MODELLING OF GAS DIFFUSION IN MESOPOROUS TIN DIOXIDE (SnO_2) AS GAS SENSOR IN DETECTING ACETONE VAPOUR

by

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KHAMINI A/P MOHAN
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LIST OF SYMBOLS

Symbol	Description	Unit
D_k	Knudsen diffusion constant	-
k	Rate constant	-
L	Film Thickness	mm
M	Molecular weight of target gas	g/mol
r	Pore radius	m
R	Ideal gas constant	J/mol.K
T	Temperature	^oC,K
t	Time	s
C_A	Concentration of target gas	ppm
E_A	Gas-dependent activation energy	KJ/mol
E_k	Temperature-dependent activation energy	KJ/mol
Ra	Resistance of gas sensor in air	Ω
Rg	Resistance of gas sensor in acetone	Ω
a_0	Pre-exponential factor	-
k_0	Pre-exponential factor	-
α	Sensitivity coefficient	-
σ_0	Conductance in air	Ω^{-1}, S
σ_x	Conductance under exposure to gas	Ω^{-1}, S

LIST OF ABBREVATIONS

CH_4	Methane
CO	Carbon Monoxide
NO_2	Nitrogen Dioxide (NO_2
ODE	Ordinary Differential Equation
SMO	Semiconducting Metal Oxide
SnO	Tin monoxide
SnO_2	Tin (IV) Oxide
TiO_2	Titanium (IV) oxide
VOCs	Volatile Organic Compounds
WO_3	Tungsten (VI) oxide
ZnO	Zinc Oxide

PEMODELAN RESAPAN GAS DALAM PENDERIA GAS TIN DIOKSIDA (SnO_2) BERLIANG MESO BAGI PENGESANAN WAP ACETON

ABSTRAK

Penderia gas berliang meso berasaskan logam oksida semikonduktor telah banyak diteliti dan digunakan dalam pengesanan jejak gas beracun dan mudah terbakar seperti nitrogen dioksida (NO_2), karbon monoksida (CO), sulfur dioksida (SO_2) dan sebatian organik mudah menguap (VOC) seperti etanol, metanol dan aseton yang risiko tinggi bagi manusia dan alam sekitar. Dalam penyelidikan ini, penderia gas berasaskan tin dioksida, SnO_2 digunakan kerana kos rendah, kepekaan tinggi dan tindak balas cepat. Bagi kaedah yang berkesan untuk meningkatkan sifat pengesan gas SnO_2 mesopori, model mekanisme penyebaran dikembangkan untuk mengkaji pengaruh kepekatan aseton dan suhu operasi terhadap kepekaan penderia gas. Mekanisme pengesanan gas dikawal oleh penyebaran gas sasaran Knudsen melalui filem berliang dan interaksinya dengan oksigen yang terserap, yang mengikuti reaksi kinetik pesanan pertama. Dalam persamaan model mekanisme penyebaran, ungkapan sensitiviti umum, S, (R_a / R_g) sebagai fungsi pemalar pra-eksponensial, α_0 dan k_0, tenaga pengaktifan reaksi untuk bergantung pada gas, E_a, pemalar gas sejagat, R, suhu, T, kepekatan, C_{A_s} , ketebalan filem, L, tenaga pengaktifan tindak balas untuk bergantung pada suhu, E_k, jejari liang, r dan berat molekul gas sasaran, M diturunkan dalam keadaan keadaan stabil. Berdasarkan teori, kepekaan penderia terhadap suhu operasi penderia menghasilkan lengkung berbentuk loceng dengan suhu optimum, sedangkan peningkatan kepekatan gas mengakibatkan peningkatan kepekaan sebelum tepu dicapai. Apabila membandingkan hasil sebelumnya dengan simulasi MATLAB, jelas bahawa kepekaan meningkat ketika suhu meningkat, menghasilkan garis lurus dan bukan lengkung bentuk loceng. Ini boleh dirumuskan

bahawa model yang dibangunkan tidak sesuai untuk pelbagai suhu operasi yang dirangsang. Dengan menggunakan model tersebut, analisis kepekaan dilakukan berdasarkan ketebalan filem, L dan radius liang, r. Berdasarkan hasil simulasi, kepekaan meningkat ketika ketebalan film menurun pada suhu 300^{o}C kerana interaksi yang lebih besar antara gas sasaran dan permukaan penderia. Sensitiviti penderia gas meningkat dengan peningkatan radius pori pada model pada suhu tertentu 300 ^{o}C, yang dapat dijelaskan dengan cukup dengan persamaan pekali penyebaran Knudsen, D_k.

MODELLING OF GAS DIFFUSION IN MESOPOROUS TIN DIOXIDE (SnO_2) GAS SENSOR IN DETECTION ACETONE VAPOUR

ABSTRACT

Mesoporous semiconductor based gas sensors have been extensively researched and employed in the detection of traces poisonous and flammable gases such as nitrogen dioxide (NO_2), carbon monoxide (CO), sulphur dioxide (SO_2) and volatile organic compounds (VOCs) such as ethanol, methanol and acetone which are dangerous to both people and the environment. In this research, mesoporous tin dioxide based gas sensor, SnO_2 is utilized due to its low cost, high sensitivity and quick response. In order to determine the most effective techniques for optimising the gas sensing properties of mesoporous SnO_2, the effect of acetone concentration and operating temperature on the sensitivity of a gas sensor was investigated using a diffusion mechanism model. The gas detecting mechanism was controlled by Knudsen diffusion of the target gas through the porous film and its interaction with adsorbed oxygen, which followed a first-order reaction kinetic. In the diffusion mechanism model equation, a general expression of sensitivity, S (R_a/R_g) as a function of pre-exponential constants, α_0 and k_0, reaction activation energy for gas dependent, E_a, universal gas constant, R, temperature, T, concentration, C_{A_s}, film thickness, L, reaction activation energy for temperature dependent, E_k, pore radius, r and molecular weight of target gas, M was derived under steady state condition. Theoretically, the variations of sensitivity with the sensor operating temperature resulted in a bell-shaped curve with optimum temperature, whereas increasing gas concentration resulted in increased sensitivity before saturation was attained. When comparing the previous result with the MATLAB simulation, it is clear that the sensitivity increases as the temperature rises, resulting in a linear line rather than a bell shape curve. This can be said the developed model is not suited for the stimulated various operating temperature. The model was used to do a sensitivity

analysis based on film thickness, L, and pore radius, r. According to simulation results, sensitivity improved with decreasing layer thickness at 300^{o}C because of greater interaction between the gas to be detected and the sensor surface. The sensitivity of the gas sensor increased with increasing pore radius in the model at a given temperature of 300 ^{o}C, which can be explained adequately by the equation of Knudsen diffusion coefficient, D_k.

CHAPTER 1

INTRODUCTION

1.1 Metal Oxide Semiconductor Gas Sensors

Gas sensors are devices which able to change the concentration of a specific sample gas to an electronic signal. There are variety of gas sensors which are classified based on sensing element such as metal- oxide based gas sensor, optical gas sensor, electrochemical gas sensor, capacitance-based gas sensor and calorimetric gas sensor. (Introduction to Gas Sensors:Construction Types and Working, 2019) Semiconducting metal oxide (SMO) is currently an important sensing material and one of the most investigated groups of gas sensors which have been widely used in portable gas detection system readily available commercially.

