MODELLING OF GAS DIFFUSION IN MESOPOROUS TIN OXIDE (SnO_2) BASED GAS SENSOR: EFFECT OF OPERATING TEMPERATURES AND GAS CONCENTRATION

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UINVERSITI SAINS MALAYSIA

2021

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by

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Project report submitted in partial fulfilment of the requirement for the degree of

Bachelor of Chemical Engineering

2021

ACKNOWLEDGEMENT

First, I would like to express my gratitude to Allah, because Allah is the only one that gives me health and strength throughout completing my final year project. After that, I would like to thank my supervisor, Associate Professor Dr. Mohamad Zailani bin Abu Bakar who had given supportive guidance in this study.

I also thank all the School of Chemical Engineering, Universiti Sains Malaysia (USM) staff for their support and assistance throughout this study. Their guidance and helps were crucial to making this study easier to be completed.

Besides, I would like to thank my family for their financial support, love, and helps throughout my study. Lastly, thanks to all my friends and postgraduate student, Erfan Hakim bin Azmal Zaid who gave me advice and guidance in this research.

Muhammad Hafizuddin bin Arshad

June 2021

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LIST OF SYMBOLS

Symbol	Description	Unit
a	Sensitivity coefficient	-
a_0	Pre-exponential constant	ppm^{-1}
C_A	Gas concentration inside the film	ppm
$C_{A,S}$	Gas concentration outside the film	ppm
D_k	Knudsen diffusion constant	m^2/s
E_a	Reaction activation energy; gas-dependent	kJ/mol
E_k	Reaction activation energy; temperature dependent	kJ/mol
k	Arrhenius Equation constant	-
k_0	Pre-exponential constant	s^{-1}
L	Film thickness	nm
M	Molecular weight of diffusing gas	g/mol
r	Pore radius	nm
R	Gas constant	J/mol.K
S	Sensitivity of sensor	-
T	Operating temperature of the sensor	˚C, K

LIST OF ABBREVIATIONS

Ag	Silver
Au	Gold
H_2	Hydrogen gas
H_2S	Hydrogen Sulfide
NO_2	Nitrogen dioxide
SMO	Semiconductor Metal Oxide
SnO_2	Tin oxide
WO_3	Tungsten trioxide

PERMODELAN RESAPAN GAS DALAM PENDERIA GAS BERASASKAN TIMAH OKSIDA (SnO_2) BERLIANG MESO: KESAN TERHADAP SUHU OPERASI DAN KEPEKATAN GAS

ABSTRAK

Kepekaan penderia gas timah oksida berliang meso telah dikaji secara teori berdasarkan dengan fenomena penyerapan gas. Model – model penyerapan yang asal dan diubahsuai telah dibangunkan dengan menganggap bahawa gas sasaran yang merupakan gas yang mudah terbakar mengalir ke dalam filem didorong oleh penyerapan Knudsen dan bertindak balas dengan spesies oksigen yang dijerap melalui reaksi kinetik bilangan pertama. Berdasarkan teori, kepekaan penderia gas menunjukkan lekukan berbentuk loceng berbanding suhu operasi Manakala kepekaan meningkat dengan peningkatan kepekatan gas dan seterusnya mencapai tahap tepu. Walau bagaimana pun, model penyerapan yang asal tidak dapat meramalkan kedua-dua hubungkait. Pengubahsuaian model persamaan penyerapan yang lama telah dilakukan di mana variasi konduktor filem terhadap kepekatan gas hidrogen didapati berkaitan dengan hukum kuasa. Hasil pengubahsuaian model tersebut, lengkung berbentuk loceng telah dihasilan di mana ianya bersamaan dengan keputusan ujikaji. Tambahan pulak, kesan perak, (Ag) dan emas, (Au) terhadap filem penderia gas SnO_2 juga disimulasikan dalam kajian ini. Hasil simulasi dalam mengesan gas 1-butanol menunjukkan bahawa untuk kedua-dua filem pengesan Ag/SnO_2 dan Au/SnO_2 didapati dapat menurunkan suhu operasi optimum sebanyak 150℃ dan menghasilkan tahap kepekaan yang lebih tinggi berbanding dengan SnO_2 tulen. Akhir sekali, kesan kesan jejari liang, (r) dan ketebalan filem, (L) terhadap kepekaan juga telah disimulasikan dalam mengesan gas hidrogen. Hasil simulasi untuk radius liang menunjukkan bahawa kepekaan meningkat apabila radius liang meningkat pada suhu tetap, yang

berhubungkait dengan persamaan Knudsen, D_k. Untuk ketebalan filem, hasilnya menunjukkan bahawa kepekaan meningkat apabila ketebalan filem berkurang kerana hubungan yang lebih kuat antara gas sasaran dan permukaan penderia.

