3-23-2005

Study of Tin Oxide for Hydrogen Gas Sensor Applications

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Study of Tin Oxide for Hydrogen Gas Sensor Applications

by

Manoj Anand

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Electrical Engineering
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Date of Approval:
March, 23rd, 2005

Keywords: Sputtered SnO₂, MOCVD SnO₂, Thin films, Oxygen Species, F↓ doped SnO₂.

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Dedication

I dedicate this thesis to my parents and my sister. I thank them for their constant support and encouragement during the writing of this thesis. I also would like to take this opportunity to thank all my lab mates and roommates who have given all the help and support I needed towards the successful completion of this thesis.
Acknowledgements

I would like to thank Dr. Christos Ferekides for giving me the opportunity to work on this project. His suggestions and guidance have been invaluable to the formulation and implementation of this thesis. I would like to acknowledge my committee members – Dr. Don Morel and Dr. E.K. Stefanakos for their comments and suggestions. I would also like to extend my gratitude to my friends at the Thin Film Electronic Material lab who have encouraged my efforts, and provided constructive criticism, Especially Lingeshwar Nemani, Gayam Sudhakar Reddy and Mathesh Jayabalan. My special thanks to Mr. Timothy Fawcett for his valuable advice and help.
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Study of Tin Oxide for Hydrogen Gas Sensor Applications

Manoj Anand

ABSTRACT

Tin oxide (SnO$_2$) has been investigated and used as a gas sensing material for numerous applications from the very start of the sensor industry. Most of these sensors use semiconductors (mostly SnO$_2$) as the sensing material.

In this work, SnO$_2$ was prepared using 2 techniques: firstly the MOCVD where we dope the sample with fluorine and secondly sputtering technique where samples are undoped in our case. These samples were tested at different conditions of temperature varying from room temperature to 150°C, in ambient gas atmosphere of 200 CC Nitrogen (N$_2$).

The typical thickness of the sputtered samples was 1500 Å with a sheet resistance of 300 $\Omega/\square$ and these sputtered samples were found to be more porous. These samples when tested in room temperature showed a change of -4 $\mu$A change for 10% and -9 $\mu$A for 90% of H$_2$. While at higher temperatures (150°C) the current change for 10% increased from -4 $\mu$A to -2 mA showing that higher ambient temperatures increased the sensitivity of the samples. The repeatability of the samples after a period of 3 days were
found to be well within 10%. The samples prepared by MOCVD were fluorine doped, the
samples were conductive to 1 order of magnitude more than the sputtered ones. 3
different samples of approximate thicknesses 3000, 6000 and 9000 Å were prepared and
tested in this work, with typical resistivity of 6 Ω/cm and the grains in this case are
typically more compact. The conductive samples showed no response at room
temperature, including the 6000 and 9000 Å samples. While at higher temperatures
(150ºC) the 3000 Å sample showed very sensitive response to H₂. Also noticed was that
the response was linear compared to the sputtered samples. The samples showed very
good repeatability and sensitivity. A added feature noticed was that the sample did not
need to be completely desorbed before detecting other (greater or lower) concentrations.
Effect of temperature was studied by conducting similar tests under similar conditions on
a sample, while varying ambient temperatures at 35, 75, 115 and 150 ºC. Results showed
increase in sensitivity of sample as temperature increased (6µA, 40µA, 150µA and
300µA change in current respectively). But the response time was seen to increase too.
Resistive Sputtered samples with 2% and 5% Zinc (Zn) deposits on it were tested but
yielded no response.
Chapter 1. Introduction

The start of industrial revolution played a very great hand in shaping our society as we see it today. Things which were considered luxury not so long ago have become so common that they have become a necessity in daily life. The rapid industrialization of our society has made it necessary for measurement technologies for monitoring of various gasses, fumes etc to grow in parallel. This chapter discusses the importance of gas sensors, and specifically hydrogen (H\textsubscript{2}) gas sensors, and the use of SnO\textsubscript{2} for these applications. Lastly it discusses various structures and architectures of sensors available.

1.1 Need for Gas Sensors

Today’s modern day society has brought numerous luxury items but with them series of problems like air pollution and emission of toxic gasses have also been introduced to our society. The necessity to constantly monitor and control these gases emitted sprouted the need for gas sensors. The various uses of gas sensors vary across a wide range and industries and applications; for example monitoring air pollution, chemical processes and exhaust from combustion engines. Sensors find applications in aerospace, laboratories, factories, Fuel cells etc.
In recent years, several types of gases have been used in different areas of industries as raw materials. It becomes really important to control and monitor these gases, as there is a huge risk of damage to property and human lives if a leak occurs. Certain gases can be toxic for humans, or corrosive gases, or explosive.

There are currently needs for 3 categories of gas monitoring [1]:

- For oxygen (O₂), in connection with the monitoring of breathable atmospheres and for the control of combustion.
- For flammable gases in air in order to protect against the unwanted occurrences of fire or explosion. In this case concentrations to be measured are in the range up to the lower explosive limit, which for most gases, is up to a few percent.
- For toxic gases in air, where the need is to monitor concentrations around the exposure limits which range from less than 1 ppm to several 100 ppb.

So we need gas sensors that can continuously and effectively detect these gasses to avoid most of the above dangers presented. The following list gives both constraints and requirements for an ideal Sensor [2]:

- Sensitivity to certain chemicals
- Reversibility
- Faster response time
- High sensitivity
• Selectivity
• Durability
• Non-contaminating
• Non-poisoning
• Simple operation
• Small size (portability)
• Simple fabrication
• Relative temperature insensitivity

All above listed characteristics have been the subject of extensive research for the past two decades. But still the quest for developing a sensor that has all the properties listed is still far from reaching an end.

1.1.1 Importance of Sensing Hydrogen

In recent years, research for a clean future fuel has been going on with extraordinary speed. The fuel should have zero emissions, be abundant in nature, and efficient. \( \text{H}_2 \) as a fuel meets all the requirements perfectly. Not only is \( \text{H}_2 \) readily available in nature but also when combustion takes place the byproducts given out are water and \( \text{O}_2 \) making it a very environmentally friendly fuel. Also \( \text{H}_2 \) dissipates very easily so in case of a leak it can be considered safer than many heavier gases as it spreads
around fast and dissipates. The amount of energy produced by H\textsubscript{2}, per unit weight of fuel, is about three times the energy contained in an equal weight of gasoline and nearly seven times that of coal [3].

Hydrogen generation can come from a variety of sources as decomposition of H\textsubscript{2} containing compounds, electrolysis of water, natural gas and many more. H\textsubscript{2} generation has the potential of being cost effective and coupled with the fact that it is renewable makes it an attractive choice as fuel in various applications. Fuel cells are designed based on H\textsubscript{2} and are considered to be “batteries of the future”. H\textsubscript{2} has a Lower Explosive Limit (LEL) of 4% [4] in air, which means accumulation of 4% concentration in air is dangerous as even a small spark can ignite the mixture. As H\textsubscript{2} is proposed to be used as the next generation’s fuel, this fact of it turning explosive in event of a leak has to be kept in mind and it therefore becomes necessary to monitor H\textsubscript{2} concentrations in air. So to detect H\textsubscript{2} at these levels, high precision sensors which can detect a leak of 0.5% - 4% are needed. The degree of leak tolerability changes with respect to the application.

Hydrogen leak-detection sensors must detect over the general level of ambient H\textsubscript{2}, and in a variety of environments. These sensors must be able to differentiate between ambient low-level sources of H\textsubscript{2} and those generated by a H\textsubscript{2} leak. Containment of H\textsubscript{2} is very difficult, since it diffuses through most materials [5].

In the US space program, H\textsubscript{2} is used by NASA primarily to launch the space vehicles. NASA has used liquid H\textsubscript{2} for the last three decades to propel the space shuttle and other
rockets into orbit. H\(_2\) fuel cells power the shuttle’s electrical systems, producing a clean byproduct (pure water), which the crew drinks [3].

Hence, it is envisaged that H\(_2\) will form the basic energy infrastructure that will power future societies. However, H\(_2\) transport and storage can be dangerous if not handled with caution. As a result, safety remains a top priority in all aspects of H\(_2\) energy, and sensing H\(_2\) leaks from storage and transportation equipment has become very essential [3].

### 1.2 Classification of Sensors

A gas sensor can be described as a device, which when exposed to a gas or a gaseous chemical compounds, alters one or more of its physical properties [6]. Sensors can be classified based on their operating principle as:

- Semiconductor gas sensors
- MOSFET Sensors
- Schottky Barrier Sensors
- Surface Acoustic Wave Sensors
- Fibre Optic Sensors

The following sections discuss these types of sensors.
1.2.1 **Semiconductor Gas Sensor**

Since the discovery made by W.H.Barttain and J.Bardeen that gas adsorption on a semiconductor surface causes a variation of the electrical conductivity. Many investigations have been carried out in order to prepare devices for the reliable detection of flammable and toxic gases in domestic environments [7]. Semiconductor gas sensors based on ZnO and SnO$_2$ were first developed by Seiyama and Taguchi in the 1960’s as detectors for Liquid Petroleum Gas (LPG) in homes. They were quite successful and have been extended to other materials like Titanium dioxide (TiO$_2$) and Indium Oxide (In$_2$O$_3$) etc [8]. Solid state sensors utilizing semi-conducting oxides generally operate at temperatures above ambient. The electrical resistance will depend on the temperature and the composition of the surrounding atmosphere most oxides will change its resistance depending on the ambient O$_2$ concentration [5].

