CHARACTERISATION AND PERFORMANCE OF SnO_2 FILM FOR DETECTION OF VOLATILE ORGANIC COMPOUNDS SYNTHESISED BY CHEMICAL VAPOUR DEPOSITION METHOD

TAN XIAN-JU

UNIVERSITI SAINS MALAYSIA

2013

CHARACTERISATION AND PERFORMANCE OF SnO_2 FILM FOR DETECTION OF VOLATILE ORGANIC COMPOUNDS SYNTHESISED BY CHEMICAL VAPOUR DEPOSITION METHOD

by

TAN XIAN-JU

Thesis submitted in fulfillment of the requirements for the degree of

Master of Science

APRIL 2013

ACKNOWLEDGEMENTS

First and foremost, I gratefully acknowledge my supervisor, Associate Professor Dr. Zailani Abu Bakar, for guiding me throughout this research diligently and patiently. He has been teaching me the correct ways to analyse a problem and relate it to the knowledge studied in order to improve my understanding on the research. His constructive ideas and motivational supports are the key factors to the success of this research. Not to forget, I would like to express my gratitude to my co-supervisor, Associate Professor Dr. Ahmad Zuhairi Abdullah for all his support, encouragement and guidance regarding this research.

Apart from that, I would like to thank School of Chemical Engineering, Universiti Sains Malaysia for giving me the great opportunity to undergo my research. It is indeed very honor to be able to complete my research under this school which provides me the facilities and comfortable working environment. For this, I wish to show my gratefulness to the Dean of School of Chemical Engineering, Professor Dr. Azlina bt. Harun @ Kamaruddin and also Deputy Dean of School of Chemical Engineering, Associate Professor Dr. Lee Keat Teong. I would like to extend my gratitude to all lecturers, technicians and office staffs for being there all the time when I need their helps in various aspects including facilities and operation as well as project related and administrative matter. Besides, my sincere thankfulness also goes to Institute Postgraduates Studies, USM for providing me financial support through USM fellowship.

Last but not least, I really appreciate the kindness and sincere effort of my family, friends and all people who has been directly or indirectly helping, teaching, guiding, supporting, caring and sharing with me throughout the project. Thank you very much!

-Tan Xian-Ju, July 2012-

TABLE OF CONTENTS

CHAPTER ONE- INTRODUCTION

CHAPTER TWO- LITERATURE REVIEW

CHAPTER THREE- MATERIALS AND METHODS

CHAPTER FOUR- RESULTS AND DISCUSSION

CHAPTER FIVE- CONCLUSIONS AND RECOMMENDATIONS

APPENDICES

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF ABBEVIATIONS

$(CH_3)_4Sn$	Tetrametyltin
$(C_2H_5)_3N$	Triethylamine
AACVD	Aerosol assisted chemical vapour deposition
Al_2O_3	Aluminium oxide or alumina
APCVD	Atmospheric pressure chemical vapour deposition
Au	Gold or Aurum
B_2H_6	Diborane
CH_4	Methane gas
C_2H_5OH	Ethanol
Cl_2	Chlorine gas
CO	Carbon monoxide gas
CO_2	Carbon dioxide gas
Co	Cobalt
Co_3O_4	Cobalt oxide
CrO_2	Chromium (IV) oxide
Cu	Copper
Cu_2O	Copper (I) oxide
CuO	Copper (II) oxide
CVD	Chemical vapour deposition
DMF	Dimethylfomamide
DMZ	Dimethyl zinc
EDX	Energy dispersive X-ray spectroscopy
FESEM	Field emission scanning electron microscope
FID	Flame ionisation detector
FSP	Flame spray pyrolysis
FTIR	Fourier transform infrared spectroscopy
GPIB	General purpose interface bus
H_2	Hydrogen gas
H_2O	Water
HF	Hydrogen fluoride vapour
H_2S	Hydrogen sulfide gas