MODELLING OF GAS DIFFUSION IN MESOPOROUS TIN OXIDE (SnO_2) BASED GAS SENSOR: EFFECT OF OPERATING TEMPERATURES AND CONCENTRATION

ABSTRACT

The sensitivity of a mesoporous tin oxide gas sensor has been theoretically investigated in relation to gas diffusion phenomena. Diffusion models that comprises original and modified diffusion models were created by using MATLAB with the assumption that the target gas which is the inflammable gas flows inside the film is driven by Knudsen diffusion and react with adsorbed oxygen species via a first-order kinetic reaction. Theoretically, the sensitivity of the gas sensor depicts a bell-curved with the variations of operating temperatures. Whilst, the sensitivity increases with the gas concentrations and subsequently became saturated. However, the original diffusion model unable to predict both trends. The modification of the former equation of diffusion model was carried out in which the film conductance variation against hydrogen gas concentration is found to coincide with the power law. With this modification, a bell shaped was obtained which is in a closed agreement with the experimental result. In additions, the effect of silver, Ag and gold, Au modification of film in SnO_2 gas sensor was also simulated. The simulated result in detecting 1-butanol gas shows that the optimum operating temperature was reduced by 150°C for both Ag/SnO_2 and Au/SnO_2 with higher sensitivity as compared to pure SnO_2. Finally, the effect of pore radius, r and film thickness, L on the sensitivity was also simulated in detecting hydrogen gas. The simulated result for the pore radius shows that the sensitivity increases as pore radius increase at the fixed temperature, which is correlate with the Knudsen equation, D_k. For film thickness, the result shows that the sensitivity increases as the thickness of the film decreases due to a stronger contact between the target gas and the sensor's surface.

CHAPTER 1: INTRODUCTION

In this study, the gas diffusion model is developed to investigate the effects of the operating temperatures and harmful gas concentrations on the sensitivity of a gas sensor. Appropriate equations based on the theory of the gas diffusion process that represent the diffusion characteristics of the mesoporous SnO_2 based gas sensor have been compiled and solved by using MATLAB.

1.1. Background

Semiconductor based gas sensors have been extensively used in domestic and industrial environments to detect flammable as well as toxic gases (Anukunprasert et al., 2005). With advantages such as a wide variety of applications, inexpensive, reliable, compact, and low-power consumption, semiconductor-based gas sensors have created huge demand from industry players. As demand for improved gas sensors is growing, rigorous efforts are being made to find the most suitable material with the necessary surface and bulk properties (Eranna et al., 2004). Semiconductor metal oxide (SMO) gas sensor is the most researched category of gas sensors, and because of its size-dependent properties where the sizes ranging from 1 nm to 100 nm are increasingly used for gas sensing (Barsan et al., 2007).

Based on various sensing materials and methods, several types of gas sensors have been designed over the past decades. There are many gas types which are catalytical combustion, electrochemical, thermal conductive, infrared absorption and paramagnetic, solid electrolyte and metal oxide semiconductor sensors (Hooker, 2002). Based on the sensing methods, researchers have categorised gas sensors and grouped them into two classes, which are based

on variation in electrical properties and based on variation in other properties (X. Liu et al., 2012). Materials such as semiconductor metal oxides, carbon nanotubes and polymers can detect gas based on variations in electrical properties. ***Table 1.1*** provides a comparison of different types of gas sensors.

Table 1.1: Comparison of various types of gas sensors (Korotcenkov, 2007)

Parameters	Types of Gas Sensor				
	SMO Gas Sensors	Catalytic Combustion Gas Sensors	Electrochemical Gas Sensors	Thermal Conductivity Gas Sensors	Infrared Absorption Gas Sensors
Sensitivity	E	G	G	P	E
Accuracy	G	G	G	G	E
Selectivity	F	P	G	P	E
Response time	E	G	F	G	F
Stability	G	G	P	G	G
Durability	G	G	F	G	E
Maintenance	E	E	G	G	F
Cost	E	E	G	G	F
Suitability to portable instruments	E	G	F	G	P

E: excellent, G: good, F: fair, P: poor

1.2. Problem Statement

The sensing mechanism of semiconductor metal oxide material is based on the change in the conductivity or resistivity of the material. The change in the conductivity or resistivity occurs when there are interactions between the target gas molecules such as hydrogen gas with the surface of the metal oxide film. When target gas is introduced, the gas molecules react with the oxygen ions adsorbed on the surface of the metal oxide and results in a change in charge carrier concentration of the materials (Sakai et al., 2001). Sensitivity can be described as Ra/Rg for the reduction of gases and Rg/Ra for the oxidation of gases, where Ra is the gas sensor's resistance in the reference gas, where air is normally being used and Rg is the sensor's resistance in the target gas (Huang & Wan, 2009).