However the most commonly used oxide material in gas sensors to date has been SnO$_2$. Non-stoichiometric SnO$_2$ is typically a n-type semiconductor in an environment containing O$_2$. The principle is based upon the initial reversible reaction of atmospheric O$_2$ with lattice vacancies in the SnO$_2$ and the concurrent reduction in electron concentration. This reaction produces various O$_2$ species at different temperatures and O$_2$ pressures, which can then react irreversibly with certain combustible species [9].
The vapor deposition technique is used to deposit SnO\textsubscript{2} thin films, either from a metallic target or an oxide target. A simple MOS gas sensor layout is shown in figure 1.2.1.1.

![Figure 1.2.1.1 A Simple Metal Oxide Semiconductor.](image)

### 1.2.2 MOSFET Sensors

One of the most important elements in microelectronics integrated circuit technologies and semiconductor gas sensor fabrication are MOSFET’s which stands for Metal Oxide Semiconductor Field Effect Transistor. The development of MOSFET gas sensors began with I. Lundstrom in 1975 with a H\textsubscript{2} sensitive MOSFET structure using a thin palladium (Pd) gate on p-type Silicon (Si) [9]. The fabrication of a typical MOSFET gas sensor includes the diffusion of the drain and source regions, the growth of a thin gate oxide, the deposition and annealing of the catalytic gate metal and deposition of source and drain contacts [9]. Figure 1.2.2.1 shows a basic structure of a MOSFET.

The response of MOSFET gas sensors is due to the dissociation of molecules into atoms on the catalytic gate metal surface (Pd). This is followed by the diffusion of these atoms
to the metal-dielectric interface, creating a dipole layer that causes a change in the electrical properties of the device i.e. the response is measured as a change in the gate voltage required to keep a constant drain current [9].

![The Basic Structure of a MOSFET Gas Sensor](image)

**Figure 1.2.2.1 The Basic Structure of a MOSFET Gas Sensor [6].**

### 1.2.3 Schottky Barrier Sensor

Under equilibrium conditions depending on n-type or p-type when a metal is brought into intimate contact with a semiconductor the Fermi levels on both sides of the junction are aligned. The Fermi level of the semiconductor adjusts itself to the dominating presence of the metal (the free carrier density of which is much higher than that of the semiconductor) and is lowered by an amount equal to the difference between the two work functions as shown in figure 1.2.3.2. This adjustment of Fermi levels occurs even if there is a thin dielectric layer, such as silicon dioxide between the metal and the semiconductor [6].
The fabrication of Schottky barrier diode gas sensors generally includes the formation of an ohmic contact followed by the deposition of catalytic metal on the topside. A simple layout of a schottky barrier sensor is shown in figure 1.2.3.1. The catalytic topside metal induces the adsorption of gases on its surface, leading to changes in electrical properties. The H atoms diffuse to the catalytic metal/semiconductor surface forming a dipole layer. And which lowers the Schottky barrier height [9].

The resultant energy band diagram depicts that of a schottky barrier structure in the absence of surface states in the semiconductor [6].
The mechanisms leading to Schottky diode sensitivity to certain ambient gas concentrations is the current transport process of the junction. This process consists of...
four basic contributions under forward bias, with the inverse processes occurring under reverse bias: (1) electron transport from the semiconductor over the potential barrier; (2) quantum mechanical tunneling of electrons through the barrier in heavily doped semiconductors; (3) electron-hole recombination in the space charge region; (4) hole injection from the metal into the semiconductor, leading to recombination in the neutral n-region [6].

There are different structures of Schottky gas sensors been used all nowadays some of them are shown in figure 1.2.3.3:

![Figure 1.2.3.3](image)

Figure 1.2.3.3 Different Structures of Schottky Barrier Gas Sensors [6].
1.2.4 Surface Acoustic Wave

It has been known since Rayleigh’s investigation in 1885 that elastic waves can propagate along the stressless boundary surfaces of isotropic solid substrates. Since then, the properties of surface acoustic waves (SAWs) have been discovered, and applications of SAW devices have been investigated. Due to their compact size and integrated circuit (IC) compatibility, SAW devices have been widely adopted in analog and digital communications. With advancement in the technique of photolithography, SAW devices can be designed to operate at frequencies higher than 1 GHz; hence, they are suitable for micro sensing applications [10].

Acoustic wave sensors are so named because their detection mechanism is a mechanical, or acoustic, wave. As the acoustic wave propagates through or on the surface of the material, any changes to the characteristics of the propagation path affect the velocity and/or amplitude of the wave. Changes in velocity can be monitored by measuring the
frequency or phase characteristics of the sensor and can then be correlated to the corresponding physical quantity being measured [11].

Virtually all acoustic wave devices and sensors use a piezoelectric material to generate the acoustic wave. Piezoelectricity was discovered by brothers Pierre and Paul-Jacques Curie in 1880, received its name in 1881 from Wilhelm Hankel, and remained largely a curiosity until 1921, when Walter Cady discovered the quartz resonator for stabilizing electronic oscillators. Piezoelectricity refers to the production of electrical charges by the imposition of mechanical stress. The phenomenon is reciprocal. Applying an appropriate electrical field to a piezoelectric material creates a mechanical stress. Piezoelectric acoustic wave sensors apply an oscillating electric field to create a mechanical wave, which propagates through the substrate and is then converted back to an electric field for measurement [11].

![Figure 1.2.4.2 Top View of a SAW Detector Setup [6].](image-url)
Since SAW devices operate by the transmission of acoustic waves across the surface, any adsorbed material will give rise to a disruption of that transmission. And keeping a track of the disruption of transmission is how the sensor detects a gas.

1.2.5 Fibre Optic Chemical Sensor

It has been demonstrated that a thin metallic film deposited on an optical fibre allows the detection of numerous gaseous species at room temperature and pressure but only Pd allows the selective detection of H$_2$. A complete understanding of the particular interaction between Pd and H$_2$ is therefore necessary for the development of a H$_2$ sensor. It has been demonstrated by Butler and others that absorption and desorption of H$_2$ in a thin layer of Pd at room temperature and pressure leads to the reversible hydride PdH$_x$ where $x$ is the atomic ratio H/Pd. The absorption of H$_2$ can be related to a crystallographic phase transition. For each isotherm corresponding to a temperature lower than 300 °C one can observe two different phases for which the ratio H/Pd increases with the pressure, separated by an isopressure zone. They are called the $\alpha$- and $\beta$-phase for pressures respectively lower and higher than the isopressure. The isopressure zone is the phase transition $\alpha \leftrightarrow \beta$ for which both phases coexist without miscibility. Without H$_2$, Pd is in the $\alpha$-phase, for all temperatures. In this phase and in the presence of H$_2$ the hydride can be considered as a solid solution of H$_2$ in the palladium lattice. At room temperature the hydridation of palladium leads to the $\beta$-phase. In most sensors based on SPR, the shift in the resonance curve is due to the variation of the refractive index of the dielectric medium surrounding the metallic layer. In this work the complex permittivity of the
metallic layer itself changes with the absorption of gaseous H\textsubscript{2}. The intensity \( I_d \) of the light transmitted through the fiber is then the detection signal from which we calculate the response \( R_{\%} \) of the sensor for a H\textsubscript{2} concentration \( c\% \) by the relation [12].

\[
R_{\%}H_2 = 100 \times \left( I_{d,c\%H_2} - I_{d,0\%H_2} \right) / I_{d,0\%H_2} \quad \text{------- (1.1)}
\]

![Figure 1.2.5.1 Setup for a Simple Optical Fibre based Gas Sensor [12].](image)

1.3 Goals

This thesis aims at achieving the following goals:

- Study the performance of thin film SnO\textsubscript{2} based H\textsubscript{2} sensors.
- Study Samples prepared by Sputtering and MOCVD.
- Compare Sputtered and MOCVD samples in varying conditions.
• Study the effect of temperature on the sensor

• Compare between normal SnO\(_2\) and Fluorine doped SnO\(_2\) samples.

• Compare the difference between samples with or without zinc metal added as in conc. of 2% and 5%.

1.4 Organization

The remaining of this thesis is organized as follows: chapter 2 deals with the working mechanism of a semiconductor gas sensor in presence of ambient gas, here we consider both the ideal case and different factors coming into play. Chapter 3 discusses the material used and its properties. Chapter 4 is the literature review. Chapter 5 describes the experimental setup, and chapter 6 reviews results and future work.
Chapter 2. Operation of SnO$_2$ Based Gas Sensor

This chapter provides an overview on the operation of a SnO$_2$ based gas sensor. As we have seen in the previous chapter there are various ways a gas sensor can be fabricated with different type of sensing capabilities. A very important common characteristic is the sensing material. The most commonly used gas sensing material for the past 3 decades has been SnO$_2$ right since W.H.Barttain and J.Bardeen proposed the adsorption theory. Since sensors were first developed by Seiyama and Taguchi in the 1960’s, SnO$_2$ has been the most commonly used sensing material.