It was first discovered by Brattain and Bardeen (W. H. Brattain and J. Bardeen, 1953) that adsorption of gases onto semiconductor surfaces which can produces a electrical conductivity of the material. Later, (Seiyama,T et al., 1962) introduced the first semiconductor ZnO and SnO_2 gas sensors, which is also known as chemoresistive gas sensors. Semiconducting metal oxides such as SnO_2, ZnO, TiO_2 and WO_3 based gas sensors offer a wide variety of advantages such as low production cost, simplicity in device manufacture, short response time and able to detect a high concentration of hazardous and volatile chemicals in the atmosphere (Tomchenko et al., 2003).

In recent years, SMO based gas sensors act as predominant devices in a variety of residential, commercial, and industrial gas detection systems. Low concentration gases such as carbon monoxide (CO), nitrogen dioxide (NO_2), methane (CH_4) and volatile organic compounds (VOCs) such as ethanol, methanol, and acetone are able to detect using SMO-based

gas sensors.(Kish et al., 2007). The SMO gas sensor undergoes reduction and oxidation process by exchanging electrons at a specific rate with the target gas which can affect the resistivity of the sensor. The detection of gas samples based on a change in the electrical resistance of the metal oxide semi-conductor. The resistance changes on the surface of metal oxide particles due to the combustion reaction occurring within lattice oxygen species (Berna, 2010). In the designing semiconductor gas sensors, high sensitivity, rapid response and recovery, and selective detection are the most critical factors that should be considered (H. Wang et al., 2014).

The basic principles of the gas sensor are sensitivity, selectivity, and reversibility of their sensing response (Kanan et al., 2009; M. Liu, 2010).The term sensitivity of gas sensor refers to the detection of gas at the lowest concentration which defined as the ratio of the device's resistance when exposed to target species to ambient air. Generally, the sensitivity of reducing gases can be defined as *Ra/Rg* while for oxidizing agent will be defined as *Rg/Ra* where the *Rg* represents resistance of target gas and the *Ra* stands for resistance of ambient air (Huang & Wan, 2009).Selectivity refers to a gas sensor's ability to distinguish different types of gases in a multicomponent gas system, whereas reversibility refers to the sensor's ability to revert to its initial condition after being exposed to a specific gas.(M. Liu, 2010). The performance of SMO sensors is influenced by several factors including their morphology and microstructure, operation temperature and various concentration of acetone to improve the sensitivity properties of gas sensor.

1.2 Synthesis of Gas Sensor

SnO_2 shows the highest potential materials because of its superior gas sensing capabilities, which include a rapid response time, high sensitivity, and chemical stability which operated at elevated temperatures. According to the International Union of Pure and Applied Chemistry (IUPAC), mesoporous SnO_2 has better permeability and exhibit superior detecting abilities toward the detection of explosives and toxic gases compared to traditional SnO_2 because it gives the target gas particles a wider surface area to diffuse into and out of the film (J.Rouquerol, 1994). Mesoporous tin oxide, SnO_2 has been commonly utilized as a gas sensing material due to large surface-to-volume ratio, highly organised porous structure with a large surface area-to-volume ratio to facilitate gas diffusion and mass transfer H. Li et al (2010).

According to Shimizu et al (2005), pore size around 4nm large mesoporous SnO_2 powders prepared by using $SnCl_2{\cdot}H_2O$ as an Sn source for phosphoric acid (PA) treatment. From the result, largest specific surface area is 253 m^2 g^{-1} was achieved at the surfactant concentration of 1.3 wt.%. The H_2 response of thick film sensors made from PA-treated big mesoporous SnO_2 powders was very high. This particularly shows that mesoporous structure can be synthesized to provide a greater specific surface area for better sensing performances.

In the article (H. Li et al., 2010), mesoporous SnO_2 was produced using the sol-gel process and attached to carbon nanotubes as a template to detect indoor air pollutants such as ethanol, benzene, and meta-xylene. Based on Figure 1.1, the mesoporous SnO_2 shows a good linear response to different concentration of ethanol and benzene. Thus, compared to traditional SnO_2, the mesoporous SnO_2 provide higher sensitivity, good repeatability and better response towards flammable gases and volatile organic compounds (VOCs).

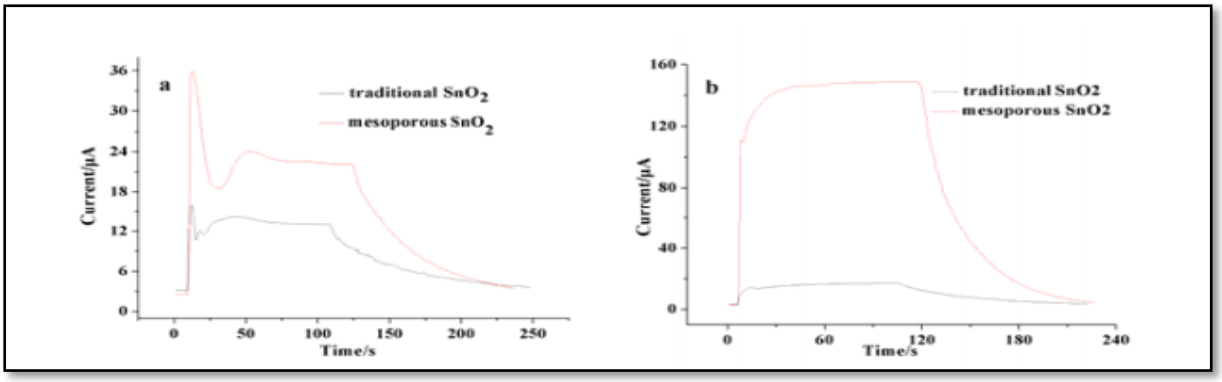

Figure 1:1: Response compares between the tradition SnO_2 sensor and the mesoporous SnO_2 sensor to (a) ethanol with concentration of 70 ppm (b) benzene with concentration of 280 ppm. (Li et al., 2010)

1.3 Application of Metal Oxide Semiconductor Gas Sensor

Detection of indoor air pollutants such as nitrogen dioxide (NO_2), carbon monoxide (CO) and sulphur dioxide (SO_2) is important for energy saving and environmental protection. This is because these indoor air pollutants are known as toxic, flammable, and explosive gases which lead to many diseases and global warming (Yi et al., 2015). Therefore, gas sensors have been developed and are being used to detect dangerous air pollutant particles in the atmosphere. SnO_2 based gas sensors are frequently used for gas leak alarms detection (G.J.Li et al., 1998) and also utilized as gas detectors such as gas chromatographic detectors to trace CO concentration (Bârsan & Ionescu, 1994). The SnO_2 based gas sensor act as pollution controller due to the great response towards reducing gases including H_2, CO, and alcohol (G.J.Li et al., 1998).

The usage of mesoporous metal oxides in gas sensor technology has certain benefits in terms of improving sensor capabilities in terms of detecting dangerous air pollutant gases in the environment. Mesoporous semiconducting metal oxides have become one of the most widely used commercial sensors due to the wide range of electronic, chemical and physical properties. These sensors are highly sensitive to the changes in their chemical environment and

utilized in various industries such as fertilizer industry, food industry and chemical technology to detect of hazardous gases in environment that harmful to human health and to trace the amount of ammonia released. Since the mesoporous semiconductor based gas sensors has a good response and reversibility, it used to detect the volatile organic compound (VOCs) such as ethanol, acetone, benzene and meta-xylene which can poses severe health issues and air pollution. (H. Li et al., 2010).