The sensitivity of the semiconductor gas sensor greatly depends on both chemisorption and diffusion activities of the gases in the material. As for chemisorption, a larger surface area of the sensing material will result in faster and higher adsorption rate. On the other hand, gas diffusion through the material strongly dominated by the porosity and surface area. The chemisorption and diffusion activities greatly depend on the physiochemical properties of the material such as surface area, porosity, crystallite, and grain sizes.

Apart from experimental investigations, the availability of good chemisorption and diffusion models can significantly contribute to the research in improving the sensitivity of semiconductor-based gas sensors. However, to date there is still lack of chemisorption and diffusion models that can be used to improving the performance of the sensor.

Owing to the fact, the present work attempts to establish the chemisorption and diffusion model by using MATLAB software. A mathematical diffusion model is proposed to study the effect of operating temperature and concentration on the sensitivity of mesoporous tin oxide (SnO_2) gas sensors. The model is then validated with experimental data in the hope that it will be successful in optimising the performance of gas sensors.

1.3. Objectives

The objectives in this study are mentioned as below:

i. To develop a gas diffusion model in predicting the sensitivity of the mesoporous SnO_2 gas sensor by using MATLAB.

ii. To study the relationship between the operating temperature, concentration of hydrogen gas, thickness, and pore size of the mesoporous SnO_2 towards the sensitivity of mesoporous SnO_2 based gas sensor on the gas diffusion model.

iii. To study the effect of Ag and Au additives on the optimum operating temperature.

CHAPTER 2: LITERATURE REVIEW

2.1. Introduction

Metal oxide gas sensors are largely used devices that are ideal for domestic, commercial, and industrial which gain many benefits such as low cost, simple manufacturing operation, and small design. The researchers have gone through deeper into the sensor's performance where it is greatly determined by the morphology and the structural properties of sensing materials, including effects of the doping agent, operating temperature, gas concentration and gas sensing system. This study will investigate the relationship between gas concentrations and the sensor operating temperature with the sensitivity of the mesoporous SnO_2 gas sensor in a gas diffusion model.

2.2. Morphology and microstructure

A researcher studied the effect of microstructure, composition, and defect chemistry on the sensing performance of a CuO-doped SnO_2-based gas sensor using nano powder derived from sol-gel (Zhang & Liu, 2000). The morphologies of SnO_2 (CuO), which were annealed at various temperatures, are shown in ***Figure 2.1***. The surface area decreased as the annealing temperature and particle size increased. Thus, it is advised to be annealed below 1000°C to create a highly porous surface that is preferred for gas sensor applications.

Another research was carried for hydrothermal processing of Nano-SnO_2 powder. ***Figure 2.2*** shows the EM micrograph of the nano-SnO_2 powder. It shows that the particles are

uniformly dispersed in shape and size and they are almost spherical with about 25-30 nm in diameter (Chen et al., 2012).

