EFFECTS OF FILM THICKNESS ON THE SENSITIVITY OF TIN (IV) OXIDE GAS SENSOR IN DETECTING VARIOUS CONCENTRATIONS OF BENZENE AND TOLUENE GASES

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by
TEOH XUAN CHEE

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LIST OF SYMBOLS

Symbol	Description	Unit
a	Sensitivity coefficient	-
a_0	Pre-exponential constant	s^{-1}
C	Targeted gas concentration	ppm
C_S	Surrounding targeted gas concentration	ppm
D_k	Knudsen diffusion coefficient	$\mathrm{nm} \cdot \mathrm{g}/J^{0.5} \cdot K^{0.5}$
E_a	Apparent activation energy	kJ/mol
E_k	Activation energy	kJ/mol
k	Rate constant	s^{-1}
k_0	Pre-exponential constant	s^{-1}
L	Film thickness	nm
M	Molecular weight	g/mol
R	Gas constant	$J/mol \cdot K$
R_a	Electrical resistance in pure dry air	Ω
R_g	Electrical resistance in targeted gas	Ω
r	Film pore radius	nm
S	Sensitivity	-
T	Operating temperature	K
t	Time	s
x	Distance from sensing layer surface	nm
σ	Electrical conductance in targeted gas	Ω^{-1}
σ_0	Electrical conductance in pure dry air	Ω^{-1}

LIST OF ABBREVIATIONS

IDLH	Immediately dangerous to life and health limit
i.e.	id est (that is)
LEL	Lower explosion limit
LOD	Limit of detection
MATLAB	Matrix Laboratory (computation software)
MOS	Metal oxide semiconductor
ODE	Ordinary differential equation
PM	Particulate matter
ppm	Parts per million
RH	Relative humidity
SOA	Secondary organic aerosol
TCO	Temperature cycled operation
TSAPV	Total surface area per unit volume
UV	Ultraviolet
VOC	Volatile organic compound

KESAN KETEBALAN FILEM TERHADAP KEPEKAAN SENSOR GAS STANUM (IV) OKSIDA BAGI PENEGESANAN PELBAGAI KEPEKATAN GAS BENZENA DAN TOLUENA

ABSTRAK

Penderia gas stanum (IV) oksida (SnO_2) adalah penderia gas semikonduktor oksida logam yang paling biasa digunakan dalam pelbagai industri. Hal ini disebabkan oleh kestabilan dan kebolehpercayaannya yang tinggi. Sebagai tambahan kepada eksperimen, model matematik juga penting dalam mengkaji tindak balas penderia gas SnO_2 ketika terdedah kepada pelbagai keadaan operasi dan gas yang disasarkan. Dalam kajian ini, satu model matematik dibangunkan berdasarkan model penyerapan Knudsen yang biasanya digunakan untuk menggambarkan mekanisme penyebaran gas. Penyelidikan sebelumnya menunjukkan bahawa prestasi penginderaan SnO_2 dipengaruhi oleh beberapa faktor, seperti suhu operasi, kepekatan gas yang disasarkan, ketebalan filem dan radius liang filem. Selain itu, untuk menentukan kebolehpercayaan dan kejituan model matematik yang dibangunkan, simulasi MATLAB digunakan untuk mengkaji kesan kepekatan gas (benzena dan toluena) yang disasarkan (C_S) dan ketebalan filem (L) terhadap kepekaan SnO_2 penderia gas (S). Dari hasil yang diperoleh, kepekaan penderia gas akan meningkat dengan kepekatan gas sasaran sehingga had penjerapan maksimum tercapai. Di samping itu, hasilnya juga menunjukkan kepekaan penderia gas SnO_2 akan adalah lebih rendah ketika filem penginderaan yang lebih tebal digunakan. Kedua-dua keputusan ini mengesahkan bahawa model matematik yang dibangunkan sesuai dengan kesahan teori. Selain itu, penderia gas SnO_2 selalu memiliki kinerja penginderaan yang lebih baik terhadap toluena daripada benzena, yang disebabkan oleh kereaktifan toluena yang lebih tinggi dibandingkan dengan benzena.

EFFECTS OF FILM THICKNESS ON THE SENSITIVITY OF TIN (IV) OXIDE GAS SENSOR IN DETECTING VARIOUS CONCENTRATIONS OF BENZENE AND TOLUENE GASES

ABSTRACT

Tin (IV) oxide (SnO_2) gas sensor is the most commonly used metal oxide semiconductor gas sensor in various industries due to its high stability and reliability. In addition to the experimental works, mathematical models are also important in studying the responses os the SnO_2 gas sensor when it is exposed to a variety of operating conditions and targeted gases. In the present study, a mathematical model is developed based on Knudsen diffusion model which is commonly used to describe tha gas diffusion mechanism. Previous researches had shown that the sensing performance of SnO_2 gas sensor is influenced by some factors, such as operating temperature, targeted gas concentration, film thickness and pore radius of the sensing film. On top of this, in order to determine the reliability and feasibility of the develop mathematical model, MATLAB simulation is used to study the effects of targeted gas (benzene and toluene) concentration (C_S) and film thickness (L) on the sensitivity of the SnO_2 gas sensor (S). From the results obtained, the sensitivity of the gas sensor will increase with the targeted gas concentration until the maximum adsorption limit is reached. At the same time, the results showed a lower sensitivity when a thicker sensing film is used. Both of these results confirmed that the developed mathematical model matches the validity of the theory. Besides that, SnO_2 gas sensor always has a better sensing performance toward toluene than benzene, which is due to the higher reactivity of toluene as compared to benzene.

CHAPTER 1 INTRODUCTION

1.1 Background

1.1.1 Gas Sensors

The rapid development of industries in recent years gives humans a better living quality by providing us all the things we need. However, at the same time, the burning of fossil fuels in the factories has given a negative impact to the surrounding environment. The exhaust gases mostly consist of CO, CO_2, SO_2 and NO_x, which are the pollutants that lead to the air pollution, greenhouse effect as well as the climate change (Bi & Hansen, 2018; Yuliarto et al., 2015).

There are many methods that can be applied to minimize the impacts brought to the environment. One of the most feasible methods is the installation of gas sensors. A sensor is the device that detects the input stimulus and transduces it into an output, usually electrical signal (Hunter et al., 2020). Gas sensors are always being designed to detect the gases that might threaten our health and safety, for instance, flammable and toxic gases, or the oxygen concentration is a certain confined space (Yuan & Shi, 2013). When the targeted gas reaches a pre-set concentration, the gas sensor will give visible or audible signals to the users to alert them about the safety issue. Hence, a reliable gas sensor is vital for the safety of the working place, especially in chemical plants that always involve hazardous gases.

