

# Development of a room temperature thin film $\text{In}_2\text{O}_3$ , $\text{ZnO}$ and $\text{SnO}_2$ ozone sensor

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**Abstract**— Thin films of Indium-zinc-tin oxide have been prepared by Vacuum Thermal Evaporation (VTE). The sensing characteristics of these films to environmentally relevant ozone concentrations were studied at room temperature. The effects of film thickness, deposition rate and annealing were investigated. The resistance of the thin film was found to be inversely proportional to the deposition rate. The highest sensitivity of the ozone sensors was found at a deposition rate of 1.2 nm/s – 1.4 nm/s. In addition the  $\text{O}_3$  sensors were found to perform best with a 40 nm thick sensing layer.  $\text{In}_2\text{O}_3$ ,  $\text{ZnO}$  and  $\text{SnO}_2$  were deposited on alumina substrates containing interdigitated electrodes by means of VTE. These results have shown that  $\text{In}_2\text{O}_3$ : $\text{ZnO}$ : $\text{SnO}_2$  thin films prepared by VTE method are promising for room temperature ozone sensing.

**Index Terms**—Thin film, Indium Oxide, Ozone sensor

## I. INTRODUCTION

Ozone is a strong clean oxidizing agent and is widely used as a disinfectant and deodorizing agent [1]. Many electronic devices such as photocopiers and laser printers produce ozone. It can have serious adverse effects on human health, such as, inflammation and congestion of the respiratory tracts, pulmonary oedema, hemorrhage and even death. Table I represents the allowed safety limits proposed by the (WHO) World Health Organization.

The field of ozone sensing has witnessed a steady development since the first International Ozone Conference held in Chicago in 1956. Several ozone-sensing techniques have been developed and are in use. So far, measurements of ozone concentration have been carried out mostly by the use of analytical instruments, which are based on photometric, chemiluminescence and fluorescence techniques, iodide methods, passive sampling, mass spectrometry and remote monitoring techniques. These techniques are very accurate and sensitive even at atmospheric ozone concentrations but require expensive equipment as well as a high degree of expertise for correct operation and subsequent data interpretation [2].

In recent years gas sensing has become more interesting to the public with the focus on health and safety. Hence sensors have been integrated into consumer and commercial

applications, e.g. carbon monoxide and carbon dioxide gas sensors for home safety and building ventilation monitoring respectively.

Ozone concentration can vary greatly from point to point in the same general area; therefore there is a need for multispot detection. Ideally these devices should have low power consumption for use as portable battery supplied instruments [1].

Table II details a selection of the techniques, materials, and the operating temperature of some thin film metal oxide ozone sensors.

Thin film sensors are generally thought to be the best choice for the detection of strongly oxidizing gases (e.g. ozone) due to the geometry of the devices [3]. Strongly oxidizing gases immediately interact with the outermost layers of the sensor, producing a resistivity change [3]. Clearly, such an effect will influence the conductance of a thin film device more than a thick-film device [3].

Most of the current metal oxide ozone sensors on the market operate at elevated temperatures (200 - 600°C) [1]. In general gas sensors working at these high temperatures use the volume effect concerning the diffusion and desorption of gas molecules. Therefore they require a heating element to be incorporated into the overall sensor design. Operating the device at room temperature has the following advantages;

- (1) Ease of implementation
- (2) More user friendly
- (3) Reduced power consumption
- (4) Reduced cost

The sensitivity and selectivity of metal oxide gas sensors is very dependent on operating temperature. Qu et al found that when operating the sensor at 200°C the sensitivity to 100 ppb ozone was 1.4, while operating the sensor at 300°C the sensitivity was increased to 2.5 [12].

There is also the possibility of operating the sensor at two different temperatures to take advantage of the greater sensitivity achieved at lower temperatures (415°C) and the faster response times which are achieved at the higher temperatures (622°C) [5].