1.4 Problem Statement

There are lot of effort done to prevent the emission of hazardous gases, but there are still harmful gases remain in the environment that led to public health issues. Acetone (CH_3COCH_3) is commonly known as volatile organic compound, which has been widely utilized in gas sensing field to dissolve plastic, purify paraffin, and dehydrate tissues in pharmaceutics. However, acetone can potentially cause a variety of health concerns, including damage to the central nervous system and liver, kidney, and pancreas (Lian et al., 2017; X. Xu et al., 2017b). Over exposure or inhalation of hazardous gases will cause health problems such as headache, allergy, eyes and skin irritation. In order to minimize the air pollutants, development of gas sensors with low production cost, small size, fast response time is very important to monitor the acetone concentration in the atmosphere for health safety purposes.

Semiconducting metal oxide (SMO) based gas sensors are considered to be best suited due to its advantageous features. The most significant parameters in constructing semiconductor gas sensors are high sensitivity, quick response and recovery, and selective detection. Tin oxide (SnO_2) is a typical n-type metal oxide with wide bandgap and promising material in gas detection due to its chemical, physical stability and ability to detect the target gas is can be improved with increasing sensitivity. (H. Li et al., 2010; H. Wang et al., 2014).

The gas sensing process of SnO_2 based sensors is strongly related to the surface reactions. The gas sensing properties of the SnO_2 sensors are influenced by the morphology and microstructures, operating temperature and concentration of the target gas since it promotes the site of the interaction between gas molecules and the surface chemisorbed oxygen species. However, the sensitivity towards target gas using metal oxides sensor is still to be improved for practical applications. This is because the lack of a general applicable model that fits the fundamental and measurable sensor parameters has hampered sensing performance development.

For safety concern, the environmental concentration of acetone monitoring is necessary using SnO_2 based gas sensor to avoid nausea, headache, fatigue, and nervous system damage. Currently, the performance parameters of the gas sensor have been observed by using simulating tool like COMSOL Multiphysics. In this research, a mathematical diffusion model is developed to study the parameters that affect the sensing behaviour such as the concentration of acetone, operating temperature, film thickness and size of porous on the sensitivity of mesoporous SnO_2 sensor which will be investigated by using MATLAB. The model is developed and validated with the experimental data and results with a hope that in the future, the model can be used to optimize the performances of the sensor by reducing the experimental and laboratory work.

1.5 Research Objective

The purpose of this study is to accomplish the following objectives.:

1. To develop a gas diffusion mechanism model that suits for mesoporous SnO_2 gas sensor.
2. To investigate the effect of acetone concentration on the sensitivity of mesoporous SnO_2 gas sensor using the gas diffusion mechanism model.

3. To study the relationship between the operating temperature and the sensitivity of mesoporous SnO_2 gas sensor based on the gas diffusion mechanism model.

4. To perform sensitivity analysis for the various of film thickness and pore radius on sensitivity of gas sensor based on the model.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Semiconducting metal-oxide based such as TiO_2, ZnO and SnO_2 have been extensively used in mobile gas detection system readily available commercially. Due to their broad variety of electrical, chemical, and physical properties, semiconducting metal oxides have become one of the most widely used commercial sensors. These sensors are extremely sensitive to changes in their chemical environment and are used in a variety of sectors and applications, including engineering, medicine, and architecture. However, the performance of SMO sensors is substantially controlled by several aspects, including the morphology and microstructure, the operating temperature, the film thickness, the pore radius, and the acetone concentration used to create the highly sensitive features. This present study will provide a gas diffusion model to develop the relationship of the concentration of target gas, operating temperature and size of porous material to the sensitivity of mesoporous SnO_2 gas sensor. The literature review below will discuss on the above statements.

2.2 Type of Gas Sensors

In general, the conductivity of semiconducting oxides is influenced by interstitial cation or anion vacancies. The gas sensing technique for semiconductor metal oxides is typically

based on changes in electrical resistance caused by the chemical interaction of specific gas molecules with the semiconductor metal oxides' surface. The targeted gas can be classified as either n-type or p-type. The oxidising gases decrease the conductivity of n-type semiconductor materials, resulting in an excess of negative electron charge carriers. For the p-type semiconductor materials, the conductance will be increase by the oxidizing gases which consist of holes as major carrier (Berna, 2010; Huang & Wan, 2009). Examples of n-type oxides are SnO_2, ZnO and WO_3 while for p-type oxide is tin monoxide, SnO. In this research, mesoporous tin oxide (SnO_2) is utilized as typical n-type metal oxide with wide bandgap and known as promising material for volatile organic compounds (VOCs) especially acetone due to its chemical and physical stability (H. Li et al., 2010; H. Wang et al., 2014).

2.3 Morphology and Microstructure

In general, hollow nanofibers of metal oxides have attracted the interest of a significant number of researchers due to their superior gas sensing capabilities, which include high surface activity, a high surface-to-volume ratio, and quicker gas diffusion. Electrospinning of SnO2 hollow nanofibers decorated with the noble metal, Ag is used to investigate the sensing capabilities of Ag-decorated SnO_2 hollow nanofibers in acetone detection (X. Xu et al., 2017b). The SEM pictures in Figure 2.1 (a) and (b) demonstrate that the tubular nanofibers structure has a large length, controllable uniform diameters of about 220 nm, and high connectivity, all of which contribute to efficient acetone vapour flow.

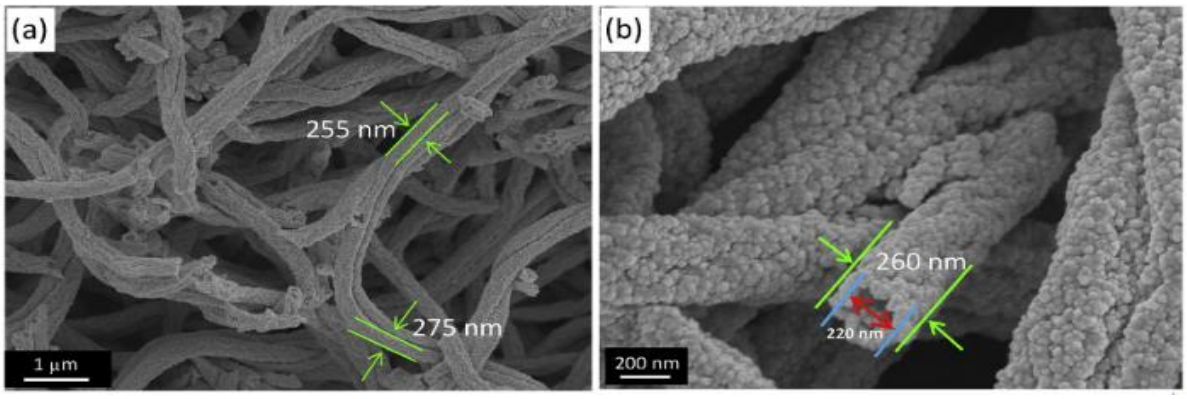

Figure 2:1 The low-resolution (a) and high-resolution (b) SEM images of Ag-decorated SnO_2 hollow nanofiber (X. Xu et al., 2017b)

A research done by (T. T. Wang et al., 2015) to enhance ethanol–gas sensing performance by electrospinning followed by calcination at 600 ˚C for 2 h using Yb-doped (0.5 wt%, 1.0 wt%, 1.5 wt%) SnO_2 hollow nanofibers. Figure 2.2 shows SEM images of as-spun nanofibers with different amount of Yb after annealing. As shown in the figure, when the doping concentration and surface roughness of SnO_2 hollow nanofibers are raised, the surface of the samples becomes uneven. The roughness of the surface is critical for gas diffusion because it increases the surface area with which the gases come into contact.