Gas sensors can be classified into several types based on their working principles, such as semiconductor-type, electrochemical-type, catalytic type, solid electrolyte-type, etc. Each of them is available in a variety of applications, where it depends on the sensing features (Nayyar et al., 2016). Some of the common applications include environmental science, medical field, automotive industry as well as the indoor and outdoor air quality monitoring. The performance of a gas sensor can be evaluated by several parameters, such as sensitivity, selectivity, accuracy, limit of detection (LOD), response time, recovery time and resolution. Besides that,

some of the key features affecting the industrial applications of a gas sensor include power consumption, cost efficiency, lifetime, miniaturization, etc (Nazemi et al., 2019). **Table 1.1** shows the advantages and disadvantages of different gas sensor types while **Table 1.2** shows performance of various types of gas sensors.

Table 1.1 Advantage and Disadvantages of Different Gas Sensor Types (Yunusa et al., 2014)

Gas Sensor	Advantages	Disadvantages
Semiconductor	● High mechanical strength ● Works well under constant high humidity	● Susceptible to environmental changes ● Susceptible to contaminants ● Non-linear response
Electrochemical	● High sensitivity ● Able to detect a wide range of gases	● Failure modes will only be revealed for advanced monitoring
Catalytic	● High simplicity ● High cost-efficiency	● Requires oxygen or air to work ● Can be poisoned by silicon, lead or chlorine
Thermal	● High mechanical strength ● High simplicity ● Wide measuring range	● High power consumption since detection involve the heating of wire
Infrared	● Only involve physical technique ● No unseen failure modes ● Able to operate in inert atmosphere	● Only applicable for gases that absorb infrared ● Slow monitoring process ● High user expertise required

Optical	• Able to operate in the absence of oxygen • Will not influenced by electromagnetic interference • Wide monitoring area	• Will be influenced by ambient light interference
Surface Acoustic Wave	• Feasible for wireless applications • Able to detect nerve and blister agent • Able to operate in harsh and rotating parts	• Difficult in handling and fabricating due to its small size

Table 1.2 Performance of Various Types of Gas Sensors (Mahajan & Jagtap, 2020)

Parameters	Gas Sensors				
	MOS	Optical	Catalytic	Thermoconductive	Electrochemical
Sensitivity	E	E	G	P	G
Stability	G	E	F	G	P
Selectivity	F	E	P	P	G
Response Time	E	F	G	G	F
Accuracy	G	E	G	G	G
Durability	G	E	G	G	P
Maintenance	E	F	E	G	G
Cost	E	F	E	G	G

* E = excellent, G = good, F = fair, P = poor

1.1.2 Metal Oxide Semiconductor Gas Sensor

Gas sensors can be made up of different construction materials, for instance, metal oxide semiconductors, conductive composites polymers, intrinsic conduction polymers, metal oxide/composite polymers, while there are many still many new materials under development for gas sensor construction in the future. Among these materials, metal oxide semiconductor (MOS) is considered as the material with the highest potential for gas sensor technology. This is due to its preferable properties, such as high sensitivity, short response and recovery time, high simplicity, low production and maintenance cost, etc (Yuliarto et al., 2015). Some examples of the MOS include SnO_2, TiO_2, ZnO, WO_3, etc (Mahajan & Jagtap, 2020).

1.1.2(a) Working Principles

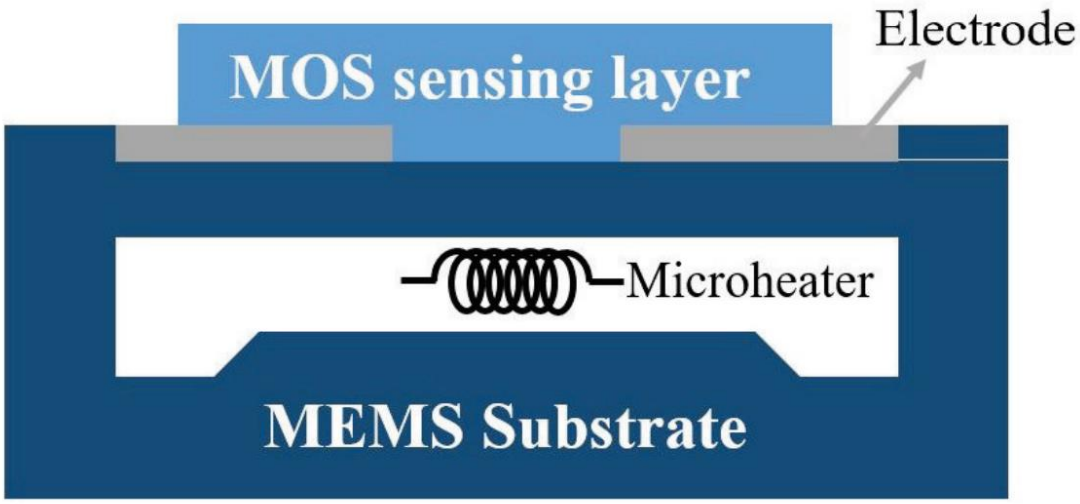


Figure 1.1 Schematic Diagram of MOS Gas Sensor (Nazemi et al., 2019)

MOS can be divided into two types, n-type (electrons as majority carrier) and p-type (holes as majority carrier). SnO_2, TiO_2 and ZnO are the examples of n-type MOS while NiO and Mn_3O_4 are p-type MOS. Both of these types operate based on the change in the

conductivity of the MOS sensing component in the gas sensor (Nazemi et al., 2019). An electric current flowing through the MOS sensing layer is set up (refer **Figure 1.1**). The heater in the MOS gas sensor will first heat up the MOS sensing layer to promote the adsorption of the oxygen in the air onto the layer. The adsorbed oxygen will bind with the electrons in the conduction band of the MOS, which leads to a reduction in the conductivity as well as an increase in the resistance of the MOS sensing layer (Nazemi et al., 2019).

For a n-type MOS gas sensor, when there is the presence of reducing gas, the oxygen adsorbed will bind with the gas and leaves the MOS sensing layer, therefore the resistance will decrease. However, when the sensor is in contact with oxidizing gas, more oxygen will bind to the sensing layer, causing a higher resistance. On the other hand, unlike n-type MOS, p-type MOS has positive holes, rather than negative electrons, as its majority charge carrier. Therefore, when it interacts with reducing gases, its resistance will rise due to its positivity decreases while its resistance will increase when come across with an oxidizing gas. These changes in resistance in both n-type and p-type MOS gas sensors reflect the concentration of the targeted gases. The greater the change is, the higher the concentration of the targeted gas (Nazemi et al., 2019). On top of this, a n-type MOS gas sensor is more suitable for reducing gas detection while p-type is more suitable for oxidizing gas detection (Yunusa et al., 2014). The increase in electrical conductivity will result in a strong optical or audible signal that is able to alert the users.