**Table I** Ozone concentration thresholds proposed by WHO (adapted from WHO)

| Threshold                | $\mu\text{g}/\text{m}^3$ | PPB   | Max. Exposure Time |
|--------------------------|--------------------------|-------|--------------------|
| Protection of Health     | 150-200                  | 64-85 | 1hour              |
| Protection of Health     | 100-120                  | 43-51 | 8hours             |
| Protection of Vegetation | 200                      | 85    | 1hour              |
| Protection of Vegetation | 65                       | 28    | 8hours             |

**Table II** Deposition techniques, materials and operating temperatures

| Ref                         | Technique  | Material   | Temperature (°C) |
|-----------------------------|------------|--|------------------|
| M. Z. Atashbar et al (1999) | Sputtering | $\text{In}_2\text{O}_3$                            | 200              |
| M. Z. Atashbar et al (1999) | Sol-gel    | $\text{In}_2\text{O}_3$                            | 200              |
| Th. Becker et al (1999)     | RGTO*      | $\text{SnO}_2$                                     | 50 - 350         |
| C. Cantalini et al (2000)   | Sol-gel    | $\text{WO}_3$                                      | 400              |
| C. Cantalini et al (2000)   | VTE        | $\text{WO}_3$                                      | 400              |
| C. Cantalini et al (2000)   | Sputtering | $\text{WO}_3$                                      | 400              |
| G.Faglia et al (1999)       | RGTO*      | $\text{In}_2\text{O}_3$                            | 400              |
| J. Frank et al (2001)       | Sputtering | $\text{In}_2\text{O}_3$<br>$\text{Ga}_2\text{O}_3$ | 25 - 650         |
| K. Galatsis et al (2002)    | Sol-gel    | $\text{TiO}_2$                                     | N/A              |
| K. Galatsis et al (2002)    | Sol-gel    | $\text{WO}_3$                                      | 150              |
| K. Galatsis et al (2002)    | Sol-gel    | $\text{MoO}_3$                                     | N/A              |
| K. Galatsis et al (2002)    | Sol-gel    | $\text{MoO}_3$ $\text{TiO}_2$                      | 150              |
| K. Galatsis et al (2002)    | Sol-gel    | $\text{MoO}_3$ $\text{WO}_3$                       | 150              |
| C. Jimenez et al (1997)     | Sol gel    | $\text{In}_2\text{O}_3$                            | 25 200           |
| W. Qu et al (2000)          | VTE        | $\text{WO}_3$                                      | 200 - 300        |

## II. EXPERIMENTAL PROCEDURE

The following sensor samples were produced from a combination of  $\text{In}_2\text{O}_3$ : $\text{ZnO}$ : $\text{SnO}_2$  (90%:5%:5%). These

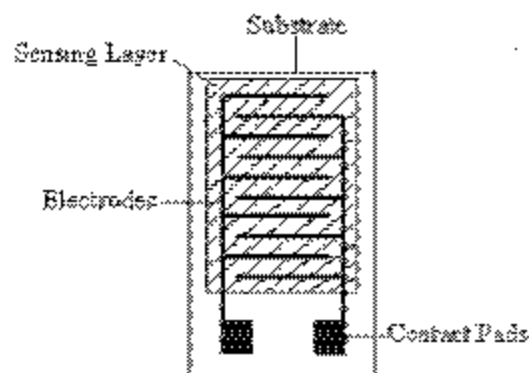
samples were fabricated by varying the deposition rates and film thickness. Table III shows the different combinations that were investigated.

**Table III.** Summary of different sensor samples produced

| Sample | Thickness (nm) | Deposition Rate (nm/s) |
|--------|----------------|------------------------|
| 1      | 100            | 0.1                    |
| 2      | 100            | 0.6                    |
| 3      | 100            | 1.4                    |
| 4      | 40             | 0.1                    |
| 5      | 40             | 0.6                    |
| 6      | 40             | 1.4                    |

### Sensor Structure

Interdigitated structures (IDS) are commonly used as a basis for gas sensitive layers [8]. The advantage of sensors based on this structure is the simple and cheap fabrication process and the ability to use the sensor in a wide range of applications without crucial changes to the sensor design [9]. The IDS is an arrangement of two comb electrodes interlocked into each other. The structure can be considered as many resistors in parallel sandwiched between the alumina substrate and the sensing layer. The oxide layer is deposited over the conductor in a rectangular pattern. The IDS measures an area of  $3\text{mm} \times 3\text{mm}$ . Each electrode has a total of 5 interdigits, with each interdigit having a thickness of 0.1 mm and a length of 2.5 mm. The space between each electrode is 0.2 mm.