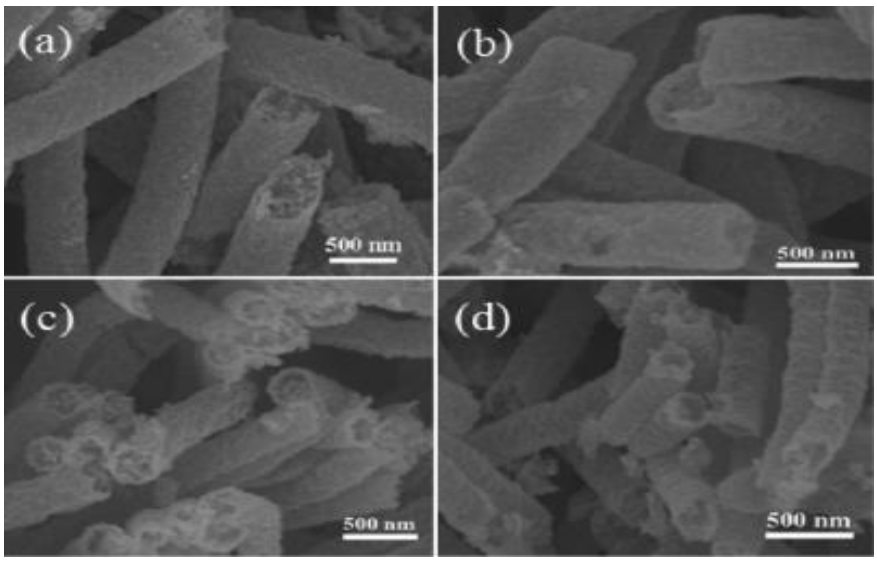

Figure 2:2: SEM images of (a) pure, (b) 0.5 wt%, (c) 1.0 wt%, (d) 1.5 wt% Yb-doped SnO_2 nanofiber (Wang et al., 2015)

In the research (G. Zhang & Liu, 2000), the influence of composition, particle size, and defect chemistry on gas sensor sensing capability is investigated using sol–gel derived CuO-doped SnO_2 and nano powders. By annealing at various temperatures, the particle size of CuO-doped SnO_2 can be adjusted. Figure 2.3 illustrates the morphologies of SnO_2 (CuO) powders that have been annealed at various temperatures. CuO-doped SnO_2 had an average particle size of 20 nm at 600°C, 100 nm at 800°C, 290 nm at 1000°C, and 6 mm at 1200°C, which increased with annealing temperature. This indicates that when the annealing temperature and particle size increased, the surface area dropped. It is recommended that it be annealed at temperatures below 1000^{o}C to create a very porous surface, which results in a higher possibility of gas interaction, which is desirable for gas sensor applications.

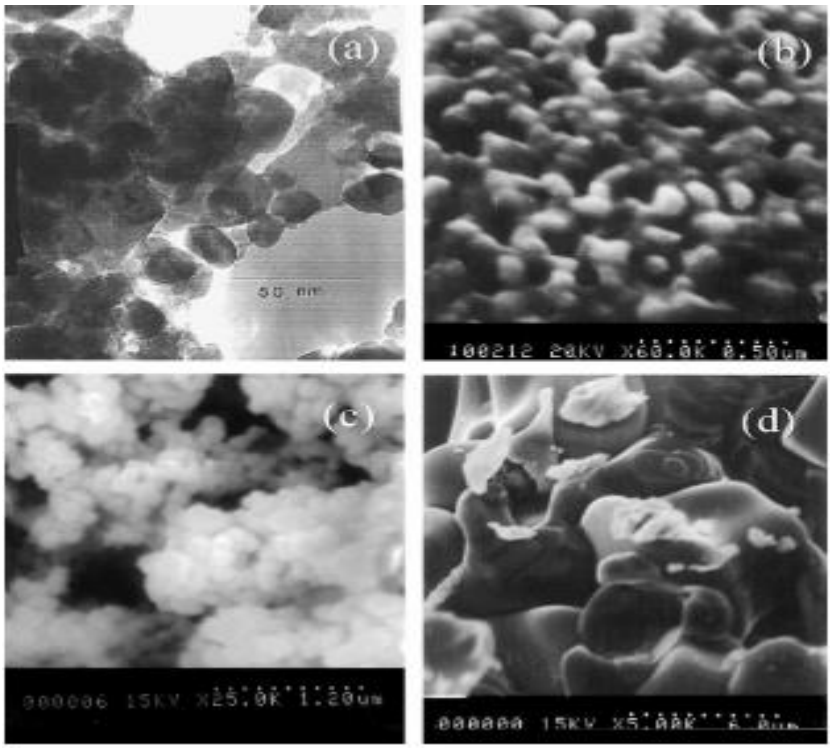

Figure 2:3: TEM and SEM micrographs of SnO_2-CuO as annealed at (a) 600^{o}C (20nm), (b) 800^{o}C (100nm), (c) 1000^{o}C (290nm) and (d) 1200^{o}C (6μm) (Zhang and Liu, 2000)

2.4 Effect of operating temperature on sensitivity of the mesoporous gas sensor

The temperature affects the fundamental properties of semiconductors and sites of reaction when the target gases are adsorbed onto the surface of the element., impacting the sensitivity and detecting system of SnO_2 based gas sensors. As a result, the operating temperature must be optimised to maximise the SnO_2 sensor's sensitivity to the target gas. In the operating temperature range of 200–300 °C, a gas sensor based on SnO_2 has been extensively utilised to detect a wide variety of oxidising and reducing gases.(Liang et al., 2017).

To determine the optimal operating temperature for improved acetone responsiveness, four samples of SnO_2 NSs coated with PdAu bimetallic nanoparticles were exposed to 50 ppm acetone at temperatures ranging from 90 to 380 °C (G. Li et al., 2019). The four sensors in Figure 2.4 showed a bell-shaped relationship between gas response and operating temperature. As the working temperature increases, the activation of absorbed molecular oxygen results in the formation of additional active O^{-2} and O^{-} species, increasing the sensitivity of four sensors. Due to the fact that acetone is more volatile, the reaction diminishes as the amount of adsorbed acetone vapour molecules getting to the sensor decreases.(Biswal, 2011).

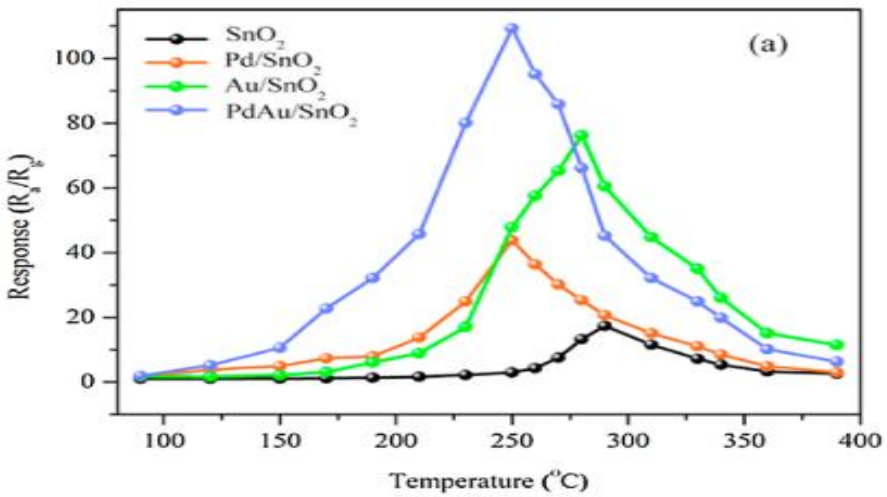

Figure 2:4: Graph of response versus operating temperature of as-prepared sensors to 50 ppm acetone(G. Li et al., 2019)

(X. Xu et al., 2017a) also showed the result of sensitivity of the Ag-decorated SnO_2 hollow nanofiber sensor increasing in proportion to the operating temperature. In this research, the concentration of acetone gas is maintained at 200 ppm and operated under different operating temperatures. Figure 2.5 shows that the gas response increases with increasing operating temperature, with the maximal sensitivity being reported at 160 ^oC (433K), indicating that the chemisorbed O^- ion equilibrium density is highest at this temperature. Then, the desorption process occurs in order to raise the working temperature further due to depletion of adsorbed acetone gas on the gas sensor and cause the response decreases.