IBA	Ion beam assisted
$InCl_3$	Indium trichloride
JCPDS	Joint Committee on Powder Diffraction Standards
L-CVD	Laser induced chemical vapour deposition
LI-PECVD	Liquid injection plasma enhanced chemical vapour deposition
LPCVD	Low pressure chemical vapour deposition
MgO	Magnesium oxide
MIM	Metal-active insulator-metal
MOCVD	Metal organic chemical vapour deposition
NDIR	Non-dispersive infrared sensor
NH_3	Ammonia gas
$Ni(CO)_4$	Nickel carbonyl
N_2O	Nitrous oxide
NO_2	Nitrogen dioxide gas
O	Oxygen
O_2	Oxygen gas
Pd	Palladium
PEALD	Plasma enhanced atomic layer deposition
PID	photo ionisation detector
ppb	Parts per billion
ppm	Parts per million
Pt	Platinum
PVD	Physical vapour deposition
RF	Radio frequency
RMS	Root-Mean-Square
Sb_2O_3	Antimony (III) oxide
SEM	Scanning electron microscopy
Si	Silicon
$SiCl_4$	Silicon tetrachloride
SiO_2	Silicon dioxide
Sn	Tin or Stannum
$SnCl_2$	Tin (II) chloride
$SnCl_4$	Tin (IV) chloride

SnO_2	Tin (IV) oxide or stannic oxide
SO_2	Sulfur dioxide gas
Ti	Titanium
Th	Thorium
TMA	Trimethylamine
TMT	Tetrametyltin
TiO_2	Titanium Dioxide
VOC	Volatile organic compound
VOCs	Volatile organic compounds
$WOCl_4$	Oxychloride
WO_3	Tungsten trioxide
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
Zn	Zinc
$Zn(CH_3)_2$	Dimethyl zinc
ZnO	Zinc oxide

LIST OF SYMBOLS

SYMBOL	**MEANING**	**UNIT**
[C]	Ethanol concentration	ppm
D	Average crystallite size	nm
eV	Energy barrier	kJ/mol
K	Constant of shape factor	Dimensionless
n	Number of moles	Mol
P	Pressure	atm
R	Gas constant	L atm mol^{-1} K^{-1}
R_a	Resistance of the gas sensor in air	Ohm (Ω)
R_g	Resistance of the gas sensor in target gas	Ohm (Ω)
S	Sensitivity	Dimensionless
$S_{acetone}$	Acetone gas sensitivity	Dimensionless
$S_{ethanol}$	Ethanol gas sensitivity	Dimensionless
$S_{methanol}$	Methanol gas sensitivity	Dimensionless
T	Temperature	K
$V_{Acetone}$	Volume of acetone in vapour sample	mL
$V_{Ethanol}$	Volume of ethanol in vapour sample	mL
$V_{Methanol}$	Volume of methanol in vapour sample	mL
λ	Wavelength of the X-ray source	Å
β	Full width at half maximum intensity (FWHM)	Dimensionless
θ	Bragg angle	Dimensionless

PENCIRIAN DAN PRESTASI FILEM SnO_2 MENGGUNAKAN KAEDAH PENGENDAPAN WAP KIMIA BAGI PENGESANAN SEBATIAN ORGANIK MERUAP

ABSTRAK

Filem SnO_2 telah berjaya diendapkan di atas substrat alumina melalui teknik pengendapan wap kimia (CVD) dengan menggunakan tetrametiltin (TMT) sebagai bahan pemula, untuk digunakan sebagai sensor kimia. Pencirian struktur filem telah dijalankan melalui pembelauan sinar-X (XRD), spektroskopi penyebaran tenaga sinar-X (EDX) dan pengimbasan mikroskop elektron jenis pancaran medan (FESEM). Filem sensor dioptimumkan dengan mengubah parameter-parameter penyediaan seperti suhu pengendapan (400 ^{o}C - 500 ^{o}C), masa pengendapan (30 min - 90 min) dan suhu penyepuhlindapan (450 ^{o}C - 550 ^{o}C). Keadaan penyediaan optimum telah dicapai pada suhu pengendapan 450 ^{o}C dan masa pengendapan 60 min tanpa penyepuhlindapan dengan menunjukkan kepekaan tertinggi bernilai 25.02 terhadap wap etanol berpekatan 500 ppm. Selain itu, didapati juga bahawa ketebalan filem meningkat secara berkadar dengan masa pengendapan, iaitu meningkat dari 0.31 µm ke 16.77 µm apabila masa pengendapan meningkat dari 30 min ke 90 min. Sementara itu, penyepuhlindapan tidak meningkatkan kepekaan filem jika dibandingkan dengan kepekaan bagi filem tanpa penyepuhlindapan. Di sebaliknya, kepekaan sensor semakin menurun apabila suhu penyepuhlindapan meningkat dari 450 ^{o}C ke 550 ^{o}C. Keputusan juga menunjukkan bahawa masa respon menurun apabila kepekatan etanol meningkat sementara masa pemulihan meningkat apabila kepekatan etanol meningkat. Sensor yang dioptimumkan juga memberi respon terhadap sebatian organik meruap (VOC) lain seperti wap metanol dan wap aseton.