1.1.2(b) Applications

MOS gas sensor was first being utilized as a safety device in the industries. It played an important role in hydrogen gas (H_2) detection when the world was transforming into a carbon-low, hydrogen-inclusive energy economy. Today, MOS gas sensors are used for

environmental monitoring purposes. It is used to detect the concentration of some common air pollutants that might cause environmental or health effects, such as NO_2, ozone, CO and volatile organic compounds (VOCs). However, the output signal of the MOS gas sensor will be affected by the interfering gas (Peterson et al., 2017). It is found that the selectivity of the MOS gas sensor is lower in the practical application for VOCs detection as compared to ideal laboratory case without background VOCs (Nazemi et al., 2019).

Some studies are done in order to improve the weaknesses of the MOS gas sensors. For instance, temperature cycled operation (TCO) is designed to increase the selectivity and sensitivity of the MOS gas sensor in the detection of VOCs, where the heater in the sensor is set to change the temperature periodically. By doing this, the sensor response to the targeted analyte in a complex environment can be correlated due to the addition of identifying parameters (Nazemi et al., 2019). In the TCO mode, the MOS gas sensor is able to detect ppb-level of VOCs, such as 20 ppb of naphthalene and 100 ppb of formaldehyde (Bur et al., 2014). Another limitation of MOS gas sensors is the requirement of high temperature, usually 150 ℃ to 400 ℃. This leads to a higher power consumption and makes it not suitable to be installed in portable electronic appliances. In order to improve this limitation, a porous sensing layer is being explored. This porous MOS sensing layer can be manufactured through the soft-templating method as well as nano-casting strategy. The porous structure with a greater surface area will promote the gas diffusion, which enhances the interaction between the MOS sensing layer and the targeted analytes. This can increase the sensitivity and selectivity while reducing the response and recovery time of the sensor (Nazemi et al., 2019).

1.1.3 Volatile Organic Compounds (VOCs)

Volatile organic compounds (VOCs) are organic compounds (up to C20) that consists of a low molecular weight as well as low boiling point, which causes them to evaporate easily under room conditions. VOCs can be emitted naturally by plants, animals and microorganisms while they can also be discharged into the atmosphere by the human activities such as the fuel combustion, industrial discharge, using of paints and aerosol, etc. (Anand et al., 2014; Bedia et al., 2018; Cheng et al., 2019; Said Ismail & Hameed, 2013). Examples of VOCs are benzene, toluene, hexane and cyclohexane (Çankaya et al., 2020).

1.1.3(a) Environmental Impacts

One of the most common environmental impacts caused by the VOCs is photochemical smog. Under the action of the ultraviolet (UV) light, the VOCs will form secondary organic aerosol (SOA), which is the major source of $PM_{2.5}$ (30-77%) in the atmosphere by reacting with ozone, OH radicals and nitrogen oxides (NO_x) (Cheng et al., 2019; Li et al., 2020). In this process, VOCs will lead to the ozone depletion, which causes the global greenhouse effects indirectly (Li et al., 2020).

Studies showed that VOCs are one of the major reasons for tropospheric ozone generation. With the presence of solar radiation, VOCs will react with NO_x and carbon monoxide to form tropospheric ozone. Aromatics and alkenes are reported as the main contributors to the tropospheric ozone generation (Li et al., 2020). Exposure to both photochemical smog and tropospheric ozone will cause eye irritation as well as respiratory effects (Louis, 1967).

1.1.3(b) Health Effects

VOCs generally have a higher concentration in an indoor environment as compared to outdoor. Homes, offices, restaurants, supermarkets are some of the common indoor microenvironments which impacted by various VOCs. This brings huge concerns because some of them are carcinogenic and teratogenic (Çankaya et al., 2020). Reports showed that exposure to the VOCs may cause skin and eye irritation, central nervous system effects as well as liver and kidney effects (Anand et al., 2014). VOCs emissions is also reported to be strongly correlated with some severe diseases of endocrine system, skin cancer and brain cancer. Life-long exposure to low level of VOCs may also lead to a high risk of suffering from asthma and rhinitis (Cheng et al., 2019).

Benzene, one of the most common VOCs, will bring hazardous health effects to human under exposure. It will bring hematologic cancers as well as functional aberration of nervous, respiratory, immune, cardiovascular and reproductive systems. In term of immune system, exposure to benzene may reduce our body immunity since the B-cell and T-cell proliferation are being affected. Benzene exposure in children may also lead to the abnormalities in hematologic, respiratory and pulmonary functions. The particular children may face a number decrease in the red blood cell, white blood cell, lymphocytes, platelets and other blood components (D'Andrea & Reddy, 2018).

Toluene is another aromatic VOC detected high level in indoor air. Individuals may expose to the toluene during their daily-life activities or in a workspace such as factories, refineries and etc. The safe exposure limit of toluene is within 10 to 100 ppm while the immediately dangerous to life and health limit (IDLH) is at approximately 500 ppm (L.Cruz et al., 2014). Toluene can cause severe effects on the nervous system which may lead to a problem of balance, vision, hearing as well as speech ability. Some of the examples of chronic effects

include cognitive impairment, ventricular enlargement as well as loss of muscle strength (L.Cruz et al., 2014; Mirzaei et al., 2018).

1.2 Problem Statement

Benzene and toluene have become the widely used industrial VOCs in the recent years. A long-term exposure to these gases may cause the accumulation of toxic in the phospholipid bilayer of our cell membrane. Benzene gas brings genotoxic and carcinogenic effects while the toluene gas is highly neutrotoxicity (Pariselli et al., 2009). MOS gas sensors with a great potential in gas sensing technology have been placed with a high hope to improve the global air quality. Tin (IV) oxide, SnO_2 gas sensor is considered as the best-understood MOS gas sensor due to its high selectivity (Barsan & Weimar, 2001). SnO_2 is a n-type MOS which has a wide band gap (Yuliarto et al., 2015), which is a high-potential gas sensor to be used in the detecting the presence and concentration of benzene and tluene gases in the surrounding atmosphere. There are many studies have been done on the SnO_2 gas sensor, however, a mathematical diffusion model that is feasible and reliable to be applied in studying the sensing performance of SnO_2 gas sensor toward benzene and toulene gases is yet to be developed. This will be an obstacle to be overcome in order to improve the quality of the surrounding air, especially around the industrial area.