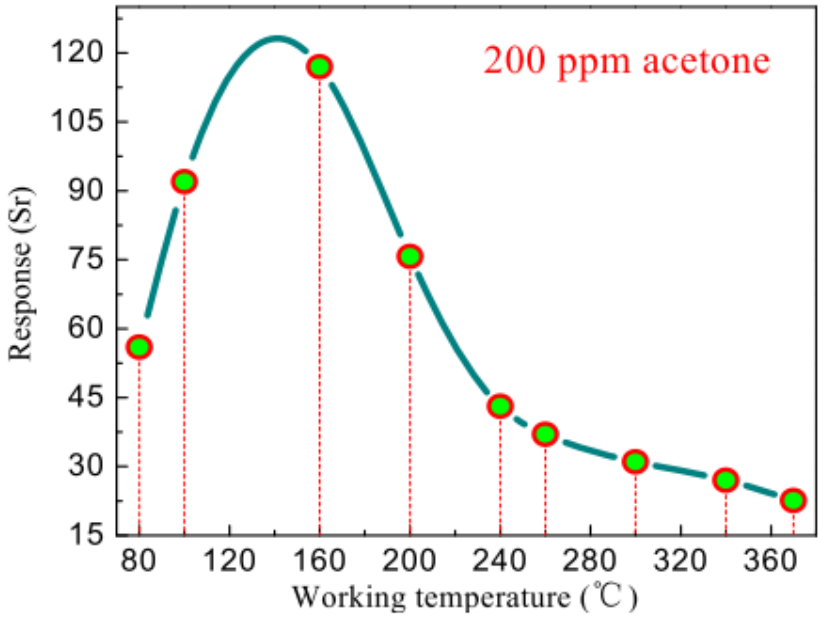

Figure 2:5: Response of Ag-decorated SnO_2 sensor to 200 ppm acetone at different working temperatures(X. Xu et al., 2017a)

Another study Guan et al (2019) found that the sensitivity increased at first as the operating temperature rose until it reached a limit. At 300°C, the greatest sensitivity was found to be 357 for the N containing SnO_2 sample and 215 for the original SnO_2 sample. Both samples exhibited comparable temperature-dependent behaviours. to 100 ppm which require a higher temperature for adequate thermal energy to surpass the barrier of activation energy of

chemisorption and surface response of the specific gases and oxygen ions. Above 300°C, the acetone gas response of SnO_2 is reduced as shown in Figure 2.6 due to the desorption of oxygen ions from the surface of SnO_2.

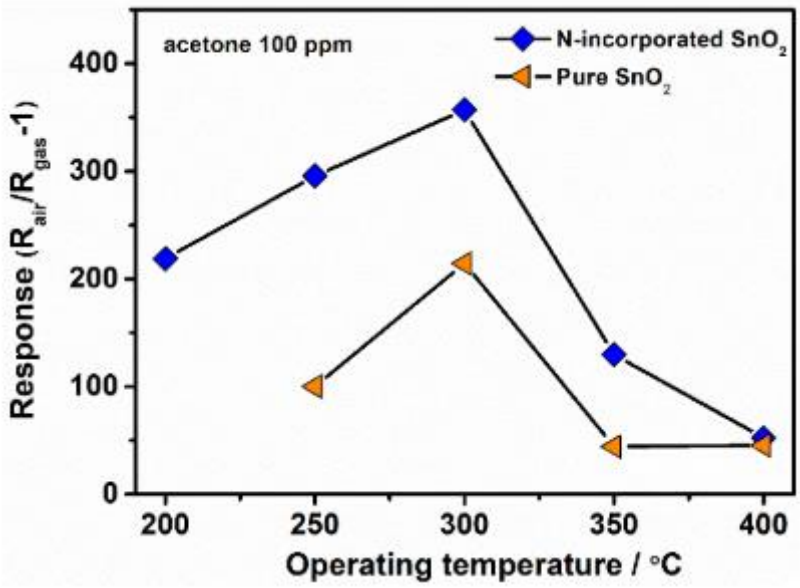

Figure 2:6: Influence of working temperature on the sensor response of the N-incorporated SnO_2 sample to 100 ppm acetone gas(Guan et al., 2019)

2.5 Effect of various gas concentration on sensitivity on sensor

The influence of different gas concentrations on mesoporous sensitivity is critical for determining a sensor's response and sensitivity. The concentration of the target gas is proportional to the sensitivity of the sensor. This was proven by the research of the high performance acetone gas sensor based on pure and Ru-doped SnO_2 nanofibers towards various acetone concentrations at 200°C through electrospinning approach was done by (Kou et al., 2020). The sensitivity of the sensor grew as the acetone concentration increased until it reached saturation at 200 ppm, as shown in Figure 2.7.It indicates that the sensor has a measurement

constraint when the majority of the adsorbed oxygen interacted with the target gas. (J. Liu et al., 2009).

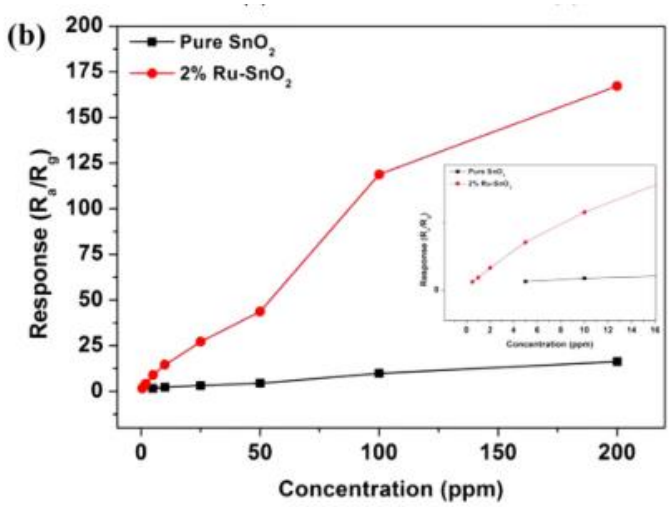

Figure 2:7: The response curves of sensors based on pure SnO_2 and 2 mol% Ru-doped SnO_2 nanofibers versus acetone concentration in the range of 0.5–200 ppm at 200℃ (Kou et al., 2020)

Another study of W. Q. Li et al (2014) demonstrated the response of hollow tin oxide (SnO_2) nanobelts based gas sensor to acetone as a target gas at 260 ˚C. The result in Figure 2.8 clearly shown the gas response increases as the increasing of gas concentration in the range 5–750 ppm. Once the concentration achieved 35000 ppm, saturation of the sensor is occur because there are sufficient of oxygen species to detect the mechanism.