**Figure 1.** Structure overview

### VTE of Cu electrodes onto alumina substrate

Short strips of Cu wire were cleaned with alcohol and DI water before being placed in a molybdenum boat, which was then placed between the electrodes of an Edwards E306A coating system. A maximum of four boats may be used for one deposition. The Alumina substrate was cleaned with alcohol and DI water before being placed in the holder approximately 12 inches directly above the boat. The vacuum process was started by producing a rough vacuum, which removes most of the air from the system [6]. After the

roughing vacuum was produced the Edwards E306A was set to high vacuum. When an appropriate vacuum was achieved, passing a current through the molybdenum boat started the deposition process. A quartz crystal was used to measure the thickness of the deposited layer. When the desired thickness was reached the shutter was closed and the current switched off.

A plastic dropper was used to deposit photoresist (AZ5214) on to the substrate containing the deposited Cu. The spin coater was then gradually stepped up from 0 – 7000 rpm to eliminate excess photoresist. Subsequently the substrate was cured at room temperature for 24 hours.

The electrode designs were drawn up and printed on acetate in preparation for UV exposure. The acetate containing the design was placed over the substrate and exposed to UV light. After the exposure the substrate was placed in a developer solution (Electrolube PDN250ML). The substrate was then rinsed in water and placed in the etching solution of SEMO 3207 fine etch crystals to reveal the electrode pattern. In order to remove the photoresist from the remaining pattern the substrate was totally re-exposed to UV light and dipped in the developer solution.

#### VTE of oxide layer

The VTE of  $\text{In}_2\text{O}_3\text{:ZnO:SnO}_2$  thin films were prepared by heating the oxide mixture in a molybdenum boat under high vacuum conditions at a deposition pressure of  $5 \times 10^{-5}$  mbar. The vapour phase was condensed on the alumina substrate, containing the electrodes, at room temperature and covering an area of  $3.0 \times 3.0$  mm. The film was deposited at various deposition rates varying from 0.1 nm/s to 1.4 nm/s. The film thickness was also varied from 20 – 100 nm, being monitored by a quartz crystal microbalance. Annealing was performed under vacuum conditions at  $300^\circ\text{C}$  for 1hr.

#### Annealing of oxide layer

In general deposited layers contain a host of structural defects. The application of a relatively mild heat treatment will anneal most of these defects out of the film. This should lead to a better adhesion of the film to the substrate surface and also to a corresponding decrease in film resistance.

Annealing was performed in a vacuum environment. Vacuum pressure was maintained at  $6 \times 10^{-4}$  mbar. Temperature inside the vacuum was gradually increased to  $300^\circ\text{C}$  and maintained for 45mins. The sensors were then left to cool to room temperature in the vacuum.

#### Experimental Set up

Ozone was generated by pumping oxygen through a quartz tube under exposure from a pen ray ultraviolet (UV) lamp (Ultra-violet Products Ltd). Ozone concentration was controlled by means of a metal shutter enclosing the UV lamp. The ozone concentration was calibrated with a UV analyzer

(Ecosensors). Figure 2 shows the basic set up.

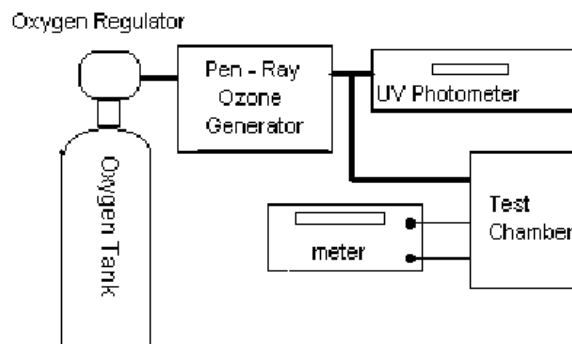


Figure 2. Experimental set up

The semiconducting sensors were mounted in a teflon chamber with inlet and outlet valves. The flow rate of the ozone over the sensor was kept constant at 0.25 l/min by an ozone regulator. The teflon chamber was flushed with  $\text{O}_2$  for 30 minutes before a measurement was taken. A thurlby multimeter was used to monitor the resistance changes.