The performance of a gas sensor can be evaluated based on three main parameters, sensitivity, selectivity as well as the response and recovery time (Mirzaei et al., 2019). According to Sakai et al. (2001), these performance parameters are affected by the operating temperature, concentration of analytes and the film thickness. In this present study, a mathematical diffusion model is developed to investigate the effect of film thickness and concentration of the targeted gases on the sensitivity of the SnO_2 gas sensor when benzene and toluene gases are exposed to it. It is hoped that this model can be used to optimize the performance of SnO_2 gas sensors in the future.

1.3 Objectives

This present study is to achieve the following objectives:

i. To develop a mathematical gas diffusion model for the sensing of benzene and toluene gases through SnO_2 gas sensors by using MATLAB.

ii. To study the relationship between the film thickness and the sensitivity of the SnO_2 gas sensor when being exposed to the benzene and toluene gases through the developed gas diffusion model.

iii. To study the relationship between the concentration of the targeted gases (benzene and toluene) and the sensitivity of the mesoporous SnO_2 gas sensor through the developed gas diffusion model.

CHAPTER 2 LITERATURE REVIEW

Among all the MOS, tin (IV) oxide (SnO_2) has become the most widely investigated material for MOS gas sensors. SnO_2 are chosen as the material for MOS gas sensors due to their parameter stability and reliability which contribute to a low failure rate. The high corrosive resistivity and good mechanical strength of SnO_2 also gives it a long operating life that requires only little maintenance (Velmathi et al., 2016). Besides that, its wide range of gas sensibility enables it to detect almost all the common target gaseous in various applications (Velmathi et al., 2016). **Table 2.1** shows the comparison of sensing behaviour toward some common target gaseous between different types of common MOS gas sensor.

Table 2.1 Sensing Behaviour of The Various Types of MOS Gas Sensor (Velmathi et al., 2016)

Target Gas	**MOS Gas Sensor**				
	Fe	**Ni**	**Sn**	**Ti**	**Zn**
Automobile Exhaust Gases			X		
Carbon Dioxide	X	X	X	X	X
Carbon Monoxide	X	X	X	X	X
Ethanol	X		X	X	X
Hydrogen Gas	X	X	X	X	X
Methane	X	X	X	X	X
Methanol			X	X	
Nitrogen Oxide (NO, NO_2, NO_3)	X	X	X	X	X
Smoke			X		
Sulphur Dioxide		X	X		

(X denotes the target gas is detectable by using the MOS gas sensor)

However, this sensing behaviour of SnO_2 toward a wide range of gaseous is a double-edged sword for SnO_2 gas sensors. It increases the applications of SnO_2 gas sensors, but at the same time, the cross-talk problem arises when there is a presence of more than one detectable gaseous. The low selectivity of SnO_2 also brings it the possibility of being influenced by ambient humidity (Velmathi et al., 2016).

The improvement in sensing properties of SnO_2 has become one of the most desirable demands to be fulfilled to ensure the gas sensor can operate under a more complicated environment. The sensing properties of SnO_2 relies on the reactivity of the sensor surface towards the molecules of the target gas. This can be improved by modifying the geometry and/or electronic structure of the sensor surface (Chen et al., 2018).

2.1 Gas Sensing Mechanism of SnO_2 Gas Sensor

The SnO_2 gas sensor is a n-type MOS gas sensor that senses target gas based on the change in conductivity. When the target gas is absent, the oxygen molecules are adsorbed on the surface of SnO_2 when it is being heated in air. The electrons of SnO_2 will be extracted from its conduction band and trapped by the O_2 molecules, causing an upward bending of the band, which reduces the conductivity (Wang et al., 2010). The oxygen molecules will form oxygen ions, O_2^-, O^- and O^{2-} after absorbing electrons from the SnO_2. This can be described by the following equations (Yuliarto et al., 2015):

$$O_2 + e^- \rightarrow O_2^- \quad (2\text{-}1)$$

$$O_2^- + e^- \rightarrow 2O^- \quad (2\text{-}2)$$

$$O^- + e^- \rightarrow O^{2-} \quad (2\text{-}3)$$

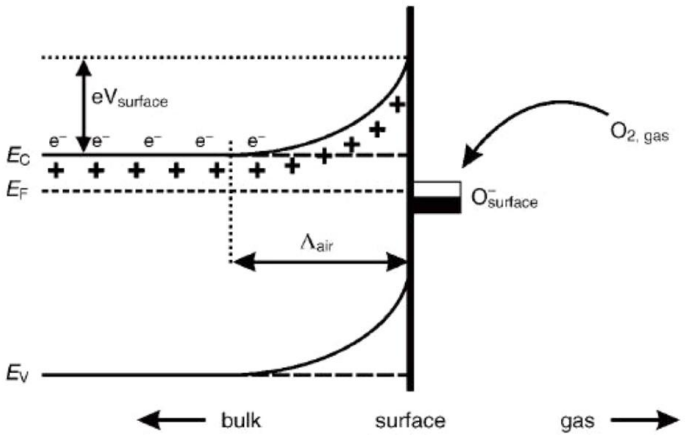


Figure 2.1 Band Bending After the Adsorption of Oxygen Molecules (Wang et al., 2010)

The O_2^-, O^- and O^{2-} are stable at temperatures of below 100 °C, within 100 and 300 °C and above 300 °C respectively while they will desorb from the sensor surface at 80, 130 and 250 °C respectively (Wetchakun et al., 2011).

The target gaseous can be classified as oxidizing or reducing gaseous. Oxidizing gases include NO_2, NO and CO while CO, CH_4 and SO_2 are examples for reducing gases. When the sensor is exposed to an oxidizing gas, the oxidizing gas will react with the oxygen ions to form a stable gas (i.e. N_2 or CO) and adsorbed onto the sensor surface (Wetchakun et al., 2011). The general equation of this reaction is as shown in **Equation(2-4)** and **Equation (2-5)**, where *A* denotes an oxidizing gas (Yuliarto et al., 2015).

$$A_x(gas) + e^- \rightarrow A^{x-}(adsorbed) \quad (2\text{-}4)$$

$$A^{x-}(adsorbed) + O^- + xe^- \rightarrow stable\ gas + xO^{2-} \quad (2\text{-}5)$$