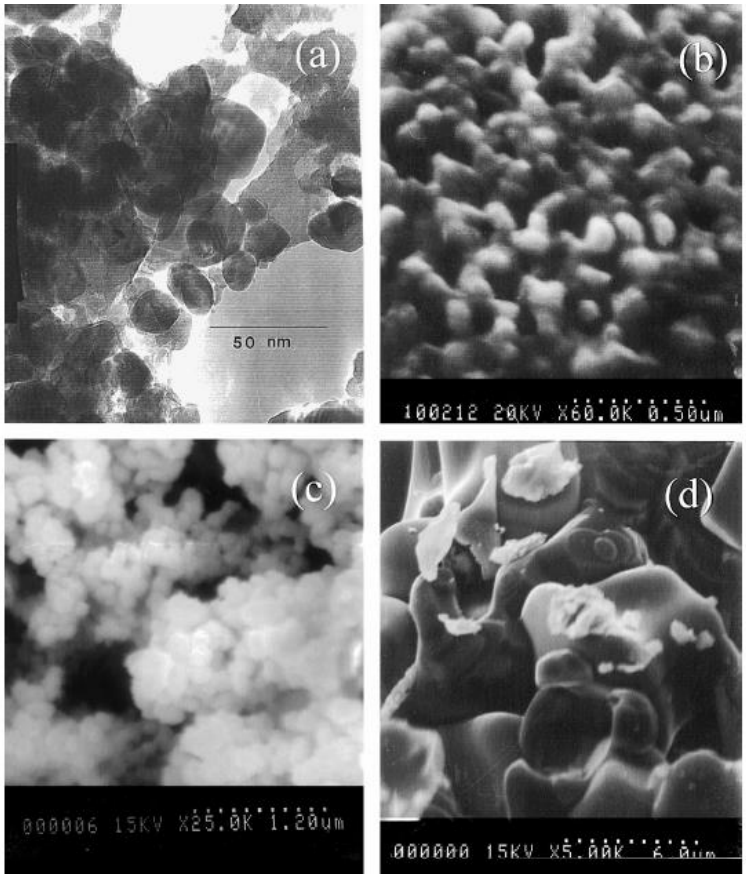

Figure 2.1: TEM and SEM micrographs of SnO_2_CuO as annealed at (a) 600˚C (20nm), (b) 800˚C (100nm), (c) 1000˚C (290nm) and (d) 1200˚C (6μm).(Zhang & Liu, 2000)

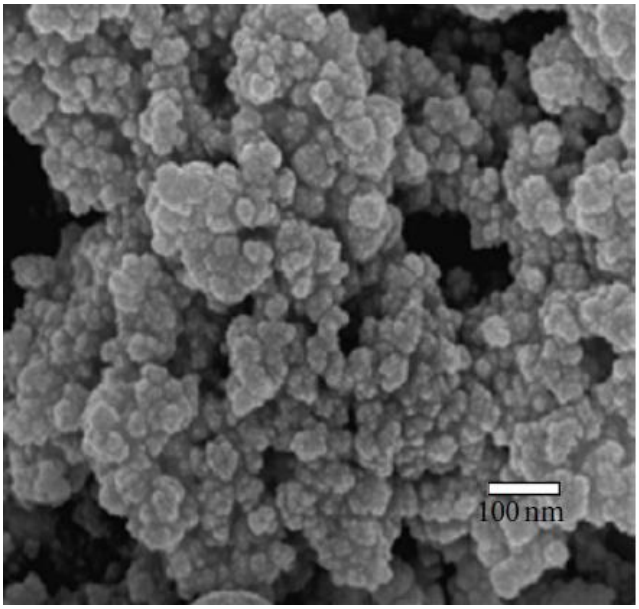

Figure 2.2: SEM micrograph of nano-SnO_2 powder. (Chen et al., 2012)

2.3. Effect of operating temperature on gas sensor

Although SnO_2 gas sensors have a high capacity to adsorb gases and can change surface conductivity during reactions, there are some disadvantages where high operating temperature is one of the drawbacks. As the target gases are adsorbed to the elemental surface, thus the operating temperature affects the physical properties of semiconductors and the reaction sites. This will affect the sensitivity and sensing mechanism of SnO_2 sensors significantly.

The sensitivity of different ethanol concentrations ranging from 500 ppm to 1000 ppm at different temperatures was studied by the researcher (Mishra et al., 2002). The highest sensitivity was observed at 623 K because most of the adsorbed oxygen species reacted with the OH group of ethanol. The highest sensitivity at 623 K was because the equilibrium density of chemisorbed O^- ion at this temperature was optimum (Mishra et al., 2002). ***Figure 2.3*** below shows that the variation of the sensitivity of SnO_2 layer with the temperature at different ethanol concentrations.

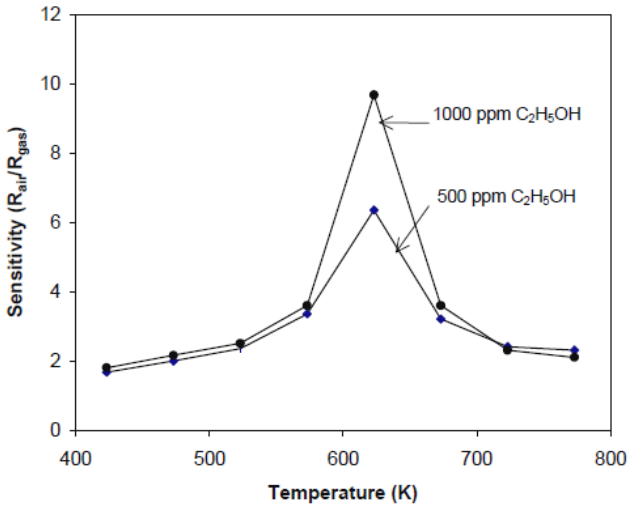

Figure 2.3: Variation of sensitivity of tin oxide layer with the temperature at different ethanol concentrations. (Mishra et al., 2002)