### III. RESULTS AND DISCUSSIONS

#### Deposition Parameters

Varying the deposition parameters has a major effect on the oxide film characteristics.

From Figure 3 it can be seen that film thickness is inversely proportional to film resistance.

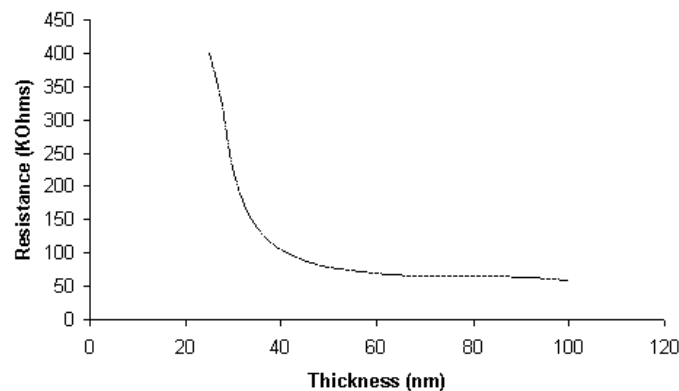


Figure 3. Resistance Vs Thickness

Film thickness can be easily controlled by either evaporating a weighted amount of material or by simply terminating the evaporation process when the desired thickness is reached. Increasing the deposition rate has the effect of decreasing the resistance of the thin oxide film (Figure 4).

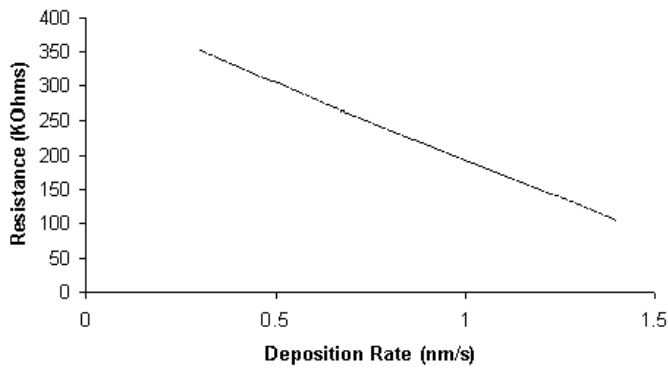


Figure 4. Deposition rate effect on resistance (40nm)

Controlling the evaporation rate is a much more complex task than thickness control because it requires the adjustment of the source (boat) temperature. The emission of the source material does not remain constant throughout the deposition. This is due to variations in the effective source area and variations in the degree of heat transfer between the evaporant and its support [7].

#### Sensitivity

The sensitivity (S) is calculated by equation (1).

$$S = RO_3/RO_2 \quad (1)$$

Where  $RO_3$  is the resistance of the sensor when exposed to ozone, and  $RO_2$  is the baseline resistance when exposed to  $O_2$ .

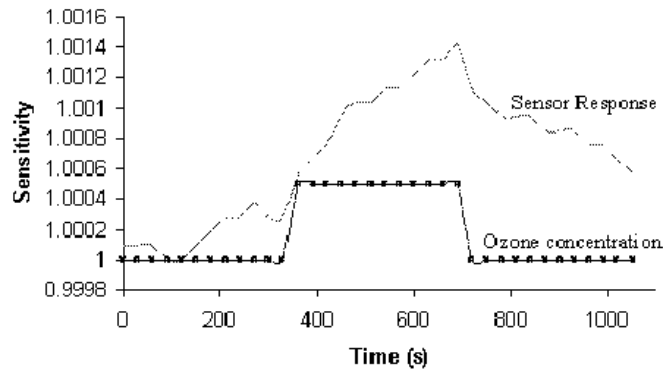


Figure 5 Response of 100 nm oxide layer deposited at 1.4 nm/s to 240ppb ozone (Sample 3)

The 100 nm  $In_2O_3:ZnO:SnO_2$  film deposited at 1.4 nm/s shows good response to 240ppb of ozone, however the recovery of the sensor is poor.