2.1 Basic Mechanisms of a SnO$_2$-Based H$_2$ Gas Sensor

The devices described in chapter 1 relied on thin film components, such as the surface metal of Schottky diodes or the gate metal and insulator layers in MOSFET’s. Thin film semiconductor films have been used by means of deposition on an insulating substrate as early as the 1960’s [6].
2.1.1 Oxygen Species

Non-stoichiometric SnO$_2$ under certain conditions behaves as an n-type semiconductor in an environment containing O$_2$ (e.g. air). The principle is based upon the initial reversible reaction of atmospheric O$_2$ with lattice vacancies in the SnO$_2$ and the concurrent reduction in electron concentration. This reaction produces various O$_2$ species at different temperatures and O$_2$ pressures, i.e. O$_2^-$, O$^-$, O$_2^2-$, which can then react irreversibly with certain combustible species [13].

The formation of these ions by O$_2$ adsorbed at the gas/solid interface extracts electrons from the bulk of the solid; the O$_2$ can thus be thought of as a trap for electrons from the bulk [1]. A detailed description can be given as:

Oxygen in a metal oxide is in equilibrium with the gaseous O$_2$ present at the solid surface. If this latter quantity is reduced, O$_2$ ions on lattice sites may be converted to the gaseous state, creating O$_2$ vacancies or point defects. The 2 remaining electrons resulting from each vacancy will have energy levels placing them in the band gap, from which they may be excited into the conduction band. In this way the bulk electrical resistance becomes a function of the O$_2$ partial pressure at the phase boundary [14]. The interaction of oxygen species with grains in the bulk is shown in figure 2.1.1.1 below:
Figure 2.1.1.1 Oxygen Species Interacting with Grains in the Bulk [1].

The relationship between the $O_2$ partial pressure and the electrical conductivity of a valence oxide is given by [1]

$$\sigma = A \exp\left(-\frac{E_A}{kT}\right)P_{O_2}^{1/N} \quad \text{(2.1)}$$

where,

$\sigma = \text{Electrical Conductivity.}$

$E_A = \text{Activation Energy for Conduction.}$

$P_{O_2} = \text{Oxygen Partial Pressure.}$

$N = \text{Constant determined by the dominant type of bulk defect involved in the equilibrium between oxygen and the sensor.}$

$A = \text{Constant.}$
2.1.2 Physisorption and Chemisorption

In environments where sensors are used to monitor exhaust gases or leaks i.e. where the ambient can be almost anything, the O\textsubscript{2} partial pressures can vary from place to place. These O\textsubscript{2} partial pressures play a very important role in sensing H\textsubscript{2} or as a matter of fact any gases as shown above.

Oxygen is desorbed into 3 temperature ranges. At low temperature range the predominant surface species is physisorped; Physisorption is caused by dispersion forces, also forces of electrostatic nature and electrical image forces. At intermediate temperature range a weak Vander walls force attaches the O\textsubscript{2} species to the surface, Chemisorbed species give rise to a second peak i.e. ones bonded with a more tougher force like covalent bonding. At higher temperature range, O\textsubscript{2} is lost from the bulk [15]. Figure 2.1.2.1 shows the 3 peaks (surface vs operating temperatures) for ZnO.

![Figure 2.1.2.1 Surface Vs the Operating Temperature for ZnO [7].](image-url)

Figure 2.1.2.1 Surface Vs the Operating Temperature for ZnO [7].
2.1.3 Grain Boundaries

The sensing layer of film sensors is very porous and consists of numerous interconnected grains. These grains can be either single crystals or polycrystalline agglomerates. The high porosity enables the ambient gases to access these intergranular connections. Because of this, a depletion layer is created around the grains, the extension of which is determined by the partial gas concentrations and the bulk characteristics of metal oxides. Figure 2.1.3.1 shows the grains and how they are depleted on the surfaces, it also shows the formation of bottlenecks between 2 grains. Therefore, grain boundaries play an important role in the sensing layer conduction and in the detection mechanism, as the grain boundaries form bottlenecks which result in electronic transfer from grain to grain. If the grains are punctually connected and the depletion layer depth $\lambda_D$ is much smaller than the grain radius $r$, a grain bulk area unaffected by the gas will still exist. In order to contribute to electronic conduction, the electrons originating from the “bulk” must overcome these depletion layers and the related potential barrier heights at the intergranular contacts. This is equivalent to a significant resistance increase of the sensitive layer.

The overall resistance $R$ is a function of the contributions of the bulk and the surface of metal oxide grains, the electrode contacts and the intergranular contacts. The resistance contribution of intergranular contacts is related to the gas dependent barriers, which have to be overcome for the numerous intergranular contacts between the electrodes [18].
Figure 2.1.3.1 Schematic Representation of Grain Structure in a Porous Solid [2].

Figure 2.1.3.1 shows a schematic of grain structure where the shaded portion for a n-type semiconductor represents the zones depleted of charge carriers. The grain junctions represent either higher resistance paths or Schottky barriers.

2.2 Operation of a Gas Sensor

The operation of a gas sensor can be branched into 2 parts.

- Chemisorption of O$_2$ species onto the surface of the SnO$_2$.
- Reaction of other gases (H$_2$ in this case) with the surface leading to change in the properties of the material involved.
Chemisorption of Oxygen Species

Tin oxide is a n-type semiconductor due to the existence of native donor levels. These have energies of 0.03-0.034eV and 0.14-0.15eV below the conduction band edge, and are generally attributed to single and double ionization of O\textsubscript{2} vacancies, as vacancies are above, i.e., within the conduction band. The position of the Fermi level is fixed and lies between the conduction band edge and the intrinsic Fermi level position, because SnO\textsubscript{2} presents a negligible concentration of electronic band-gap states at their geometrically ideal surfaces.

Oxygen in a metal oxide is in equilibrium with the gaseous O\textsubscript{2} present at the solid surface. If this latter quantity is reduced, O\textsubscript{2} ions on lattice sites may be converted to the gaseous state, creating O\textsubscript{2} vacancies or point defects. If the temperature is high enough, such vacancies, although created at the surface, may diffuse into the bulk until full equilibrium is reached.

The two remaining electrons resulting from each vacancy will have energy levels placing them in the band gap, from which they may be excited into the conduction band. Therefore, the bulk electrical resistance becomes a function of the O\textsubscript{2} partial pressure at the phase boundary. This mechanism is thought to predominate at temperatures above 700 °C, This model requires O\textsubscript{2} to cross the phase boundary in order to change the carrier concentration and hence the electrical resistance.
In contrast, the effect of the surrounding atmosphere on the electrical resistance of metal oxide semiconductors at temperatures below 500 ºC is rarely explained in terms of the formation and annihilation of point defects. Tin oxide provides a classic case of surface effects on the electrical resistance of such materials. Here, gaseous O₂ may become chemisorbed on the surface, with the formation of species such as O₂⁻, O⁻, O₂²⁻, so that electrons may be removed from the conduction band at the surface and a depletion layer can be created [14].

Nevertheless, the above discussion is not valid for a polycrystalline material, due to primarily two effects: a) The presence of grain boundaries and the b) crystallite size. Grain boundaries are formed by several layers of atoms displaced from their original positions, thereby allowing the coupling between the crystalline lattices of both crystals. The natural disorder of grain boundaries results in the modification of the local band structure of the material due to the appearance of interfacial energetic levels within the band gap. The origins of these levels lead the grains to act as acceptor or donor levels.

There exist surface and interface traps acting as acceptor or donors, each of them having a certain density of states and certain parameters of emission and capture. The charge trapped at grain boundaries or surfaces is compensated by opposite charged depletion regions surrounding them. However, a direct association between the created states, their activity, and their location in the band gap and the type of defects from where they are caused cannot be predicted a priori. However, for an n-type semiconductor, the position of the Fermi level in the grain boundary has to be lower than the corresponding position in the bulk material just to generate the band bending of the surface, this is shown in figure 2.2.1.1[16].
With respect to the influence of crystal size, it is mainly due to the fact that as grain size is reduced, the number of ideal surfaces (i.e., those with negligible band gap states) reduces as well, and in the case of nanoparticles, these ideal surfaces do not exist, thereby increasing the number of unreconstructed surfaces, dangling bonds, and surface vacancies, that induce acceptor or donor levels at the grain surface.

Figure 2.2.1.1 was with respect to a single grain, when we take in consideration multiple grain interfaces we see that, charge in the depletion regions causes curvature of the

Figure 2.2.1.1 Band Diagram of SnO₂ Ideal, Polycrystalline [16].
energy bands, leading to potential barriers (opposing Schottky barrier at an interface), which prevent the movement of any remaining majority free carriers from one grain to another, as shown in figure 2.2.1.2 [16].