The results of the sensitivity of mesoporous WO_3 thin film rising with the operating temperature was also studied by another researcher (Teoh et al., 2003). In this analysis, the NO_2 gas concentration is maintained at 3ppm and various operating temperatures which is 35°C, 50°C, 70°C and 100°C, are operated. ***Figure 2.4*** shows that 226 is the highest sensitivity which is at 100°C (Teoh et al., 2003).

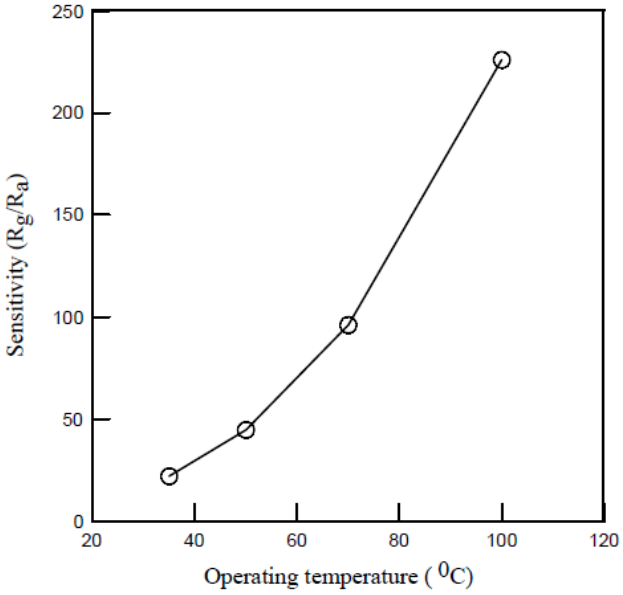

Figure 2.4: Sensitivity of mesoporous WO_3 thin film upon operating temperatures from 35 to 100 ◦C. (Teoh et al., 2003)

Another researched by Sakai et al., 2001 shows that bell shaped was formed for both experimental and simulated results as can be seen in ***Figure 2.5***. The experiment was conducted at 800 ppm of H_2 with 1000 nm film thickness. From ***Figure 2.5***, it is shown that the simulated results were plotted which is the solid line can fit satisfactorily to the experimental result which is the open circle legend. The highest sensitivity is found at the range of 350-400˚C of operating temperature. It shows that when the gas sensor operates at the optimal operating temperate, the sensitivity would be more efficient.

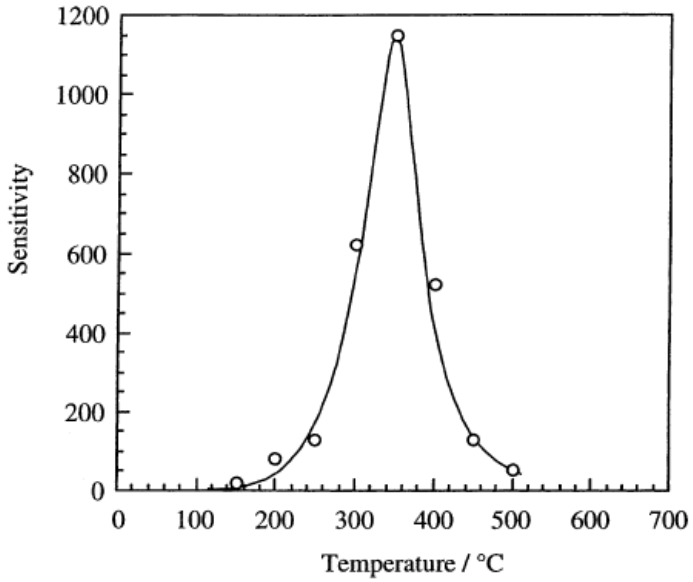

Figure 2.5: The gas sensitivity of thin film to 800 ppm H_2 as correlated with temperature. (Sakai et al., 2001)

2.4. Effect of various gas concentration on sensitivity of gas sensor

Researchers had analysed the sensor response at various H_2S gas concentrations and temperatures which is 30°C, 150°C and 250°C (J. Liu et al., 2009). ***Figure 2.6*** indicates that the sensor response increases as the temperature rise and saturation at higher concentration. This can be inferred that it has sensor response limits because most adsorbed oxygen reacted with the target gas (J. Liu et al., 2009).