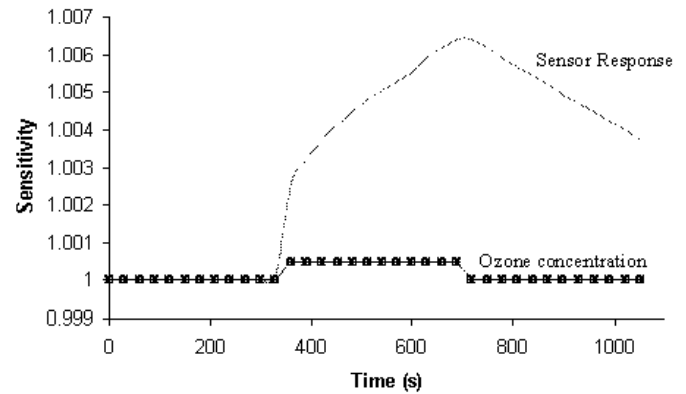


Figure 6. Response of 40 nm oxide layer deposited at 1.4 nm/s to 240ppb ozone

The 40 nm  $In_2O_3:ZnO:SnO_2$  film deposited at 1.4 nm/s shows good response time and good sensitivity but the recovery of the sensor is poor.

As can be seen from Figures 5 and 6 the sensor response does not return to baseline resistance after ozone has been switched off. This makes it difficult to continuously measure the ozone concentration with any great accuracy or confidence.

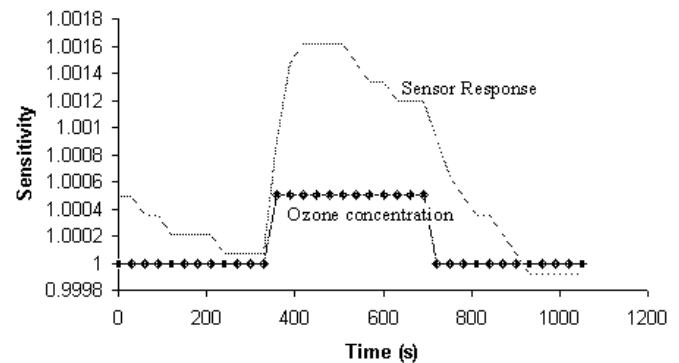


Figure 7. Response of 40 nm oxide layer deposited at 0.6 nm/s to 240ppb ozone (Sample 5)

From Figure 7 it can be seen that the  $In_2O_3:ZnO:SnO_2$  (90%:5%:5%) sensor deposited at a rate of 0.6 nm/s yields a reasonable value of ozone sensitivity with a recovery time ( $T_{90}$ ) of approximately 210 seconds. Therefore making it useful for environmental ozone detection.

Although the sensitivity of the sensor deposited at 1.4 nm/s is higher the reaction with ozone cannot reach equilibrium and the sensor recovery cannot return to its initial state.

Figure 8 shows how the sensitivity of the device is affected by the change in thickness of the  $In_2O_3:ZnO:SnO_2$  layer.