![Figure 2.2.1.2](image.png)

*Surface or interface traps create a potential barrier and a depletion region. Under gas adsorption, as grain boundaries are less exposed, barrier height should be different at grain boundaries and at surfaces, as shown in this figure.*

**Figure 2.2.1.2 Opposing Schottky Barrier at an Interface [16].**

### 2.2.2 Effect of Target Gases, Temperature and Moisture on SnO₂ Surface

The interest in sensing materials lies in the fact that electrical properties change in the presence of a determinate gas. Depending on the materials, this change can be due to Surface or Bulk effects. The following section discusses in detail the material used in this thesis. We will discuss the role of surface effects, specifically changes in surface conductance.
Because of the natural non-stoichiometry of SnO$_2$, it presents an n-type character. Therefore the species that tend to trap electrons from the semiconductor are those who are easily adsorbed. This implies that, under usual operating conditions (understood as an ambient such as synthetic air (79% N2 + 21% O2), in which some small quantity of other gas is introduced and certain humidity conditions), the surface of SnO$_2$ is mainly covered by oxygen and water species. So, the oxygen available as well as the different species resulting from water are crucial for the understanding of the operating behavior.

2.2.2.1 Surface Conductance Effects of Target Gas in Presence of O$_2$

SnO$_2$ is a good choice for detecting, oxidizing or reducing gases. In order to describe the surface conductance effects in the presence of gases we have taken H$_2$ acting as a reducing gas as an example. The dependence of the electrical conductivity $\sigma$ on H$_2$ partial pressure $P_{H_2}$ can be characterized by a parameter $m_\sigma$.

$$m_\sigma = \left( \frac{\partial \log \sigma}{\partial \log P_{H_2}} \right)^{-1} \quad \text{(2.2)}$$

The theoretical values of $m_\sigma$ can be found depending on the gas-solid state interaction that occurs on the semiconductors surface.

Under the presence of O$_2$ in atmosphere, the sensing material chemisorbs it on its surface. O$_2$ can be adsorbed in several forms such as O$_2^-$, O$, O^2-$. The interaction between a semiconductor surface and H$_2$ (with reducing properties) can be explained in terms of the reaction of H$_2$ molecules with the preadsorbed O$_2$. 
The following reactions could take place [17]:

\[
O_2^- + 2H_2(g) = 2H_2O(g) + e^- 
\]  \hspace{1cm} (2.3)

\[
O^- + H_2(g) = H_2O(g) + e^- 
\]  \hspace{1cm} (2.4)

\[
O^{2-} + H_2(g) = H_2O(g) + 2e^- 
\]  \hspace{1cm} (2.5)

As seen from the 3 equations the interaction between chemisorbed O\textsubscript{2} and the reducing gas (in this case H\textsubscript{2}) results in a decrease of surface chemisorbed O\textsubscript{2} and in an increase of electrical conductance. An important factor to be taken in to account is the presence of water vapor at the sensor surface, since the formation of hydroxyls is in competition with the O\textsubscript{2} adsorption; the OH\textsuperscript{-} group does not influence directly the surface reactions but affects the reaction rate [7].

### 2.2.2.2 Moisture Effects

Water can be adsorbed in two states: Molecular water, H\textsubscript{2}O (physisorption), and hydroxyl groups, OH\textsuperscript{-} (Chemisorption). Adsorption of water vapor always produces a large increase in electronic conductivity in SnO\textsubscript{2}. This is because chemisorbed hydroxyl groups are bound to Sn atoms and the remaining H\textsubscript{2} ions reduce the O\textsubscript{2} atoms, creating donors for Sn dioxide [16].

The adsorption of hydroxyls follows the reaction [7]:

\[
H_2O + O^-_{ad} + e^- = 2OH^-_{ad} 
\]  \hspace{1cm} (2.6)
2.2.2.3 O₂-Effect on the Surface

Adsorbed O₂ species transform at the surface of an oxide according to the general scheme $\text{O}_2 \text{ads} \rightarrow (\text{O}_2 \text{ads})^- \rightarrow (\text{Oads})^- \rightarrow (\text{Olattice})_2^-$, in which they are gradually becoming richer in electrons. At room temperature all the forms are adsorbed, being the coverage of the species at the surface restricted by Weisz limit. In fact, at room temperature, the equilibrium of the $(\text{O}_2 \text{ads})^-$ coverage with gaseous O₂ is approached slowly. With increasing temperature $(\text{O}_2 \text{ads})^-$ converts to 2$(\text{Oads})^-$ by taking one electron from the bulk, thereby causing (at constant O₂ coverage) an increase of surface charge density with corresponding variations of band bending and surface conductivity. Oxygen desorbs with a maximum temperature of desorption as physisorbed O₂ at 80 °C, as O₂⁻ at 150 °C and O⁻ or O²⁻ at 520 °C, while at temperatures higher than 600 °C the thermal reduction of the SnO₂ occurs and lattice oxygen is desorbed. $(\text{Oads})^-$, which is a very reactive specie, is the dominant specie in the case of SnO₂ for temperatures between 423 and 933 K [16]. While O₂⁻ species are highly unstable and do not play much role in determining the sensitivity. In fact, this is the least stable form of O₂ in the gas phase, and becomes stabilized only in the crystal lattice by the electric field created by its neighboring actions [16].

The net effect of surface states (coming either from adsorption of O₂ molecules or from crystal structure defects) is, when a high concentration of surface states is present, a pinning of the Fermi level within the band gap [16].
2.2.2.4 Effects of Temperature on SnO$_2$ Surface

Temperature has pronounced effects on the sensitivity of thin film gas sensors, as it influences the physical properties of semiconductors (change of the free carrier concentration, Debye length, etc.). However since sensor operation is influenced primarily by surface processes, their dependence on temperature is more critical. Temperature dependent surface mechanisms include: adsorption, desorption, surface coverage by molecular and ionic species, chemical decomposition, reactive sites. In this way, dynamic properties of the sensors such as response and recovery time and the static characteristics of the sensor depend on the temperature of operation, and a temperature for which the sensitivity of a Semiconductor Gas Sensor (SGS) is maximum, is always observed.

There are different possible temperature-dependent elementary steps of molecular recognition with semiconductor gas sensors that have to be optimized for the specific detection of a certain molecule. These steps firstly involve the low-temperature surface reactions. Examples are adsorption and catalytic reactions at active sites (the latter involving intrinsic point defects, such as O$_2$ vacancies, and/or extrinsic point defects, e.g., segregated metal atoms) and similar reactions at grain boundaries or at three-phase boundaries (e.g., at metallic contacts or at surface metallic clusters). All of these reactions involve adsorbed negatively charged molecular (O$_2$-) or atomic (O-) species as well as hydroxyl groups (OH-) at different surface sites. These steps secondly involve the high temperature bulk reactions between point defects in the SnO$_2$ crystal and oxygen (O$_2$) in the gas phase. The key for the controlled operation of such sensors is the careful
adjustment of the operation temperature, since conduction changes upon exposure to
different gas components usually showing different maxima as a function of temperature
[16].
Chapter 3. Materials and Their Properties

A material is selected for a specific application on the basis of its intrinsic properties. The material properties can be divided into bulk and surface properties. For this thesis the surface properties are looked into in detail, although bulk properties cannot be ignored. It must be stated that the current status of physics and chemistry are not fully developed and understood, to know clearly the effects of surface properties on gas sensitivity. This section describes the most accepted theories to-date.

3.1 Structural Properties of SnO₂

Tin (Sn) is a naturally occurring element that appears in group 14 (4A) of the periodic table at the boundary between metals and non-metals. Various organic and inorganic compounds can be formed with Sn. The divalent and tetravalent oxidation states can be designated using the names stannous and stannic, respectively, in the name of the compound. Another commonly encountered nomenclature system, the stock oxidation-number system, denotes the divalent and tetravalent tin as Sn (II) and Sn (IV).

Tin is a silver-white metal that is malleable and somewhat ductile. It has a crystalline structure and exists in two allotropic forms at normal pressures. Gray or α Sn exists below 13.2 °C and has a cubic structure. At 13.2 °C, gray Sn is converted to white or β
Sn, which has a tetragonal structure. In compounds, Sn can exist in the +2 or +4 oxidation state [18].

Sn (IV) oxide is the subject of this work; it is normally called Tin oxide, stannic oxide, or stannic anhydride with a chemical formula SnO₂.

Tin oxide is a semiconductor; it’s an anisotropic polar crystal, which crystallizes with tetragonal rutile structure. The unit cell contains six atoms, two Sn, and four O₂. Each Sn atom is at the centre of six O₂ atoms placed approximately at the corners of a regular slightly deformed octahedron, and three Sn atoms approximately at the corners of an equilateral triangle surround every O₂ atom; resulting in a 6:3 coordination [18]. this is shown in figure 3.1.1.

Figure 3.1.1 Rutile Structure of SnO₂ [18].
The lattice parameters are \( a = b = 4.737 \, \text{Å} \) and \( c = 3.185 \, \text{Å} \). The \( c/a \) ratio is 0.673. The ionic radii for \( \text{O}^{2-} \) and \( \text{Sn}^{4+} \) are 1.40 and 0.71 Å, respectively. The metal atoms (cations) are located at positions \((0, 0, 0)\) and \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) in the unit cell, and the \( \text{O}_2 \) atoms (anions) at \( \pm (u, u, 0) \) and \( \pm (\frac{1}{2}+u, \frac{1}{2}-u, \frac{1}{2}) \), where the internal parameter, \( u \), takes the value 0.307. Each cation has two anions at a distance of \( \sqrt{2}ua \) (2.053 Å) and four anions at \([2(\frac{1}{2}-u)^2 + (c/2a)^2]^{\frac{1}{2}}a\) (2.597 Å).