This causes a drop in the electron concentration on the SnO_2 surface, which increases the resistance while reducing the conductivity. This change in resistance contributes to a sensing response for SnO_2 gas sensor, which can be expressed as (Wetchakun et al., 2011):

$$S_{ox}^{SnO_2} = \frac{R_{og}}{R_a} \quad (2\text{-}6)$$

where $S_{ox}^{SnO_2}$ = sensing response for SnO_2 gas sensor to oxidizing gas

R_{og} = electrical resistance in the presence of oxidizing gas

R_a = electrical resistance in pure dry air

On the other hand, when the gas sensor is exposed to reducing gases, the gas will react with the adsorbed oxygen ions to form stable gas (i.e. N_2 or H_2O). In this reaction, the reducing gas will release electrons to SnO_2, which increases the electron concentration and enhances the conductivity of the sensor while reducing its resistivity. **Equation (2-7)** and **Equation (2-8)** show the general equation for this reaction while **Equation (2-9)** shows the relationship between sensing response for SnO_2 gas sensor and the electrical resistance with and without the presence of the reducing gas (Wetchakun et al., 2011; Yuliarto et al., 2015).

$$B(gas) + yO^-(adsorbed) \rightarrow stable\ gas + ye^- \quad (2\text{-}7)$$

or

$$B(gas) + yO^{2-}(adsorbed) \rightarrow stable\ gas + 2ye^- \quad (2\text{-}8)$$

$$S_{rd}^{SnO_2} = \frac{R_a}{R_{rg}} \quad (2\text{-}9)$$

where $S_{rd}^{SnO_2}$ = sensing response for SnO_2 gas sensor to oxidizing gas

R_a = electrical resistance in pure dry air

R_{rg} = electrical resistance in the presence of reducing gas

The presence of either oxidizing or reducing gas will alter the band bending extent. The oxidizing gas will increase the bending while the reducing gas will decrease or reverse the band bending (Wang et al., 2010).

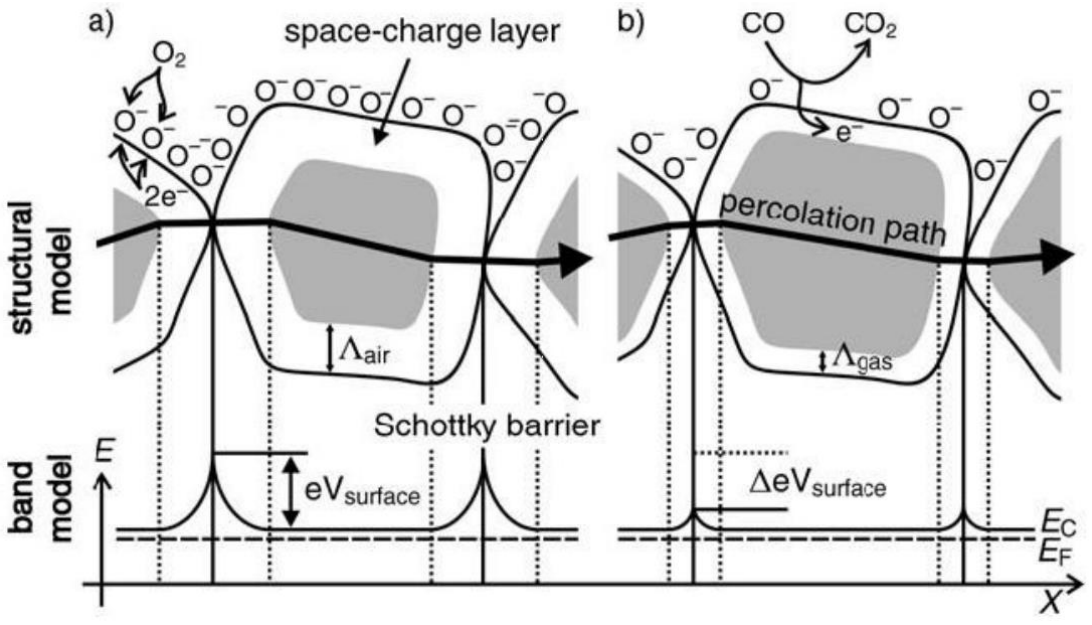


Figure 2.2 Band Models of Conductive Mechanism of SnO_2 Gas Sensor under the conditions of (a) Absence and (b) Presence of a Reference Gas (Wang et al., 2010)

2.2 Effect of Temperature on Sensitivity of SnO_2 Gas Sensor

Effects of temperature on sensitivity of SnO_2 gas sensor has been studied by many researchers to understand the sensing performance of SnO_2 gas sensor under a variety of temperature. **Figure 2.3** shows a graph illustrating the relationship between operating temperature and sensitivity of SnO_2 gas sensor when it is exposed to a 800 ppm of H_2 gas. We can see that the optimum operating temperature for the SnO_2 gas sensor is approximate 350 ºC, which drops within the general operating temperature range for metal oxide gas sensor (25 – 500 ºC) (Mirzaei et al., 2019).

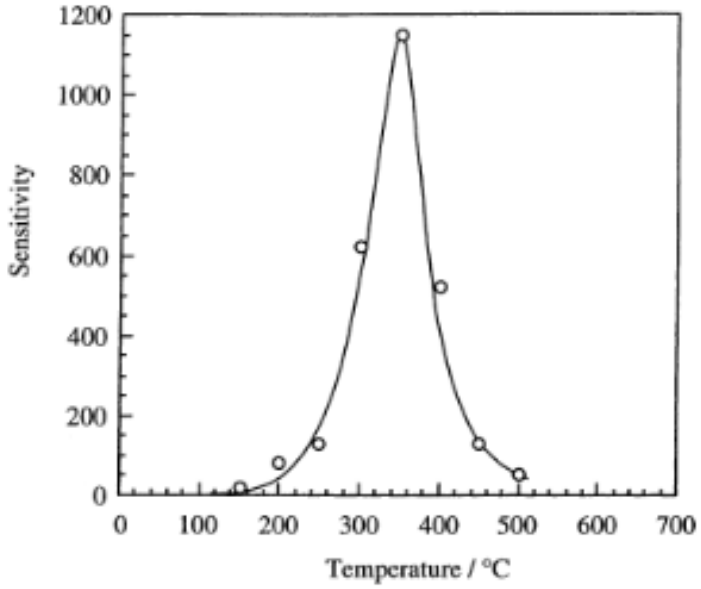


Figure 2.3 Graph of SnO_2 Gas Sensor Sensitivity vs Operating Temperature (Sakai et al., 2001)

Operating temperature brings a huge effect to gas sensor sensitivity because both of the gas diffusion and reaction of targeted gas with the sensing layer are temperature-dependent. From 100 to 350 ºC, the sensitivity of SnO_2 gas sensor increases with increasing temperature. When temperature increases, the amount of H_2 gas adsorbed onto the sensing film increases, this is due to the rate of gas molecules diffusion increases with the temperature. At optimum temperature, the rate of adsorption and desorption of the gas molecules reach equilibrium,

contributing to the highest number of gas molecules adsorbed and hance, the highest sensitivity achieved (Chen et al., 2018; Mirzaei et al., 2019).