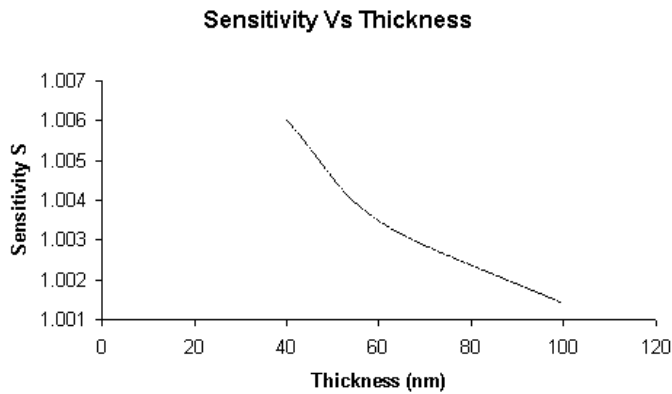


Figure 8. Sensitivity Vs Thickness for deposition rate of 1.4 nm/s

The sensitivity of the device is greatest at 40 nm. The grain size of the deposited oxide layer also affects the sensitivity of the sensor. The grain boundaries act as scattering centers for the electrons [10]. The ratio of the grain size ( $D$ ) to the electron depletion layer thickness ( $L$ ), ranging below  $D/2L = 1$  i.e. the depletion region extends over the entire grain, governs the sensitivity of the sensor [11].

Figure 9 shows the effect of thickness and deposition rate on the overall sensitivity of the ozone sensor to 240ppb. By obtaining a surface plot of thickness vs deposition rate, the interaction between both parameters can be observed.

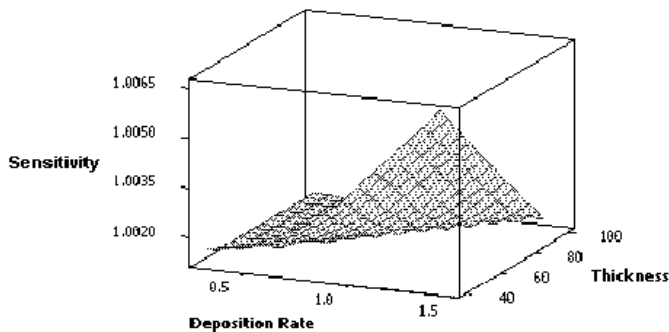


Figure 9. Surface plot of deposition rate and thickness Vs Response to 240ppb ozone

From Figure 9 it can be seen that in order to obtain good sensitivity measurements both the deposition rate and the thickness must be controlled. High deposition rate combined with relatively thin sensing layer yields best response.

#### IV. CONCLUSION

Frank et al [4] and Jimenez et al [14] have operated  $\text{In}_2\text{O}_3$  based ozone sensors at room temperature without much success.  $\text{In}_2\text{O}_3:\text{Ga}_2\text{O}_3$  and  $\text{In}_2\text{O}_3$  sensors prepared by the sputtering technique showed 0 response to ozone at temperatures between 25 – 200°C [4]. Jimenez et al prepared  $\text{In}_2\text{O}_3$  sensors by the sol – gel process (Table II). It was deduced that the sensors could not be operated at room

temperature due to slow response and poor recovery features, therefore the sensor had to be operated at elevated temperatures (100 - 200°C) [14].

In this work, an investigation was conducted into the use of thin films of  $\text{In}_2\text{O}_3:\text{ZnO}:\text{SnO}_2$  as a room temperature ozone sensor. The results have indicated that the 40 nm  $\text{In}_2\text{O}_3:\text{ZnO}:\text{SnO}_2$  layer deposited at a rate of 0.6 nm/s showed the best potential for use as an ozone sensor. All the samples exhibited sensitivity to ozone, with the lowest ozone sensitivity attributed to 100nm  $\text{In}_2\text{O}_3:\text{ZnO}:\text{SnO}_2$  deposited at a rate of 0.1 nm/s.

In general two statements can be made concerning the deposition parameters effect on the sensitivity of the device: firstly decreasing the thickness of the sensing layer increases the sensitivity, and secondly increasing the deposition rate increases the sensitivity (Figure 9).

Films deposited at a rate of 1.2 - 1.4 nm/s showed the highest sensitivity to ozone but with poor recovery features. Films deposited at 0.6nm/s show a good response and recovery time with the trade off being the sensitivity of the device.

These results have shown that  $\text{In}_2\text{O}_3$  based thin films prepared by VTE are promising for room temperature ozone sensing.

Compared with much of the existing devices, the advantages of these sensors include room temperature operation, reduced power consumption and reduced cost.

It is our intention to explore the effect of different molar percentages of  $\text{In}_2\text{O}_3:\text{ZnO}:\text{SnO}_2$  on the sensitivity to ozone.

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