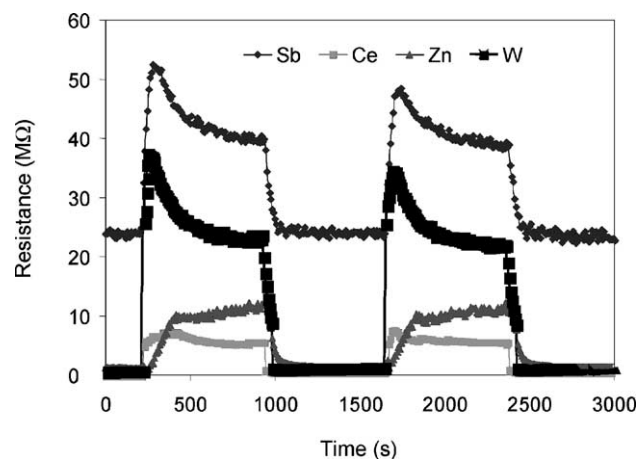


Fig. 2. Dynamic electrical response of the doped Ga<sub>2</sub>O<sub>3</sub> films at an operating temperature of 500 °C (1000 ppm O<sub>2</sub>).

pure N<sub>2</sub> and then to oxygen pulses of 1000 ppm. It is observed that sensor doped with Sb has a much higher base resistance than the other sensors at this operating temperature. The sensors doped with Ce, W and Zn have a base resistance of similar order of magnitude at this operating temperature. Even though the resistances of all doped Ga<sub>2</sub>O<sub>3</sub> sensors are lower than that of pure Ga<sub>2</sub>O<sub>3</sub> one (60 MΩ at an operating temperature of 470 °C [12]). It is also evident from Figs. 1 and 2 that despite having a lower response, the Ce doped sensor has a much faster response time.

Stability and repeatability are important aspects of sensor performance. These aspects are also highlighted in Fig. 2. The response of all the sensors tested were reproducible, returning to the baseline value following each successive pulse of analyte gas. It is noted that the sensors doped with Sb and W have an initial spike when exposed to the analyte gas whereas the sensors doped with Ce and Zn logarithmically approach their response resistance. The sensors were also exposed to carbon dioxide and propane gas, yet there was no significant response at the operating temperatures tested.

Ga<sub>2</sub>O<sub>3</sub> is an n-type semiconducting material, i.e. its conductance increases with the temperature. Additionally, its conductivity also increases when the oxygen partial pressure decreases, which is consistent with a conduction mode in which the charge carriers are electrons, generated from oxygen vacancies ionization. Ga<sub>2</sub>O<sub>3</sub> has a high resistivity making it difficult to integrate into modern electrical circuits without the addition of circuitry. Therefore, doping with Zn and Ce is significant for gas sensing applications.

#### 4. Conclusions

Gas sensors based on Ce, Sb, W and Zn doped Ga<sub>2</sub>O<sub>3</sub> semiconducting thin films have been fabricated. The sol-gel process was employed to prepare the gas selective layers. The sensors were exposed to various concentrations of oxygen gas in an ambient of nitrogen and the gas sensing performance has been examined. It was observed that sensors doped with Zn showed preferred gas sensing at operating temperatures below 450 °C. Sensors doped with Ce had lower response than that of Zn films and operated at higher temperatures, however, they possess very fast response times (typically 40 s). W doped films required

higher operating temperatures yet showed the higher response to the oxygen gas. Sb doped films had small response in comparison to the other sensors and had the highest base resistance. The responses of sensors doped with Ce, Sb, W and Zn were stable and reproducible at their respective operating temperatures.

We have found that by doping the gallium oxide thin films with Zn, W and Ce, the base resistance was lowered and the operating temperature of sensors was decreased. We believe that compositional analysis of the films as a function of annealing temperature can provide valuable information regarding the thin films ability to interact with different analyte gases. It is concluded that  $\text{Ga}_2\text{O}_3$  films doped with Ce, Zn and W are promising for oxygen gas sensing applications, however, further investigation of doping levels is required to optimize the sensors responses to oxygen gas.

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