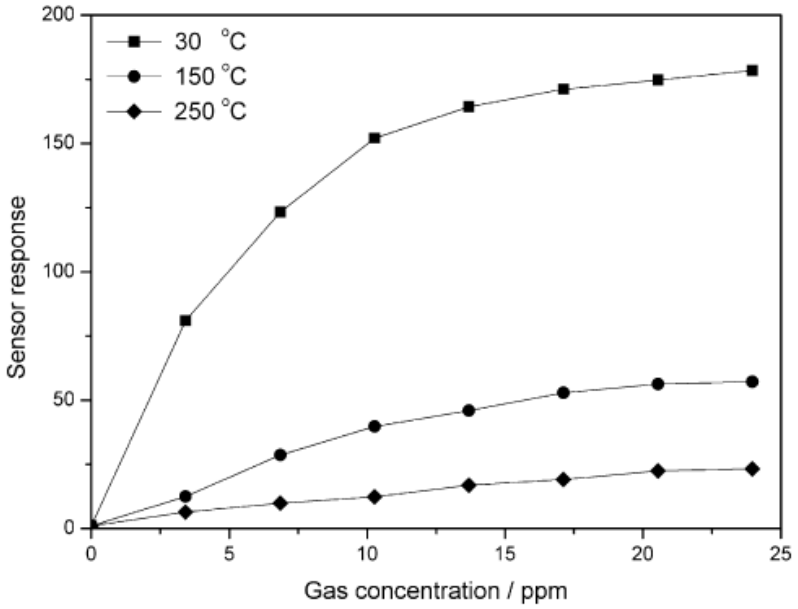

Figure 2.6: Sensor response of thin films at different temperatures of 30, 150 and 250 °C. (J. Liu et al., 2009)

The sensor performance of the mesoporous ZnO2-SnO_2 nanofibers in different ethanol concentrations has been investigated further by another researcher (Song et al., 2009). Based on the results obtained, high sensitivity was observed when in the range of concentrations of 3 to 500 ppm ethanol at 300°C. The responses of m-Z–S nanofibers film were 4, 12.8, 21, 88, 155, 268, and 423 to 5 ppm, 50 ppm, 100 ppm, 500 ppm, 1000 ppm, 2000 ppm, and 4000 ppm of ethanol gas, respectively. It is concluded that as the ethanol concentration increased, the

sensitivity of the sensor increased up to saturation of 10000 ppm. ***Figure 2.7*** below shows the four cycles of response–recovery characteristics of m-Z–S nanofibers exposed to different ethanol concentrations and graph of sensitivity versus ethanol concentration in the range 5-10000 ppm.

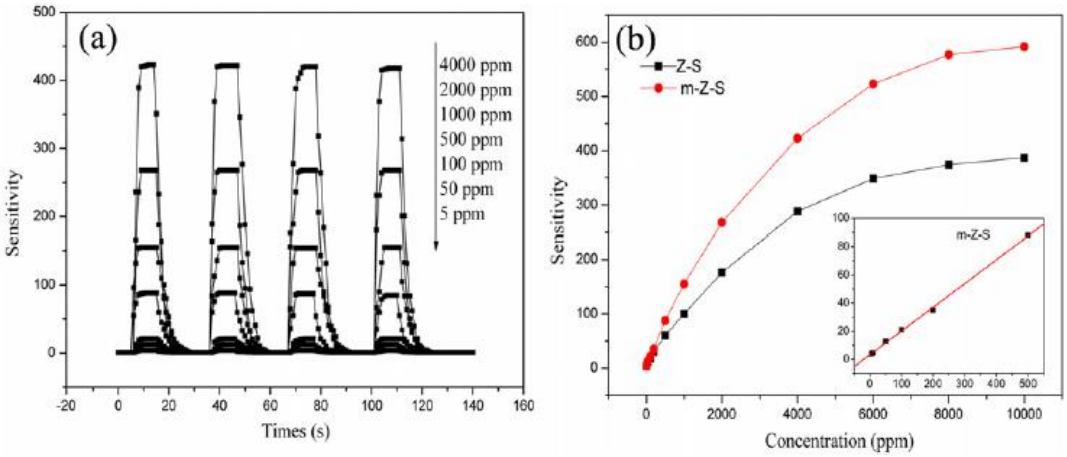

Figure 2.7: (a) Four cycles of response–recovery characteristics of m-Z–S nanofibers exposed to different ethanol concentrations, and (b) sensitivity versus ethanol concentration in the range 5–10 000 ppm. (Song et al., 2009)

Another study indicates that the rise in the alcohol concentration would increase the sensitivity of the gas sensor as shown in ***Figure 2.8***. The graph shows an increase in sensitivity until 1150 ppm and it becomes saturated after that. The sensitivity becomes constant after concentration is 1150 ppm due to the absence of oxygen species to detect the mechanism (Mishra et al., 2002).