CHARACTERISATION AND PERFORMANCE OF SnO_2 FILM FOR DETECTION OF VOLATILE ORGANIC COMPOUNDS SYNTHESISED BY CHEMICAL VAPOUR DEPOSITION METHOD

ABSTRACT

SnO_2 films were successfully coated on alumina substrate by using tetramethyltin (TMT) as the precursor via chemical vapour deposition (CVD) technique, to be used as chemical sensor. Characterisation of the films was performed by using X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX) and field emission scanning electron microscope (FESEM). The sensor was optimised by varying parameters such as coating temperature (400 ^{o}C - 500 ^{o}C), coating time (30 min - 90 min) and annealing temperature (450 ^{o}C - 550 ^{o}C). The optimum coating condition was achieved at coating temperature of 450 ^{o}C and coating time of 60 min without annealing with highest sensitivity of 25.02 towards 500 ppm of ethanol vapour. It was also found that film thickness increased linearly from 0.31 µm to 16.77 µm as the coating time increased from 30 min to 90 min. Meanwhile, annealing temperature of 450 ^{o}C to 550 ^{o}C did not improve the sensitivity when compared to the sensitivity of the film without annealing. Instead, an increase of annealing temperature lowered the sensor sensitivity. The results also showed that response time decreased with increasing ethanol concentration meanwhile the recovery time increased with increasing ethanol concentration. The optimised sensor also responded to other volatile organic compounds (VOCs) such as acetone and methanol vapour.

CHAPTER ONE

INTRODUCTION

Volatile organic compounds (VOCs) are organic chemical compounds that have high vapour pressures and low water solubility under normal conditions to significantly vaporise and enter the atmosphere (EPA, 2009). A wide range of carbon-based molecules, such as aldehydes, ketones, and other light hydrocarbons are VOCs. VOCs are widely found in chemical industry and daily activities. Some VOCs that are toxic can cause water and air pollution as well as resulting in various types of disease on either animal or human health. Diseases such as conjunctival irritation, dyspnea, nausea, visual disorders, memory impairments and cancer are caused by VOCs. For instance, cleaning solvents, paints, and wood preservatives from certain furniture would emit VOC compounds, which may contribute to sick building syndrome and other effects such as allergic sensitisation or asthmatic symptoms (Dales *et al.*, 2008; Yu *et al.*, 1998). Irigaray *et al.* (2007) states that long term exposure of VOCs also can cause leukemia and lymphoma. And, aromatic VOCs such as toluene, benzene and xylene are carcinogenic (Bernstein *et al.*, 2008). The effects of VOCs on human health or animals depend on the level and time of exposure (EPA, 2009).

Since the VOCs can cause so much adverse effects on health, precautions should be taken in order to control the VOCs level in the surrounding. One of the precautions is to monitor and detect the VOCs contents from time to time by using effective gas sensor so that proper action can be done if the VOCs level exceeds the safe level. Hence, VOCs gas sensors are essential in this technological world in order to maintain a safe environment.

1.1 Types of Gas Sensor

There are several common types of gas sensor which are widely used in industry. These sensors include flame ionisation detector (FID), non-dispersive infrared sensor (NDIR), photo ionisation detector (PID), infrared spectrophotometry, electrochemical sensor, catalytic sensors, metal oxide semiconductor, gold film (mercury), detector tubes and portable gas chromatography (OSHA, 2009).

Among these gas sensors, it’s found that the metal oxide based semiconductor gas sensors are playing an important role in the detection of toxic pollutants and the control of industrial processes (Arshak and Gaiden, 2005). This is because metal oxide semiconductor gas sensors provides small grain size, low energy consumption and higher surface area to volume ratio which results in better sensitivity and selectivity at low gas concentration (Carotta *et al.*, 1999; Zhao *et al.*, 2002; Yamazoe *et al.*, 2003; Arshad *et al.*, 2008).