Once the temperature is further increased beyond the optimum temperature, the equilibrium achieved is interrupted (Mirzaei et al., 2019). After the optimum temperature, the desorption is more favorable since adsorption is an exothermic reaction. Hence, the gas molecules adsorbed on the sensing layer decreases and causes a drop in the sensitivity of SnO_2 gas sensor (Chen et al., 2018).

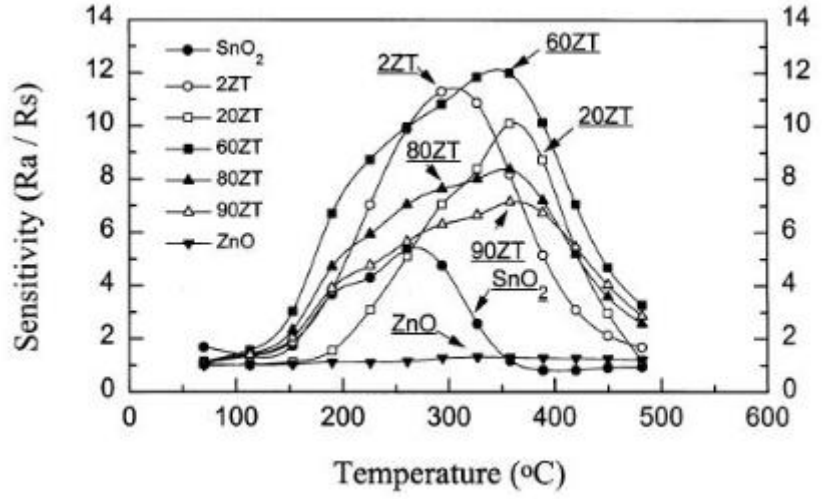


Figure 2.4 Graph of Sensitivity vs Temperature for Different Gas Sensor in Detecting Carbon Monoxide Gas (Wang et al., 2010)

A similar sensitivity curve (**Figure 2.4**) is obtained in a study done by Wang et al. in 2010. The graph shows the effects of temperature on different gas sensors when they are exposed to 200 ppm of carbon monoxide gas. By comparing **Figure 2.3** and **Figure 2.4**, we can conclude that the relationship between temperature and gas sensor sensitivity can be applied to various gas sensors. Besides that, we also can say that when SnO_2 gas sensors show different sensitivity toward different targeted gas. This is due to different sensitivity coefficient possessed by different targeted gases, which can be explained by **Equation (2-17)** in **Section 2.6**.

2.3 Effect of Film Thickness on Sensitivity of SnO_2 Gas Sensor

The understanding of the influence of the film thickness of SnO_2 gas sensors on its gas sensing properties is essential. However, there are not many studies to find out the relationship between the sensing properties and the film thickness, instead, most of the researchers have studied the sensing properties of the gas sensor with a fixed thickness. Furthermore, there are some disagreements among the studies done. Some of the reports show that the sensitivity of the gas sensor will increase with the film thickness while some found an opposite result. These disagreements infer that a deeper understanding on the effect of film thickness on SnO_2 gas sensors is necessary (Korotcenkov & Cho, 2009).

According to Masaaki et al. (1994), the sensitivity of SnO_2 gas sensor decreases when the film thickness increases. A 5 – 10 nm film has very high sensitivity, where its sensitivity can reach about 100 for 2000 ppm 2-methyl-2-butene as well as more than 1000 for 10^4ppm hydrogen, and the sensitivity drops drastically when the film thickness increases. Since both hydrogen and 2-methyl-2-butene gas are reducing gas, the sensitivity of SnO_2 gas sensors can be expressed as **Equation (2-9)**. This is also proven by the study. **Figure 2.5** shows the resistivity of SnO_2 film with different thickness.

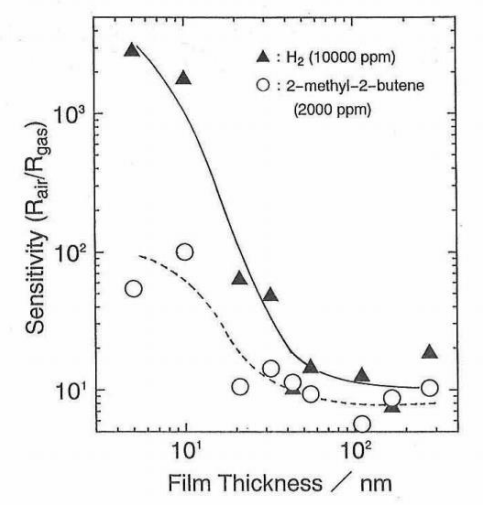


Figure 2.5 Graph of SnO_2 Sensitivity vs Film Thickness (Masaaki Kanamori, Yoshiki Okamoto, 1994)

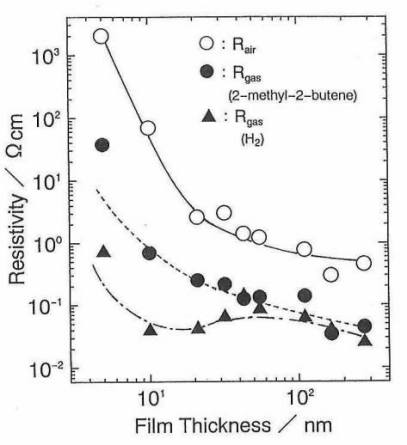
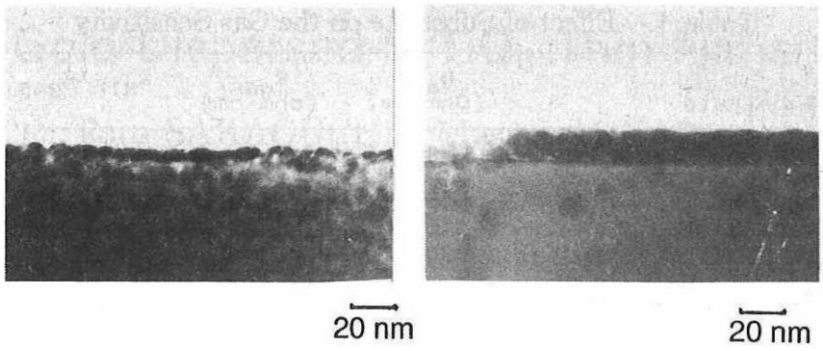


Figure 2.6 Graph of SnO_2 Resistivity vs Film Thickness (Masaaki Kanamori, Yoshiki Okamoto, 1994)

From **Figure 2.6**, we can see that the electrical resistance in pure air (R_a) has a higher film thickness dependency as compared to electrical resistance in the presence of target gas (R_{rg}) (Masaaki Kanamori, Yoshiki Okamoto, 1994). Since the R_a drops significantly when the thickness increases, according to **Equation (2-9)**, the sensitivity of SnO_2 will reduce accordingly, which suits the results in this study. The study also found that the crystallite size of SnO_2 film will decrease with the thickness (Masaaki Kanamori, Yoshiki Okamoto, 1994). A smaller SnO_2 crystal gives a larger total surface area per unit volume (TSAPV) for the oxygen adsorption, hence results in a higher value of R_a.