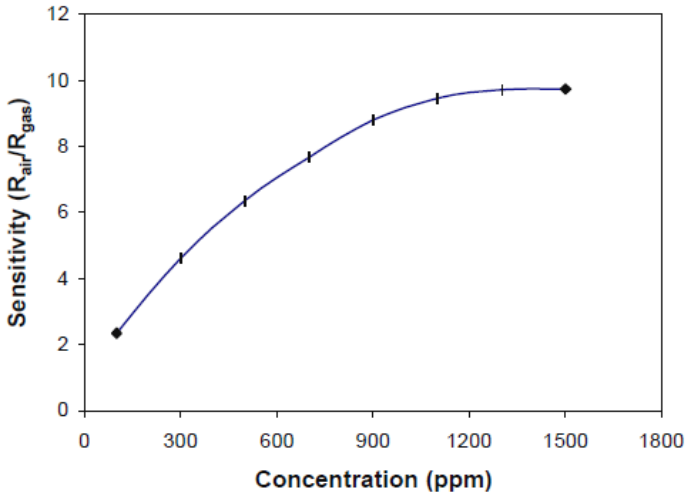

Figure 2.8: Variation of sensitivity with ethanol concentrations at 623 K.

2.5. Reaction kinetics and gas sensing mechanism of mesoporous SnO_2

2.5.1. Gas sensing mechanism

The concept of the sensing system is the chemiresistive property change in the conductivity associated with the adsorption and desorption of gas molecules on the surface of metal oxide which in this study is tin oxide. SnO_2 gas semiconductor sensors have been thoroughly studied and used for practical applications such as detectors for gas leakage and environmental control. Most of the harmful gas emissions from different sources arise at low concentrations, so the detecting of these gases requires great sensing characteristics.

The gas molecules interacting with metal oxides behave either as a donor or as an acceptor of charge carriers known as the receptor function and modify the resistivity of the metal oxide known as the transduction function (Shankar & Rayappan, 2015). ***Figure 2.9*** illustrate the schematic of metal oxide thin film gas sensor. The resistance of the metal oxide thin film to increase or decrease depends on the form of majority carrier in the semiconducting

film and the existence of the gas molecules, whether they are oxidising or reducing in the ambient atmosphere. Oxidating gases increase the resistance of thin films with n-type materials while reducing gases reduce thin film resistance (Fine et al., 2010). The receptor function and the transduction function explain the chemiresistive behaviour of the gas sensors of metal oxide.

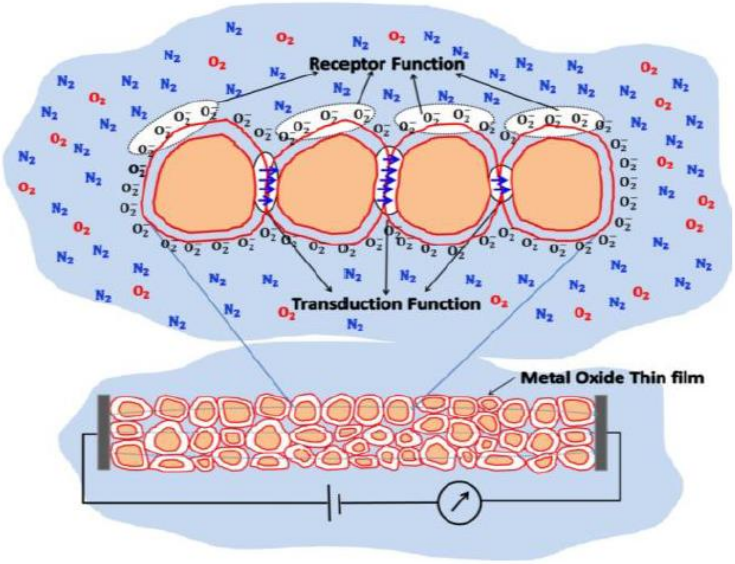

Figure 2.9: Schematic of metal oxide thin film gas sensor. (Shankar & Rayappan, 2015)

2.5.2. Gas diffusion model

A semiconductor gas sensor is commonly agreed to detect targeted gases based on a mechanism that involves a gas reaction with the adsorbed oxygen on the surface of the semiconducting oxide used. The target gas molecules diffuse within the sensor film as they are consumed by the surface reaction at a certain rate. This means that the gas sensing mechanism is an occurrence in which diffusion and reactions are connected to a semiconductive metal oxide gas sensor at the same time.