### 3.2 Electrical Properties

\( \text{SnO}_2 \) is a good gas sensor due to the combined effect of bulk and surface properties. These are discussed separately and in detail in this section.

#### 3.2.1 Bulk Effects

The conductivity of a semiconductor crystal can be given as the sum of electronic conductivity (\( \sigma_e \) and \( \sigma_p \)). If the conduction processes are considered independent,

\[
\sigma_{\text{tot}} = \sigma_e + \sigma_p + \sum \sigma_{\text{ion},i} \approx \sigma_e + \sigma_p
\]

\[
\text{--------- (3.1)}
\]

The resistance of homogeneous bulk material with bulk conductivity \( \sigma_b \), mobility \( \mu \), length \( l \) and cross section \( A \) can be calculated according to:

\[
R_b = \frac{1}{\sigma_b \cdot l \cdot A} = \frac{1}{\sigma_b \cdot A}
\]

\[
\text{--------- (3.2)}
\]
Where \( \sigma_b = \sigma_e + \sigma_p = n \mu_e e + p \mu_p e \)

The charge carrier concentrations \( n \) and \( p \) for an intrinsic semiconductor can be calculated with Fermi-Dirac distribution \( f(E) \) and the density of states \( D(E) \).

The \( n \)-type behavior of \( \text{SnO}_2 \) is associated with \( \text{O}_2 \) deficiency in the bulk [18].

The relationship between \( \text{O}_2 \) partial pressure and the electrical conductivity of a mixed valence oxide is given by equation 3.3.

\[
\sigma = A \exp\left( -\frac{E_d}{kT} \right) \frac{P_{\text{O}_2}^{1/N}}{a_2} \quad \text{--------- (3.3)}
\]

\( N \) in the equation above is a constant determined by the dominant type of bulk defect involved in the equilibrium between \( \text{O}_2 \) and the sensor [17].

### 3.2.2 Surface Effects

The reactivity of a gas with a sensor material depends on the species adsorbed on the surface of the material. In general, most target gases are detected via the influence that they have on the \( \text{O}_2 \) stoichiometry of the surface. In this way, \( \text{H}_2 \) for example can reduce the surface of \( \text{SnO}_2 \) taking chemisorbed \( \text{O}_2 \), and thus, giving electrons to the bulk of the semiconductor, decreasing barrier height and increasing surface conductance. The reaction product leaves the surface and enters the gas phase, and the \( \text{H}_2 \) chemisorption is the rate-limiting step [17]. A detailed description of this is given in section 2.2.1 of this thesis. However, gas detection cannot yet be completely explained by only taking into account the charge transfer occurring at the surface of the semiconductor.
In order to modify or control the surface properties of the SnO$_2$, introduction of metal additives is usually performed. The most important effects of metal addition are the increase of the maximum sensitivity and the rate of response, as well as the lowering of the temperature of maximum sensitivity. All these effects arise as a consequence of promoting catalytic activity when loading with noble metals. A great amount of additives have been studied, with Pd and Pt being the most commonly used.

![Formation of Schottky Barrier upon Introduction of Metals](image)

**Figure 3.2.2.1 Formation of Schottky Barrier upon Introduction of Metals [16].**

In general, under metal loading the formation of clusters takes place. Depending on the noble metal deposited, the loading, and the interacting gas, these clusters will be in metallic or oxidized form. In any case, the contact of the additive with the semi-conducting oxide creates a barrier that is fully characterized by the electron affinity of the semiconductor, the work function of the metal and the density of surface states of the semiconductor that are located inside the energy band gap. All of these three contributions create a Schottky barrier through the formation of a depletion region in the
semiconductor surface in contact with the cluster. Eventually, the surface states created by the presence of the additive can pin the Fermi level of the semiconductor to that of the additive (figure 3.2.2.1) [16].

Two mechanisms have been proposed to explain the observed results of the influence of additives on SnO$_2$:

*Chemical sensitization.* The action of the additive is in general two-fold: a) the metallic cluster presents a higher sticking coefficient (to gases) than the semiconductor and b) on the cluster, nearly all the gas molecules are dissociated; being the dissociation products spill over the semiconductor support and sometimes diffuse. Because the activation energy for desorption is much higher than for diffusion, the support can act as source of reactant supply. Moreover, normally the support is assumed to be catalytically inactive, but not always. It is evident why selectivity and lowering of the operation temperature are obtained by this mechanism. For example, in the case of, H$_2$, oxides are not very active for H$_2$ activation, but the gas is activated by the deposited metal, and the activated fragments (H) migrate to the semiconductor surface by spill-over mechanism, thereby reacting with the adsorbed O$_2$ as shown in figure 3.2.2.2. In this way, reactions that occur on the oxide surface and need H$_2$ can proceed at lower temperatures, and are favored over reactions that do not consume H$_2$. This type of mechanism occurs for example in Pt-loaded SnO$_2$, where Pt is known to remain in metallic form under most reaction conditions [16].
Electronic sensitization: In this, there is an electronic interaction between the added particles (for example pt) and the semiconductor through the space charge created in the semiconductor by the presence of the surface clusters. Additives at the surface of the semiconductor act as receptors while the semiconductor acts as a transducer of the changes taking place at the surface under gas adsorption. This type of sensitization has so far been observed in SnO$_2$ elements impregnated with Ag, Pd and Cu, which form stable metal oxides when exposed to air. The electronic interactions actually appear between the metal oxides and SnO$_2$ and disappear when the oxides are converted to metals (Ag and Pd). Thus, the oxidation state of the particles changes when it comes in contact with a gas, inducing the corresponding change in the electronic state of the semiconductor [16].

The process explained above is shown in figure 3.2.2.3.
In spite that the above mechanisms are the most accepted ones to explain most of the investigations; some authors propose other mechanisms to explain their results. Thus, for example, it has been claimed that under certain conditions for the distribution and size of the metallic clusters, tunneling occurs between the discrete islands, dominating the normally considered thermionic emission carrier transport. Other authors consider that, in some cases, the effect that the depletion region created by the presence of additives at the surface of the semiconductor has on decreasing the effective grain size is more relevant [16].
Chapter 4. Literature Review

This chapter reviews work done by other researchers in the field of H\textsubscript{2} sensors, it discusses different methods and materials used by researchers in this area. We know how a SnO\textsubscript{2} based gas sensor functions and all the factors that affect the working of a gas sensor. The main drawback observed in SnO\textsubscript{2} based gas sensors are low selectivity and cross sensitivity. The main areas of research in improvisation of gas sensors has been going on in trying to make them more sensitive by using different materials or adding catalysts or using different technologies. Or even by varying various parameters like temperature or thickness of the film. In this chapter we will summarize different literature by previous researchers sorted out by case numbers.

4.1 Case 1: Thickness Dependence on Selectivity.

The setup used in this particular case is shown below.
In this case a mathematical model for simulation of the steady state gas sensitivity \( S = \frac{G_g}{G_a} \) of a thin film resistive gas sensor is presented. The sensitive semiconductor film was modeled as a multi layer polycrystalline structure, the target gas was assumed to affect the inner layers either by penetration through the grain boundaries or by direct interactions with all the layers at their exposed edges. The effect of micro-cracks and open pores were quantitatively accounted for as the providers of extra exposed edges. The simulation carried out predicted that in the micro-crack-free sensitive films, in general, the sensitivity reduces exponentially as the total thickness of the film increases. But in this case they also have shown that this trend can be altered by the presence of the structural defects. Also they proved that in micro-cracked or porous films the relationship between sensitivity and thickness is strongly dependent on the nature of the target gas; considerably different thickness dependencies were predicted for the sensitivity to different target gases [21]. Figure 4.1.2 depicts the sensitivity vs. thickness graph obtained in this case.
4.2 Case 2: Conduction Model of Metal Oxide Gas Sensors

It is well known that sensor selectivity can be changed over a wide range by varying the SnO$_2$ crystal structure and morphology, dopants, contact geometries, operation temperature or mode of operation, etc. The elementary reaction steps of gas sensing itself can take place at different sites of the structure depending on the morphology. A simple distinction can be made between compact layers and porous layers.

- Compact layers: The interaction with gases takes place only at the geometric surface (figure 4.2.2).

- Porous layers: the volume of the layer is also accessible to the gases and in this case the active surface is much higher than the geometric one (figure 4.2.3).

Figure 4.2.1 shows the 2 types of layers and gas interactions within them.
For compact layers, there are at least two possibilities: completely or partly depleted layers, depending on the ratio between layer thickness and Debye length $\lambda D$. For partly depleted layers, when surface reactions do not influence the conduction in the entire layer ($z_g > z_0$ see figure 4.2.2), the conduction process takes place in the bulk region (of thickness $z_g - z_0$, much more conductive that the surface depleted layer). Two resistances occur in parallel, one influenced by surface reactions and the other not; the conduction is parallel to the surface, and this explains the limited sensitivity. Such a case is generally treated as a conductive layer with a reaction-dependent thickness. For the case of completely depleted layers in the absence of reducing gases, it is possible that exposure to reducing gases acts as a switch to the partly depleted layer case (due to the injection of additional free charge carriers). It is also possible that exposure to oxidizing gases acts as a switch between partly depleted and completely depleted layer cases.
Figure 4.2.2 Schematic Representation of a Compact Sensing Layer Geometry and Band Diagram [22].