(a) (b)

Figure 2.7 TEM Images of the Cross-Sectional View of SnO_2 Film with thickness of (a) 5 nm and (b) 14 nm (Masaaki Kanamori, Yoshiki Okamoto, 1994)

There was another research done by Hossein-babaei and Orvatinia (2003) that shows the sensitivity of SnO_2 gas sensors is dependent on the film thickness. The sensing performance of SnO_2 gas sensors with various film thickness is assessed by exposing them in 2000 ppm acetone contamination. **Figure 2.8** shows the results obtained from the study, where the sensitivity of the gas sensor decreases exponentially when the film thickness increases. This can be explained by the fact that a thinner film possesses a greater TSAPV. From the graph, a higher sensitivity is expected by further reducing the film thickness, however, the attempt to deposit a thinner film by the research team was unsuccessful due to the low stability of the thinner film. This implies that the sensitivity of the SnO_2 gas sensor is practically limited by the electrical conduction instabilities of the thin film.

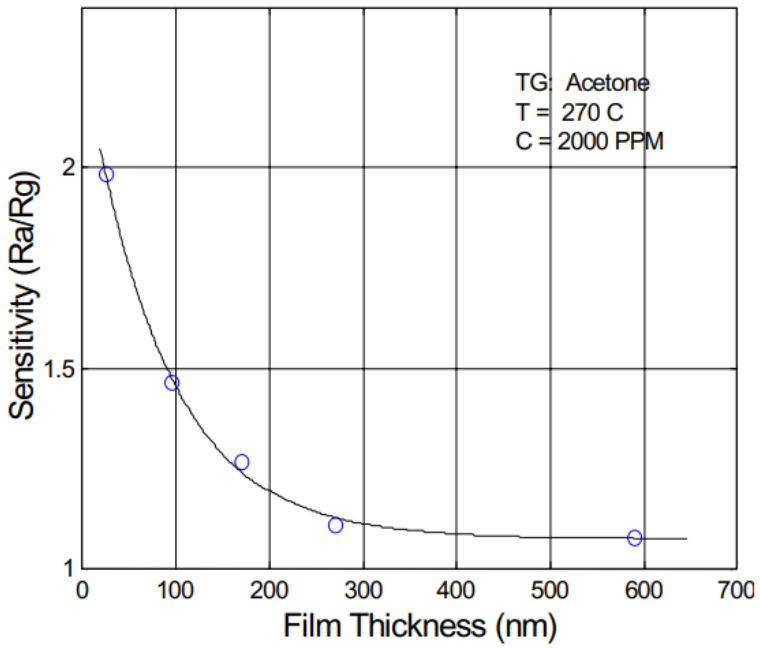


Figure 2.8 Relationship between Sensitivity of SnO_2 Gas Sensor and Film Thickness (Hossein-babaei & Orvatinia, 2003)

From **Figure 2.8** we also can see that when the film thickness is greater than 300 nm, the sensitivity of the gas sensor experiences negligible reduction even though the thickness is further increased. This is due to the high stability of the thick film. Therefore, the selection of

film thickness will be a trade-off between the sensitivity from one side as well as the stability, reproducibility and reliability from the other side (Hossein-babaei & Orvatinia, 2003).

Experiment by Korotcenkov et al. (2009) obtained a different result from both of the previous studies. The researchers found that the increase in the film thickness of the SnO_2 gas sensor will result in a reduction in the sensitivity toward ozone (oxidizing gas) but an improvement in the sensitivity toward hydrogen gas (reducing gas). According to the authors, this implies that a "thick film" gas sensor has a higher sensitivity toward reducing gas while the "thin film" gas sensor shows a higher sensitivity toward oxidizing gas. Furthermore, the presence of humidity in both cases give an opposite result too. The presence of water vapor will increase the sensitivity of the gas sensor toward ozone while decreasing that for hydrogen gas. The results are as shown in **Figure 2.9**.

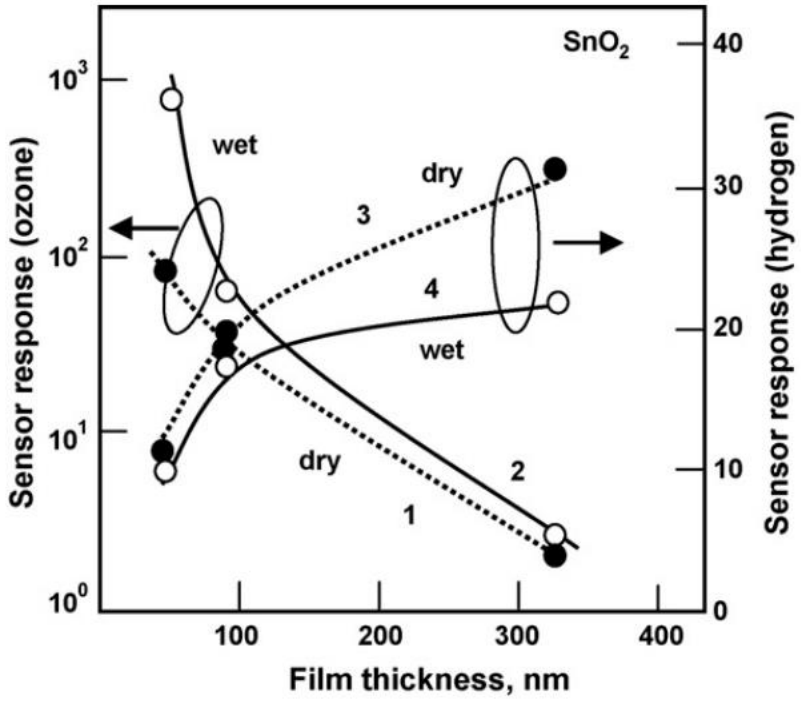


Figure 2.9 Sensitivity of SnO_2 Gas Sensor toward Different Gaseous at Different Film Thickness (Korotcenkov & Cho, 2009)

This result deviates from the conclusion made in both of the reports stated previously, which is the grain size must be minimized in order to get a maximum sensitivity. This conclusion only suits the condition when an oxidizing gas is exposed to the gas sensor in this experiment. Thus, the authors made a conclusion that stated that the grain size (or film thickness) is critical in determining the sensitivity of a SnO_2 gas sensor, however, it is not always a determinant (Korotcenkov & Cho, 2009).