The mechanism of gas diffusion through a porous material depends on the size the of porous involved. Besides the surface reaction, Knudsen diffusion and molecular diffusion occurs when the pore size increase. Diffusion of Knudsen is known to occur in pores ranging from 1 or 2 to 100 nm in radius, so called mesopores regularly. ***Equation 2.1*** shows the formula of Knudsen diffusion constant (D_K) (Sakai et al., 2001).

$$D_K = \frac{4r}{3}\sqrt{\frac{2RT}{\pi M}} \qquad \textit{Equation 2.1}$$

Where,

D_K = Knudsen diffusion constant

r = Pore radius

T = Temperature

M = Molecular weight

R = Gas constant

It is assumed that the surface reaction of the target gas molecules and the adsorbed oxygen is first order kinetics. The diffusion equation is formulated with the two assumptions Knudsen diffusion and a first-order surface reaction. The diffusion equation shows in ***Equation 2.2*** as shown below (Sakai et al., 2001).

$$\frac{\partial C_A}{\partial t} = D_K \frac{\partial^2 C_A}{\partial x^2} - kC_A \qquad \textit{Equation 2.2}$$

Where,

C_A = Concentration of target gas

D_k = Knudsen diffusion coefficient

t = Time

k = rate constant

x = distance (depth) from the top surface of the sensing layer

Figure 2.10 shows the models of gas sensing film of actual model and equivalent model.

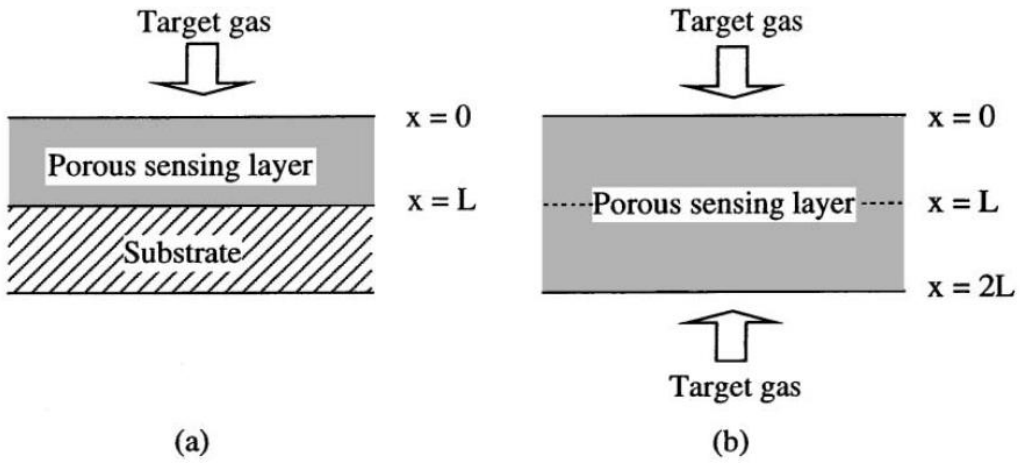

Figure 2.10: Models of gas sensing film: (a) actual model, (b) equivalent model

At steady state, $\partial CA/\partial t = 0$, hence ***Equation 2.2*** is converted to ***Equation 2.3*** as shown below.

$$D_K \frac{\partial^2 C_A}{\partial x^2} - kC_A = 0 \qquad \textit{Equation 2.3}$$

The general solution of this equation is then represented as below, taking boundary conditions, where C1 and C2 represent integral constants:

$$C_A = C_1 \exp\left(x\sqrt{\frac{k}{D_K}}\right) + C_2 \exp\left(-x\sqrt{\frac{k}{D_K}}\right) \qquad \textit{Equation 2.4}$$

2.5.3. Dependence of Sensitivity on Gas Concentration

The concentration of gas in the sensor film is not constant but decreases due to the surface reaction with an increasing diffusion depth. The electrical conductance is given by σ(x),