For porous layers the situation may be complicated further by the presence of necks between grains (Figure 4.2.4) as 3 cases come into picture: surface/bulk (for large enough necks \( z_n > z_0 \)), grain boundary (for large grains not sintered together), and flat bands (for small grains and small necks).
What was mentioned for compact layers, i.e. the possible switching role of reducing gases, is also valid for porous layers. For small grains and narrow necks, when the mean free path of free charge carriers becomes comparable with the dimension of the grains, a surface influence on mobility should be taken into consideration. This happens because the number of collisions experienced by the free charge carriers in the bulk of the grain becomes comparable with the number of surface collisions; the latter may be influenced by adsorbed species acting as additional scattering centers [22].

Figure 4.2.3 Schematic and Band Diagram for a Porous Sensing Layer [22].
The importance of this paper is that it shows us that the base of the gas detection is the interaction of the gaseous species at the surface of the semi conducting sensitive metal oxide layer. It is important to identify the reaction partners and the input for this is based upon spectroscopic information. Using this input, one can model the interaction using the quasichemical formalism. As a consequence of this surface interaction, charge transfer takes place between the adsorbed species and the semi conducting sensitive material. This charge transfer can take place either with the conduction band or in a localized manner [22].
4.3 Case 3: High Surface Area SnO\textsubscript{2} [23]

In this study as reaction between the surface O\textsubscript{2} species and reducing gases are of extreme importance for gas sensitivities, the authors (G. J Li et.al.) believes that sensor sensitivity can be improved by increasing the sensor surface areas in order to provide more surface sites available for O\textsubscript{2} to be adsorbed and make contact with the surrounding gases [23].

SnO\textsubscript{2} based sensors are generally prepared by, sol-gel method or thin film deposition techniques. According to this work these methods are usually quite complicated and it is difficult to control the experimental conditions. So the author here uses a method called surfactant synthetic strategy which produces high surface area SnO\textsubscript{2}.

![Figure 4.3.1 Sensitivity vs Surface Area of SnO\textsubscript{2} [23].](image-url)
Figure 4.3.1 shows the results obtained, as we can see the sensitivity increases as the surface area increases.

In addition The paper discusses the preparation method for surfactant treated SnO$_2$, how it gives more uniform mesopores and how acidity of the starting synthesis mixtures substantially affects the surface areas of the resulting material (i.e. as acidity increases surface areas increase); And higher surface areas have higher sensitivities.

4.4 Case 4: Selective Gas Sensors

One major requirement of gas sensors in addition to sensitivity is selectivity. A study by A. Katsuki et. al., we see work done on a SnO$_2$ based gas sensor to make it more selective by using a hot wire model. Commercially available SnO$_2$ was sintered in a bead covering over a platinum wire coil. The gas sensor was operated by a bridge electric circuit. A dense layer near the surface of the porous bead was formed by chemical vapor deposition of hexamethyldisiloxane (HMDS). The dense layer functioned as a molecular sieve; thereby the diffusion of gasses with large molecular diameters, except for H$_2$, was effectively controlled, resulting in a prominent selectivity for H$_2$. On the other hand, diffusion control of O$_2$ caused a strong H$_2$ reduction of the SnO$_2$ in the inner layer covered with the dense layer, resulting in decay in sensor output and irreversible reduction of the H$_2$ sensitivity (deactivation of SnO$_2$)[24]. The setup is shown in figure 4.4.1.
As a counter measure against the damage, the effect of cerium oxide from 0.5% to 5.0% was investigated. The $\text{H}_2$ selective gas sensor thus obtained had significantly lower humidity dependence and prominent long term stability [24]. The output of the work for 2% Ce: SnO$_2$ is shown below in figure 4.4.2.
4.5  **Case 5: Behavior of \( \text{SnO}_2 \) Thin Film Gas Sensor Prepared by MOCVD [25]**

As we have seen in one of the cases above porous materials are preferred because they improve the sensitivity, and a lot of research has been dedicated to studying of these type of materials. J.R. Brown et. al. the authors of this work, looked into relatively non-porous thin films grown by the MOCVD method. MOCVD is a deposition technique, which allows fairly precise control of the microstructure of the resultant thin films through the process parameters. Films produced by this method have low porosity compared to those deposited by sputtering or thick-film preparation techniques. This method of deposition also allows controlled introduction of dopants in a one step deposition process. For this study films were produced from tetratertiarybutoxytin at 350 °C. The authors found that the films act as selective sensors at room temperature with higher sensitivity above 200 °C. The effect of water vapour on the response was found to be negligible [25]. Figure 4.5.1 shows response to \( \text{H}_2\text{S} \) at room temperature.

![Figure 4.5.1 Response at Room Temperature [25]](image-url)

**Figure 4.5.1  Response at Room Temperature [25].**
4.6  **Case 6: Influence of Metal Nanoclusters on Sensing Behavior of SnO$_2$ [26]**

The incorporation of a second component in metal oxides as bulk doping or surface modification is becoming one of the most attractive methods of optimization of the gas sensing properties of solid state gas sensors. This work shows how nanoclusters of various additives like transition metals (Fe, Mn, Co, Ni, Cu), oxides (SiO$_2$, Al$_2$O$_3$), and noble metals (Ag, Pd, Pt) can be used depending on the required result.

These additives can be used as promoters, catalysts, surface sites for adsorption of O$_2$ and detected gas with following spill over of adsorbed species, or as elements promoting the improvement of porosity, thermal stability, and gas-sensing characteristics.

Successive Ionic Layer Deposition (SILD) is the method used for surface modification. SILD is used because it’s a method for deposition of metal oxide nanoclusters and nanolayers on textured surfaces i.e. on porous materials. It does not provide a high deposition rate in comparison with other techniques.

For surface modification a high deposition rate is not needed, precise monitoring of both the size and composition of deposited clusters and nanolayers is more important [26].

The author concludes that the surface coverage achieved by the SILD method on the surface of the gas sensing metal oxide films can act as an active filter improving gas selectivity. Figure 4.6.1 shows the response of various metal additives at different cycles of deposition to H$_2$. 
4.7  Case 7: Study of SnO$_2$ and SnO$_2$: Cu Thin Film Gas Sensors

In this study the authors show how O$_2$ deficient films are fabricated. They use 2 different approaches to do this: 1. Deposition of Sn in Ar atmosphere followed by annealing in an O$_2$ atmosphere, and 2. Deposition in Ar/O$_2$ mixture. Both methods help in making polycrystalline films with a high sensitivity to reducing gases. The method used for deposition is r.f.magnetron sputtering.

It was noticed that the long term instability of the film conductance caused by O$_2$ diffusion at advanced operating temperatures did not appropriately meet the sensor requirements. Doping of the films with copper atoms was shown to be a useful method of stabilizing the electrical characteristics [27].
4.8  Case 8: Selective Filter for SnO$_2$ Based Gas Sensor

In this case the author has tried to make SnO$_2$ based gas sensors very selective by treating them with hexamethyldisiloxane (HMDS) at high temperatures i.e. 500-600 °C. After this treatment it was noticed that the electrical properties of sensors are greatly modified. The sensitivity towards H$_2$ is markedly increased and a high selectivity to H$_2$ is achieved. It was noticed that response and recovery times are longer for treated films than untreated ones. But if the temperature is increased from 450 to 550°C the response time notably decreases and the detection of H$_2$ trace as low as 250 ppb is seen with high stability. It’s seen that surface hydroxyl groups are involved in the HMDS-SnO$_2$ interaction. It could be that a weakly porous Si-based coating film overlaps the treated SnO$_2$ material and acts as a molecular sieve. H$_2$ can pass easily through the dense filter whereas the diffusion of other gases, and especially O$_2$, is considerably reduced [28].

![Figure 4.8.1 Time Vs Conductance of Treated Film [28].](image)
Figure 4.8.1 shows how the conductance increases with introduction of H$_2$ and falls with it been cutting off.

![Graph showing conductance over time with H$_2$ introduction and removal.]

Figure 4.8.2 Response to H$_2$ for Treated Films at 500 and 600ºC [28].

Figure 4.8.2 compares the graphs for samples treated at different temperatures.
Chapter 5. Preparation of Samples and Experimental Setup

This chapter describes the experimental setups and procedures used for this thesis. It also describes sample preparation by MOCVD and sputtering, and the experimental test bed that was setup to test the H₂- sensitivity of the SnO₂ thin films

5.1 Preparation of Samples

The samples used in this thesis were SnO₂ thin films. Tests have been conducted on both doped and undoped samples; in this section we will review how samples are prepared. The substrates used were Corning 7059 borosilicate glass (1.25” X 1.45” X 0.032”). These substrates were cleaned in a 10% by volume HF solution by dipping them twice for 5 sec and then thoroughly rinsing them in deionized water. They were subsequently dried with compressed N₂.