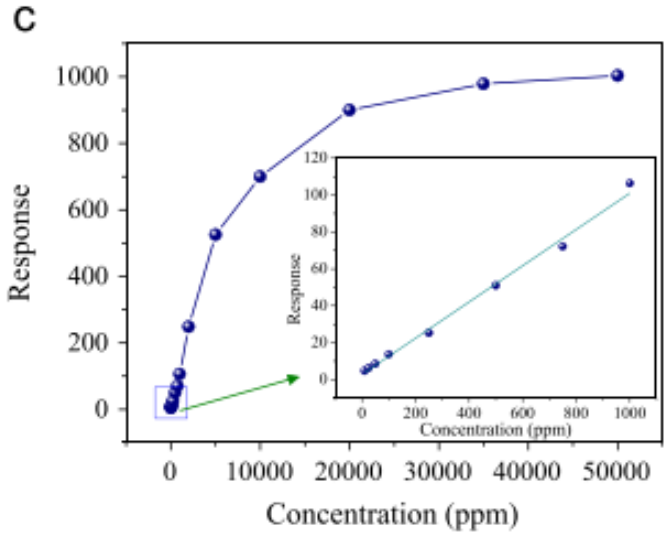

Figure 2:8: The response of sensor to acetone concentrations in the range from 5 ppm to 50,000 ppm at 260 ˚C (W. Q. Li et al., 2014)

In the research of (Patil et al., 2007), using cobalt-doped tin oxide (Co–SnO_2) thin films, the sensitivity of sensor was examined for different acetone gas concentrations. As illustrated in Figure 2.9, for all temperatures between 50 and 300˚C, the variation in sensor response as a function of acetone vapour concentration follows the same pattern, initially increasing with concentration and eventually reaching saturation at higher concentrations..

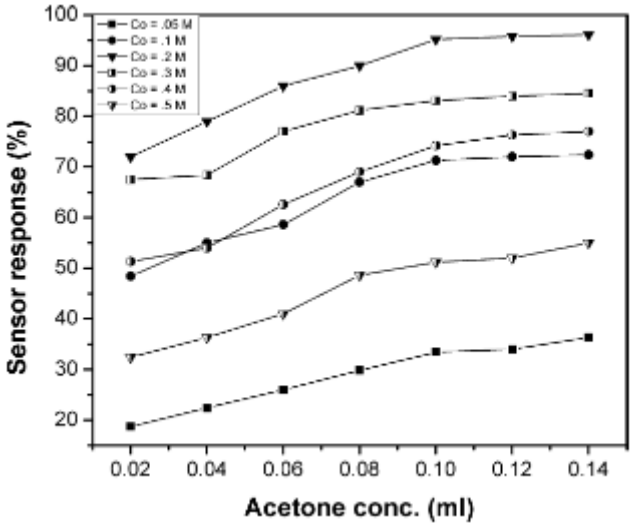

Figure 2:9: Variation in sensor response (S_R) of spray deposited cobalt-doped SnO_2 thin films to different concentrations of acetone vapour measured at 300˚C(Patil et al., 2007)

A study on the sensing behaviour of SnO_2 thin film towards the ethanol vapour by using sol–gel process was conducted (Mishra et al., 2002). The SnO_2 thin film was prepared through spin coating method and the sensitivity of the film was measured at different temperatures and concentrations of ethanol ranging from 500ppm to 1000ppm. The ethanol detection result demonstrates the greatest sensitivity at 623 K, as the majority of adsorbed oxygen species reacted with the OH group in ethanol vapour, indicating that the equilibrium density of chemisorbed O– ions is greatest at this temperature. Figure 2.10 depicts the SnO_2 film's gas sensitivity as a function of alcohol concentration at 623 K. The concentration of ethanol is

linearly proportional to the sensitivity up to 1150 ppm of C_2H_5OH, at which point it saturates due to a lack of adsorbed oxygen species to contribute to detection processes.

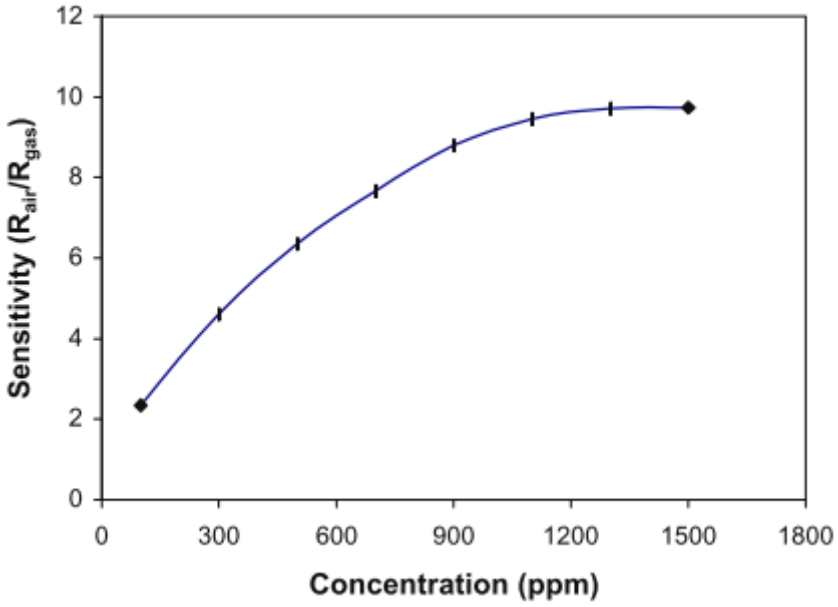

Figure 2:10: Variation of sensitivity with ethanol concentrations at 623 K (Mishra et al., 2002)

2.6 Reaction Kinetics and Gas Sensing Mechanism of Mesoporous SnO_2

2.6.1 Gas Sensing Mechanism -Acetone

Semiconductor-based gas sensors, such as ZnO, SnO_2, and In_2O_3, are useful for detecting dangerous and explosive gases in the environment. Among the semiconductor oxide, SnO_2 based gas sensors have been broadly adopted as gas sensing materials due to their superior sensing features, which include high sensitivity, high selectivity, and the ability to detect both low and high concentrations of target gases such as carbon monoxide, ethanol, methane, and acetone.

In this study, acetone which is a highly volatile and flammable liquid chosen as a target gas that has low boiling point in atmosphere and readily evaporates at ambient temperature. Acetone inhalation can result in headaches, allergies, fatigue, and narcosis when the acetone concentration exceeds 1000 ppm in air (Chen et al., 2018; Wang et al., 2016). A sweet, fruity odour is a sign of ketoacidosis, an acute complication of diabetes due to the presence of acetone (*What Does Bad Breath Have to Do with Diabetes?*, 2017). Acetone concentrations in the breath of healthy individuals range between 0.3 and 0.9 ppm, while diabetic patients' exhaled air exceeds 1.8 ppm.(Chen et al., 2018; WANG et al., 2016). Since acetone is an effective breath marker for diabetes detection, there is a need to create acetone sensing materials and detection devices with a high sensitivity, which is preferable for safeguarding the environment.