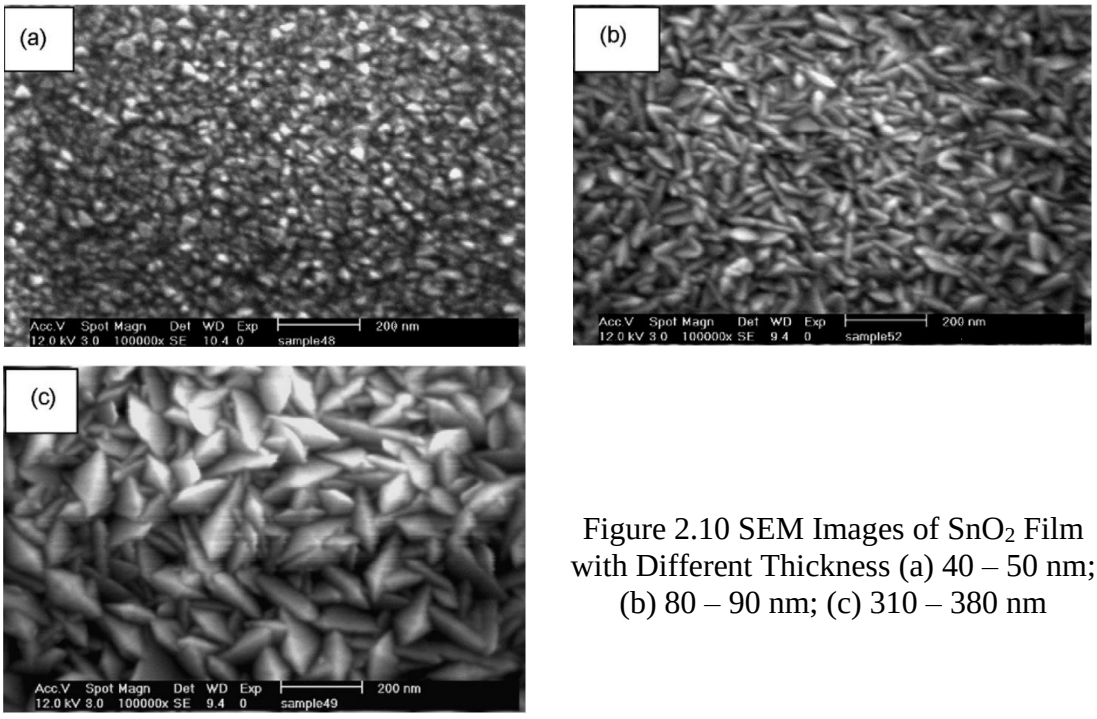


Figure 2.10 SEM Images of SnO_2 Film with Different Thickness (a) 40 – 50 nm; (b) 80 – 90 nm; (c) 310 – 380 nm

2.4 Effect of Target Gas Concentration on Sensitivity of SnO_2 Gas Sensor

The target gas concentration is another parameter that affects the sensitivity of the SnO_2 gas sensor. However, unlike the film thickness, the effect of gas concentration on the gas sensor sensitivity does not come along with any disagreement. It is well accepted that the sensitivity of the gas sensor will increase with the gas concentration until it reaches its maximum sensitivity.

An experiment by Basu et al. (2013) has studied the effect of ethanol concentration on the SnO_2 gas sensor sensitivity. The results obtained demonstrated that the increase in ethanol concentration (target gaseous) will increase the gas sensor sensitivity, no matter the gas sensor is operating under what temperature. A higher ethanol concentration allows more ethanol molecules to be absorbed onto the SnO_2 surface per unit time, and contributes to a higher electron transport kinetics. Hence, this enhances the gas sensor sensitivity.

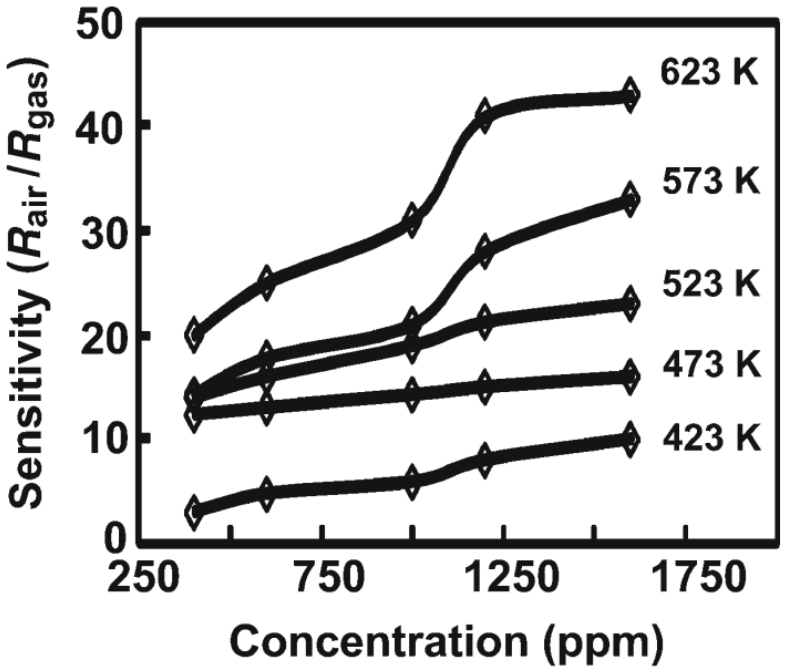


Figure 2.11 Effect of Ethanol Concentration and Temperature on SnO_2 Gas Sensor Sensitivity (Basu et al., 2013)

However, at an ethanol concentration of 1250 ppm, the curves are almost flattened. This shows that the maximum sensitivity of the gas sensor is achieved. At this point, the oxygen ions on the SnO_2 surface are insufficient to react with all the ethanol molecules, hence the sensitivity can no longer be improved to a higher value (Basu et al., 2013).

Similar results are obtained in the experiment done by (Hossein-babaei & Orvatinia, 2003). In this experiment, the sensitivity of a SnO_2 gas sensor is evaluated in different acetone