SnO₂ thin films were prepared by 2 methods

[i] Sputtering and

[ii] MOCVD.
5.1.1 Sputtered Samples

Magnetron Sputtering is a vacuum process used to deposit thin films on a substrate. The functioning principle here can be summarized as a very high voltage being applied across a low pressure gas (generally in millitorr) to create a plasma which consists of electrons and gas ions in a high energy state. During sputtering energized plasma ions strike a target, composed of the desired coating material, and cause atoms from that target to be ejected with enough energy to travel and bond with the substrate. The magnets help in creating a magnetic field which helps the ions to travel straight to the target. Figure 5.1.1.1 shows a schematic of working of magnetron sputtering.

![Figure 5.1.1.1 Magnetron Sputtering Process](image_url)
For this thesis RF- Magnetron sputtering was used to reactively deposit SnO$_2$ thin films from a Sn target in an Ar/O$_2$ (20) ambient. The vacuum chamber was a Consolidated Vacuum Corp. model; the sputtering guns were Kurt J.Lesker Torus TRS3FSA models; Advanced Energy RFX-600 power supplies supplied the RF power. The sputtering sources were positioned such that the center line of each source created an angle of approximately forty degrees with respect to a plane parallel to the substrate holder. The substrate holder was rotated to ensure uniform film thickness [29].

The total pressure in the chamber was maintained at 3.0 mT in all cases. Before each deposition, the chamber was pumped down to a background pressure in the low 10$^{-5}$ Torr range [29]. The target used was Tin (Sn) which is 99.99% pure and 25% O$_2$ in an ambient of argon which react to form SnO$_2$. Figure 5.1.1.2 shows how the positioning of targets and holders are done in this case to prepare samples.

![Figure 5.1.1.2 Arrangement of Sputtering Sources and Substrate Holders [29].](image)
5.1.2 MOCVD Samples

MOCVD stands for Metal Organic Chemical Vapor Deposition; this method is frequently used in many areas of the semiconductor industry to grow thin films. Figure 5.1.2.1 shows the main components of an MOCVD system.

**Figure 5.1.2.1 Block Diagram of a MOCVD System.**

The use of each block from above can be described as follows:

a) Gas handling system: Deals with the whole ambient gas inlet pipe system, including the gas cylinders.

b) MO Source: Deals with the target and lines used to introduce the MO source.

c) Temperature controller: Maintain and control the temperature.

d) Reactor: The glass chamber where sample is housed and the reaction takes place.

e) Vacuum and Exhaust: Vacuum system and exhaust for gasses.
(SnO$_2$ was deposited on the substrates by chemical vapor deposition technique). The reactor consisted of a quartz tube which was heated by RF coils to above 450 °C. The organometallic Sn source used was Tetra Methyl Tin (TMT); ultra high purity He was used as a carrier gas, and O$_2$ served as the oxygen source. The fluorine dopant used was halocarbon 13B1 (CBrF$_3$). The samples were placed on a graphite susceptor and loaded into the chamber. At the end of the deposition process the O$_2$ was kept on for an extra min after the TMT was shut off at 450°C. Figure 5.1.2.2 shows a schematic of the system used in this work.

Figure 5.1.2.2 Schematic of a MOCVD Setup [29].
5.2 Experimental Setup

The prepared samples were placed in a test bed prepared only for the purpose of testing i.e. to see how the samples react in different atmospheres and different conditions of temperature etc.

The experimental setup included 2 high pressure cylinders as source of N₂ and H₂; which acted as the carrier gas and target gas. Lines were connected from the cylinders to the UFC 1100A model Mass Flow Controllers of specification 200 standard cubic centimeters per minute (SCCM) and 1000 SCCM. The MFC’s were controlled through a Tylan UNIT 1000 power supply. Shut off manual valves were used to turn on and off the gas flow by the user. All gas lines are connected to a manifold which leads to the test chamber or reactor. Figure 5.2.1 shows a schematic of the test bed designed.

![Figure 5.2.1 Original Test Bed Setup.](image-url)
Inside the reactor tube we have the sample placed on a graphite plate, the setup includes 2 graphite plates 1 above the other with slots for thermocouples. Nickel wires are used as contacts, nickel was was used since it can sustain high temperatures.

Pressure contacts are used in this case to make the electrical contact between the Ni-wires and the sample. The pressure contact was designed by making a quartz glass in the shape as shown in figure 5.2.2, so it applies pressure right on the edges of the sample with the contact wires in between. The 2 graphite plates are on top and bottom and 4 screws are tightened on the 4 sides of the graphite plate which creates the necessary pressure for the contacting of the wires and the sample edges.
The wires are in turn connected to probes which are connected to a 2410 Keithley Sourcemetre. The sourcemetre was operated in 4 wire mode.

Heating lamps are used to Heat up the graphite and therefore the sample under test.

Temperature control was achieved using type K thermocouples and Omega T.C CN4400 PID controller so the temperature can be maintained constant.
Chapter 6. Results and Discussion

This chapter deals with the results obtained from the experiments conducted in our Thin Film Electronic material Laboratory.

6.1 Properties of Sputtered SnO$_2$ Samples

The sputtered samples were prepared with a target of SnO$_2$ at a temperature of 330 °C, other process parameters are as follows:

Thickness monitor settings

- Density - 6.95 g/cm$^3$
- Tooling - 84%

Other settings

- Pressure - 2 milliTorr
- Power - 101/7 watt = incident/reflective power.

The sample was prepared in an atmosphere of Argon which was flowed at a rate of 17.9 cm/min and the substrate was rotated at a speed of 75 rotations/min to ensure even deposition on the substrate. The deposition was done at a rate of 1.2 Å/sec. The total thickness of the film was measured to be 1500 Å. Sputtered SnO$_2$ samples are very
resistive with the sheet resistance being approximately 300 $\Omega/\square$ sometimes. Resistive samples are considered suitable for gas sensor applications. Also sputtered films have been found to be more porous [22].

6.2 Properties of MOCVD SnO$_2$ Samples

MOCVD samples are prepared at a temperature of 470 °C with TMT (tetra methyl tin) as the tin source and 13B1 halocarbon as fluorine dopant, in an O$_2$ ambient. Films of three effective thickness were prepared of approximate thicknesses 3000, 6000 and 9000 Å. Typical film resistivity were found to be 6 $\Omega$/cm. These samples are significantly more conductive (approximately 1 order of magnitude) compared to sputtered samples. The grains are typically more compact.

6.3 Results of Sputtered Samples as Sensors

Sputtered sample 1 was placed on the graphite plate and pressure contacts were applied using the setup shown in chapter 5, section 5.2, and placed in the test tube (approximate volume 150 cm$^3$). First the test bed was purged with 100% N$_2$ (200 SCCM) for 40 mins, while at room temperature, the voltage applied through the sourcemetre was typically 0.30 mV and I compliance was set to 1.00105 mA. The measurement was carried out in a 4-wire mode.
The initial current measured was approximately 118.24 µA. After the 40 mins purge H₂ was introduced in the chamber at measured amounts. The total flowrate was maintained at 200 cc/min and H₂ and N₂ flowrate were adjusted to yield 10 / 50 / 90% H₂ partial pressure. After shutting the H₂ off, the tube was purged for 6 mins prior to reintroducing H₂.

![Time - Current Graph](image)

**Figure 6.3.1** Response of Sputtered Sample 1 to H₂ in Room Temperature.

Figure 6.3.1 shows the total current measured through the SnO₂ films as a function of time; The ON and OFF times are marked. As seen in the graph, there is a slight increase in current when the system is being purged with N₂. According to the literature there maybe a residue of contaminants on the surface of the film which escape during the purge process leading to higher current. A 40 min purge time was selected as suitable since
current was found to saturate. Figure 6.3.2 shows a graph of change in current vs time for the data in Figure 6.3.1.

![Time - Change in current graph](image)

**Figure 6.3.2 Time vs. Change in Current Graph of Sample 1.**

It can be seen that the change in current when 10% of H₂ is sensed is shown to be -4 µA and -9 µA for 90% of H₂. It is known that at room temperature physisorbed O₂ is present on the SnO₂ surface; therefore the sensitivity is low which explains some of the observed noise in our data.

To evaluate the SnO₂ films response at higher temperatures, another sputtered film (prepared under identical conditions) was tested under the same conditions at 150 ºC.
As was the case at room temperature the current was found to increase during N\textsubscript{2} purge. Now the graph of time vs. change in current shows a very interesting response we see that the change in current tremendously increases from -4 µA to -2 mA. The reason for this increase in sensitivity is role of the chemisorbed O\textsubscript{2} species which occur at higher temperatures, while at room temperature only physisorbed O\textsubscript{2} species are involved as mentioned above.

If we refer back to figure 2.1.2.1 in chapter 2 pg 27 in this thesis, a graph was presented which explains how temperature influences O\textsubscript{2} physisorption and chemisorption.

The change in current for the data in 6.3.3 is shown in figure 6.3.4.
Based on the results in figures 6.3.2 and 6.3.4 it appears that both films sense H$_2$ but the response is not proportional to the H$_2$ partial pressure.