The semiconductor oxide gas sensor detects gases by charge-transfer interactions that are primarily induced by oxidation or reduction reactions between the sensor and gas molecules on the sensing material's surface. The mechanism of the SnO_2 is the charge-transfer interactions which are mainly caused by oxidation or reduction reactions between the sensor and gas molecules on the surface of the sensing materials (Lian et al., 2017). It involves the gas adsorption, charge transfer and desorption process which can be described by the following steps(Z. Zhang et al., 2014). At first step, oxygen is adsorbed on the SnO_2 layer when the sensitive film is heated at ambient at a temperature of 473–723 K and forming oxygen ions (O^{2-}, O^{-}_2, O^{-}). Then, the ions undergo desorption which takes place at 323 K, 373 K, and 723 K respectively.(Mishra et al., 2002) The adsorption and desorption processes cause the conductance of the SnO_2 layer to rise or decrease depending on the composition of the gas. Conductivity typically increases when exposed to reducing gases and decreases when exposed to oxidising gases. The reaction kinematics will proceed as below (Mishra et al., 2002; Sun et al., 2012; H. Wang et al., 2014):

O_2 (gas) ↔ O_2 (absorbed) **2.1**

O_2 (absorbed) + e^- ↔ O^-_2 **2.2**

O^-_2+ e^- ↔ $2O^-$ **2.3**

When the acetone gas is introduced, oxygen ions (O^{2-}, O_2^- or O^-) would react with the reducing target gas. The electrons returned to the SnO_2 during the process which can lowering the sensor's resistance. When the sensor was re-exposed to air, the gases are desorbed as H_2O and CO_2.The following equation illustrates the reaction:(Lian et al., 2017; WANG et al., 2016; Z. Zhang et al., 2014):

CH_3COCH_3 (ads) + $8O^-$ (ads) → $3CO_2$ + $3H_2O$ +$8e^-$ **2.4**

2.6.2 Surface Reaction Model

Gas-sensing mechanism of metal oxide semiconductor gas sensor involves of physisorption and chemisorption. The term "physisorption" refers to the exothermic process of gas species adhering to the sensor surface. Chemisorption is an endothermic reaction that involves the exchange of electrons between adsorbed species and the material surface.. (Huang & Wan, 2009).

The metal oxide gas sensor operates on the chemiresistance principle, which is defined as the change in electrical conductivity caused by the chemical interaction of gas molecules with the surface of semiconductor metal oxides.(Shankar & Rayappan, 2015; H. Wang et al., 2014). For n-type materials, the oxidizing gases act as an acceptor to increase the resistance of thin film while, the reducing gases act as donor to decrease sensitivity. When exposed to air, the SnO_2 semiconductor film physisorbed oxygen gases generating oxygen ions (O_2^-, O^-, O^{2-}) via electron trapping in the conductance band of SnO_2.These adsorbed molecules act as a potential barrier between particles by generating an electron depletion layer just beneath the

surface of the SnO_2 particles, resulting in the formation of a high-resistance state SnO_2 film in air.(Mishra et al., 2002).

2.6.3 Gas Diffusion Model

In general, semiconductor metal oxide-based gas sensors detect the targeted gas through an interaction between the gas and adsorbed oxygen on the surface of the semiconducting oxide. The target gas molecules diffuse into and out of the semiconductor layer throughout the response and recovery processes. When gas molecules disperse within the sensor element, they are consumed at a certain rate as a result of surface response. It indicates that the target gas diffusion and reaction with adsorbed oxygen happen at the same time in semiconductor metal oxide gas sensors (Matsunaga et al., 2002) . Mesoporous SnO_2 is used as materials for gas sensing since it provide large space for gas diffusion and have better response to target gas.(Sun et al., 2012)

(Sakai et al., 2001a) discovered that the size of the pore had a key role in the gas diffusion mechanism, which improved the sensitivity of gas sensors. As the pore size increase, surface diffusion, Knudsen diffusion, and molecular diffusion take place. Knudsen diffusion is known to occur in mesoporous pores, which range in size from 1 to 100 nm. Sakai and co-workers provide a diffusion equation based on a first-order reaction of the target gas to explain gas diffusion dynamics in the response process. In the mesopores, Knudsen diffusion constant (D_K) is determined by temperature (T), pore radius (r) and molecular weight (M) of the diffusing gas, as follows (Sakai et al., 2001a) :

$$\boldsymbol{D_K = \frac{4r}{3}\sqrt{\frac{2RT}{\pi M}}} \qquad \textbf{(1)}$$

Here R is Gas constant.

The molecules of the targeted gas permeate into the surface of the mesoporous SnO_2 film and then react with the oxygen on the surface of the SnO_2 chains, which is follow a first order kinetic reaction (Sun et al., 2012). Assume that a target gas A diffuses into a porous film, as shown in Figure 2.11. A well-known diffusion equation is developed by combining the Knudsen diffusion with a first-order surface response. (Sakai et al., 2001a):

$$\frac{\partial C_A}{\partial t} = D_K \frac{\partial^2 C_A}{\partial x^2} - kC_A \qquad \textbf{(2)}$$

Here (C_A) is concentration of target gas, (t) is time, (D) is Knudsen diffusion coefficient, (x) is distance or depth from the top surface of the sensing layer and (k) is rate constant.

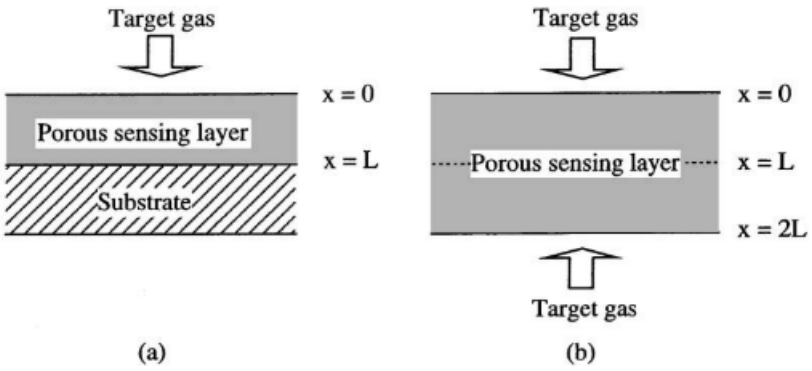

Figure 2:11:Model of gas sensing film: (a) actual model, (b) equivalent model (Sakai et al., 2001)

At steady state, $\frac{\partial C_A}{\partial t} = 0$, therefore

$$D_K \frac{\partial^2 C_A}{\partial x^2} - kC_A = 0 \qquad \textbf{(3)}$$

By taking boundaries conditions, the general solution of this equation is then expressed as below:

$$C_A = C_1 exp\left(x\sqrt{\frac{k}{D_K}}\right) + C_2\, exp\left(-x\sqrt{\frac{k}{D_K}}\right) \qquad \textbf{(4)}$$

Here, C1 and C2 are integral constants.