To test repeatability and proportionality of the sensor response another set of measurements were carried out. For this experiment the H$_2$ partial pressure was varied as 10%, 20%, 50%, 75% and 100% also we go back to 25% and 75% just to check how it works when percentages are reduced after an increasing trend. The voltage applied here was 0.1 V. Now H$_2$ is said to touch the surface but when its purged its supposed to remove all the H$_2$ off the surface, but we noticed that there is some residue left on the surface and that doesn’t let the sensor to reach the exactly same response as the before cycle. The results are shown in figure 6.3.5.
The change in the signal is not linearly proportional to the amount of H$_2$. However the film appears to follow a consistent trend based on the amount of H$_2$.

The repeatability was tested by repeating the same test procedure after 3 days. The results shown in figure 6.3.6 suggest that repeatability is well within 10%.
Figure 6.3.6  Response on the Same Sample 1 after a Period of 70 Hours.

6.4  Results of MOCVD Samples.

The samples prepared by MOCVD are more conductive than the ones prepared by sputtering, and as we are trying to compare the sensing properties of both the samples we noticed that MOCVD samples don’t respond to H₂ at room temperature. The reason could be that sputtered samples are more porous while MOCVD samples are more compact than sputtered and this kind of structure doesn’t allow physisorbed O₂ species to react with H₂. The graph for this is not presented because there was no change in current and if there was any it was more random than other samples seen.
We prepared 3 different samples made by MOCVD with different thickness; the time the MOCVD process was tested was varied to change the thickness. The thickness was 3000, 6000 and 9000 Å.

The difference in response was tabulated when the total flow rate is not maintained constant. As can be seen initially $\text{H}_2$ is sensed in the first cycle, but thereafter the response just randomly changes. Figure 6.4.1 shows the graph for 1 such sample.

![Graph showing response of MOCVD Sample to $\text{H}_2$ in 150ºC (flow rate not constant).](image)

**Figure 6.4.1** Response of MOCVD Sample to $\text{H}_2$ in 150ºC (flow rate not constant).

The 6000 and 9000 Å thickness sample were tested but they did not show any response to $\text{H}_2$. The reason for this is unknown as it could be either a flaw in the preparation of samples or in the testing procedure (contacts). The 3000 Å samples responded to $\text{H}_2$. The graph for a 3000 Å doped sample tested at 150 ºC is shown in Figure 6.4.2. The initial current was measured to be 1.033 mA and the source voltage applied was 0.30mV.
Figure 6.4.2  Response of 3000 Å Doped Sample 1 at 150ºC.

Figure 6.4.3  Time vs. Change in Current Graph for the Same Sample as Above.

Figure 6.4.2 and 6.4.3 show the current and the change in current.
As we see in these graphs the response of this film to H\textsubscript{2} is approximately linear, which was not the case for the sputtered samples. The initial drop in current can only be explained by the presence of contaminants on the surface.

As can be seen the response (i.e. change in current) when compared to the sputtered sample under the same conditions is relatively lower (i.e. less sensitivity). This as suggested in literature is because of the grain size having larger grain boundary surface areas.

In order to check the stability of the sample, it was used in 6 different runs during a span of 10 days. The results from the last run are shown in figure 6.4.4 demonstrating repeatability. It should also be noted that the level of noise decreased from run to run.

![Time - Current Graph](image)

**Figure 6.4.4** Response of the same MOCVD Sample as Previous but on the 6\textsuperscript{th} Run.
Figure 6.4.5 Graph of Time vs. Change in Current for the Same as Above.

The Sensor was exposed to a different H\(_2\) test flow rate pattern in order to determine if purging is critical between sensing cycles. A test was conducted with no purging in between hiking intervals but maintaining the total flow rate constant in the first run of the same sample as shown above. The data is given in Figure 6.4.6.
Figure 6.4.6  Step Response of Sample with no Purge in Between (except the end).

The results are shown in figure 6.4.6. This data was obtained by increasing the H₂ flow rate in steps of 10% H₂ OFF. Even though the data appears noisy, this was expected based on the overall results (i.e. see single H₂ cycle in figure 6.4.3). Since the noise level was found to improve the same experiment was repeated after the sensor was tested under various conditions over a period of 10 days. In figure 6.4.7 it is clear that the noise has decreased. For this experiment the H₂ was also gradually turned OFF, and as the results show the film provides consistent response. It should also be noted that the sensitivity changed (i.e. change in current increased). Explanation for this is out of scope of this work.
As indicated in section 2.2.2.3 of this thesis, sensor sensitivity is temperature dependent. To evaluate the effect of temperature we applied the same conditions of temperature and voltage to the same sample and exposed to H₂. The temperatures were: 35, 75, 115 and 150 ºC.

The results are summarized in figure 6.4.8 and 6.4.9 and table 1.
Figure 6.4.8  a) Response at 35 °C (b) 75 °C (c) 115 °C and (d) 150 °C.
As seen in figure 6.4.8 the response increases as temperature is increased. Presented
below (figure 6.4.9) is a graph which combines each of them together so we can see the
variation in response much clearer.

![Time vs. Temperature Graph](image)

**Figure 6.4.9 Comparison Graph of Different Temperatures.**

As seen in the comparison graph there is a difference in response time and also the
sensitivity.

The response time seems to increase with increasing temperatures. And this change is in
accordance with some of the literature (refer to chapter 2) where they claim that changes
affect the response time and sensitivity of materials as it changes the number of active
charge carriers or change the Debye length.
6.5 Conclusions

The main purpose of this work was to study the use of SnO$_2$ prepared in our thin films and materials lab as a H$_2$ sensing material. As shown above in this chapter, Primarily 2 types of processes were used to prepare the samples; MOCVD and Sputtering. We have conducted tests separately on both types of samples for the sole reason of determining which is better suited for sensing purposes. A point needed to be highlighted is that the data were collected manually (not automated), therefore possibility of human error during collection of some data points is highly possible.

Analyzing the results we can see that the sputtered samples prepared when tested under room temperature showed a -4 µA change in current to 10% of H$_2$ which is very low compared to the change in current of -2 mA noticed for samples tested at 150 °C. Literature suggests that the reason for this low and almost negligent sensitivity to H$_2$ is attributed to presence of physisorbed O$_2$ species which exist only at room temperatures, while the increase in sensitivity is because of the presence of chemisorbed O$_2$ species which exist at higher temperatures.

Tests for analyzing repeatability and proportionality were conducted which showed that samples were sensitive to H$_2$ but the sensitivity wasn’t exactly proportional to the H$_2$ partial pressures the samples were exposed to. And the repeatability was noticed and measured to be within 10%.
The MOCVD samples were found to be insensitive to H₂ at room temperatures. The explanation for this can be given as the same as before but also because of the samples being less resistive than the sputtered samples. The same samples at higher temperatures (150 °C) showed good sensitivity and better response time than sputtered samples. We had tested 3 categories of samples of varied thicknesses to see the effect on thickness on sensitivity. The three samples fabricated were of thickness 3000, 6000, and 9000 Å.

When the three samples were analyzed we noticed that the 6000 and 9000 Å samples didn’t respond to H₂ even at higher temperatures, hence proving the fact stated in the literature that the surface area of the film are supposed to be as small as possible for better sensor results.

Another interesting fact noticed in this work was that samples didn’t respond well if the total flow rate was not maintained constant. The doped films showed high repeatability, and response of these samples when compared to the sputtered sample under the same conditions is relatively lower (i.e. less sensitivity). This as suggested in literature is because of the grain size having larger grain boundary surface areas.

The response was found to be linear to H₂ partial pressures introduced to the sample which was not the case in sputtered samples. The data showed a frequent case of noise level being greatly reduced as more and more runs were conducted on the same sample, leading us to believe that more runs tends to clean the sample of contaminants slowly.
Analysis was also conducted on the importance of purging cycles, and samples were continuously hiked in H$_2$ partial pressure at equal intervals without purging. The data obtained showed a very important feature noticed about the doped samples; the samples could sense continuous change in H$_2$ partial pressures proportional to the change in percentages either increasing or decreasing.

Effect of temperature on sample sensitivity was deeply studied in earlier sections of this thesis; analysis of effect of temperature was done at a wide range of temperatures 35, 75, 115 and 150 ºC. Analyses of the data obtained have been tabulated in table 1.

<table>
<thead>
<tr>
<th>Table 6.5.1 Responses at Various Temperatures.</th>
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<tr>
<td>Response at 35 ºC temperature</td>
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<tr>
<td>Response at 75 ºC temperature</td>
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<tr>
<td>Response at 115 ºC temperature</td>
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<tr>
<td>Response at 150 ºC temperature</td>
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Metal additives (Zn) were also deposited on the sample films but these samples showed no response whatsoever. The explanation for this insensitivity to metal additive to films can only be explained as; metal additives did not form clusters on the film as required, instead it formed a film coating on SnO$_2$. 
The study of effect of moisture on the films and testing of the samples in low pressures are some of the recommendations put forward, to complete this effort of study of SnO$_2$ for H$_2$ gas sensor applications.
References