2.6.4 Dependence of Sensitivity on Gas Concentration

As the diffusion depth of a sensor film increase, the gas concentration drops due to surface reaction. Assume the film is a uniform stack of infinitesimally thin sheets with an electric conductance of (x), where x is the distance from the film surface. (Sakai et al., 2001a).By integrating (x) over the entire range of x (x = 0 – L), the conductance of the entire film is obtained. Consider that the sheet conductance under gas exposure, (σ_x), is linear to the target gas concentration C_A when normalised by that in air (σ_0) (Sakai et al., 2001a).

$$\boldsymbol{\sigma(x) = \sigma_0(1 + \alpha C_A)} \quad \textbf{(5)}$$

The constant here is $\boldsymbol{\alpha}$, which is also known as the sensitivity coefficient. The following are the formulae for the film's total resistance in air (Ra) and in air containing the target gas (Rg). (Sakai et al., 2001a).

$$\boldsymbol{\frac{1}{R_a} = \int_0^L \sigma_0 \, dx} \quad \textbf{(6)}$$

$$\boldsymbol{\frac{1}{R_g} = \int_0^L \sigma_x \, dx = \int_0^L \sigma_0 \, (1 + \alpha C_A) \, dx} \quad \textbf{(7)}$$

Performing integration of both resistance,

$$\boldsymbol{\frac{1}{R_a} = \sigma_0 \, L}$$

$$\boldsymbol{R_a = \frac{1}{\sigma_0 \, L}} \quad \textbf{(8)}$$

$$\boldsymbol{R_g = \frac{1}{\sigma_0 \, L + \sigma_0 \alpha C_{A_s} \, tanh\left[L\sqrt{\left(\frac{k}{D}\right)}\right]}} \quad \textbf{(9)}$$

$\boldsymbol{C_{A_s}}$, which is the concentration of the diffusing gas outside the film

Here, L is the thickness of the film. As a result, the film's gas sensitivity, S, is defined as the ratio of Ra to Rg in terms of gas concentration which as expressed as follows (Sakai et al., 2001a):

$$\boldsymbol{S = \frac{R_a}{R_g} = 1 + \frac{\alpha C_{A_S}}{L} tanh\left[L\sqrt{\left(\frac{k}{D}\right)}\right]} \quad \textbf{(10)}$$

where $\boldsymbol{\alpha}$ is sensitivity coefficient

2.6.5 Dependence of Sensitivity on Operating Temperature

Operating temperature is an important factor that should be considered for the highest sensitivity of semiconducting metal oxide (SMO) based gas sensors. It can be clearly seen that Knudsen diffusion coefficient, D_k and rate constant, k depends on temperature. Based on equation (1), the D_k is proportional to $\sqrt{T}$, while k can be expressed as below (Sakai et al., 2001a):

$$\boldsymbol{k = k_0 exp\left(-\frac{E_k}{RT}\right)} \quad \textbf{(11)}$$

Here, E_k is activation energy of first order reaction and k_0 is pre-exponential constant. Since the thickness dependence is important when T increase, compared to D_k, the k is more dependent T.

The sensitivity coefficient $\boldsymbol{\alpha}$ converts the gas-solid interaction into a relative change in electrical sheet conductance ($\sigma(x)/\sigma_0$) based on equation 5. The steady-state concentration of adsorbed oxygen can be estimated from the rates of adsorbed oxygen consumption by the target gas and supply of adsorbed oxygen from the gas phase. As a result, the sensitivity coefficient a can be written as follows:(Sakai et al., 2001a).

$$\boldsymbol{\alpha = \alpha_0 exp\left(-\frac{E_k}{RT}\right)} \quad \textbf{(12)}$$

The Knudsen diffusion coefficient, Arrhenius Equation, and sensitivity coefficient determine the sensitivity's dependence on sensor operating temperature, according to equation (9). However, the relationship between the sensor's sensitivity and the operating temperature could not be explained sufficiently by the previous theory, thus a modification of the equation is presented. Here, introduced $\Phi = \sqrt{kL^2/D}$ known as Thiele Modulus, which is a dimensionless group that differentiate the response rate to the diffusion rate into equation (9) and the equation becomes:

$$\boldsymbol{S = \frac{R_a}{R_g} = 1 + \frac{\alpha C_{A_S}}{L\Phi} tanh\left[L\sqrt{\left(\frac{k}{D}\right)}\right]}$$

$$\boldsymbol{S = \frac{R_a}{R_g} = 1 + \frac{\alpha C_{A_S}}{L\left[\sqrt{\left(\frac{kL^2}{D}\right)}\right]} tanh\left[L\sqrt{\left(\frac{k}{D}\right)}\right]} \quad \textbf{(13)}$$

2.7 Effect of Various Film Thickness on SnO_2 Sensitivity

The influence of film thickness is necessary to enhance the sensitivity and selectivity of the materials. Previous research into the relationship between metal oxide semiconductor gas sensor film thickness and sensitivity was conducted. The gas sensing properties were studied using porous WO_3 film and sputtered WO_3 film at various operating temperatures (Zeng et al., 2012). From the Figure 2.12, result shows that the porous WO_3 achieved its maximum response value of 41.2 at 150 ˚C, and 7.2 for the sputtered WO_3 film at 200 ˚C. Due to the huge number of gas molecules absorbed on the surface per unit area, the porous WO_3 sensor exhibits a greater response value at a lower ideal operating temperature than the sputtered WO_3 sensor.

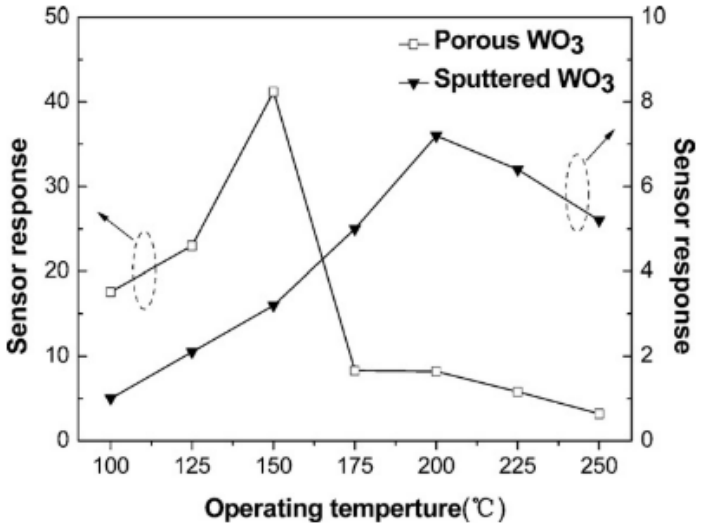

Figure 2:12: Relationship between operating temperature and the sensor responses for the porous WO_3 and sputtered WO_3 film to 1 ppm NO_2 (Zeng et al., 2012)

The effect of thickness and calcination temperature on SnO_2 thin film H_2S gas sensor was explored by (Mochida et al., 1995) .At the working temperature of 600°C, the sensitivity rose as the film thickness decreased. The Figure 2.13 shows the thinnest film affords the highest sensitivity and selectivity due to rise in depletion region caused by chemisorbed oxygen.

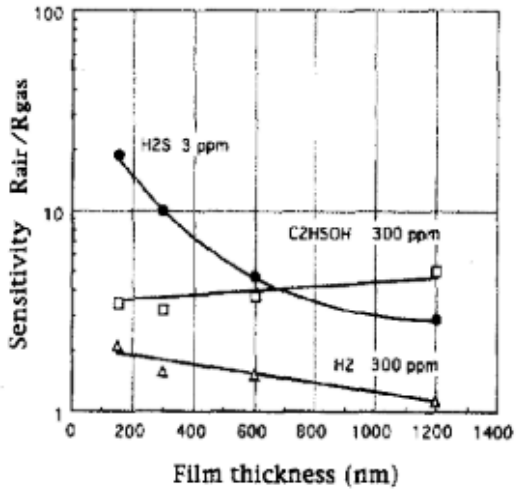

Figure 2:13: Relationship between film thickness and sensitivity to 3 ppm H_2S, 300 ppm of H_2 and C_2H_5OH at calcination temperature of 600°C. (Mochida et al., 1995)