1.2 Semiconductor Metal Oxide Gas Sensor

In general, commonly used semiconductor metal oxides for gas sensors can be categorised into two types which are the n-type and p-type. N-type oxides normally are SnO_2, ZnO, TiO_2 and WO_3 whereas p-type oxides are NiO and Co_3O_4. Several researches (Seiyama *et al.*, 1962; Morrison, 1982; Ihokura & Watson, 1994; Zhao *et al.*, 2006; Paraguay-Delgado *et al.*, 2008) show that sensing effect existed in metal oxides and is affected by the reactive gas in the environment. It has been found that SnO_2 film can be used as sensor in detecting the VOCs gas due to their high sensing ability (Ihokura and Watson, 1994).

Both of the n-type and p-type semiconductor metal oxide sensor are basically operated using the adsorption and desorption of the target gas on the layer surface by analysing the electrical conductivity or resistivity of the materials (Shilbayeh and Iskandarani, 2006). The adsorption or desorption process either involves formation or cleavage of bonds between the gas and the material surface in which transferring of electrons occurs. Hence, the electrical charge on the material will be affected and results in its conductivity changes. This changing property of the material electrical conductivity during the gas adsorption and desorption process makes it possible in the detection of gases. Typically, the resistance of n-type metal oxides decrease meanwhile the resistance of p-type metal oxides increase when interact with reducing gas (Korotcenkov, 2007). Besides, n-type metal oxides are found to be more thermally stable and work better under lower oxygen partial pressure as compared to p-type metal oxides (Gordon *et al.*, 1996).

1.3 Preparation Techniques of Semiconductor Metal Oxide Gas Sensor

There are various techniques of film deposition such as electroplating, liquid phase epitaxy, sol gel, physical and chemical vapour deposition (PVD and CVD), Radio Frequency (RF) ion plating and ion beam assisted (IBA) (Kamijo, 2002; Pauleau, 2002; Takano *et al.*, 2002).

Among these techniques, CVD is one of the most popular deposition methods. CVD is chemical reactions which transform gaseous molecules, called precursor, into a solid material, in the form of film or powder, on the surface of a substrate. The precursor gases (often diluted in carrier gases) are delivered into the reaction chamber at approximately ambient temperatures. As they pass over or come into contact with a heated substrate, they react or decompose forming a solid phases which are deposited onto the substrate. The substrate temperature is critical and can influence what reactions will take place. The major challenges of this technique are to obtain the optimum parameters of the process in order to produce highly sensitive film.

From the economic wise, CVD is a versatile process for depositing the desired element on the surfaces or parts. The CVD process can be carried out to deposit the coating onto many parts at once. It will save the time and energy in the particular industry. Therefore CVD is widely used in semiconductor industry, as part of the semiconductor device fabrication process to deposit various films. The synthesis and deposition of the sensing layer material by using the CVD is done in one step, in which the particles are immediately deposited onto the sensor substrates upon formation; which is saving a lot annealing energy and time as compared to other method of deposition. CVD coatings are generally deposited in the order of a few hundred microns per hour in order to achieve the metal oxide gas sensing layer in nano-size layer. The time needed for the deposition to complete is short within 1 hour and reduce the cost of the production in the overall.

In this work, it is proposed to use CVD technique to produce the film sensor due to its versatility to deposit any element or compound such as silicon dioxide, silicon germanium, tungsten, tin oxide, silicon nitride, silicon oxynitride and titanium nitride (Bessergenev, 2006). By using CVD, the film of the microstructure and porosity that are stable to thermal cycling can be controlled. This process is based on gas phase in nature and therefore given a uniform temperature with the coating retort and similarly uniform concentrations of the depositing species then the deposition rate will be similar on all surfaces. Therefore, variable shaped surfaces such as powder, plate, monolithic parts can be coated evenly without build-up on edges.

1.4 Problem Statement

Recently, effort towards the development of simple, inexpensive and reliable devices have been increased with the aim of controlling air pollution and to detect toxic or volatile organics compounds (VOCs) at low levels in the air, in the field of domestic and industry applications. A variety of semiconductor metal oxides such as SnO_2, ZnO, WO_3 and TiO_2 are reported to be usable as gas sensors.

In the previous work, the thick film sensors have been developed based on 4 semiconductor oxides such as SnO_2, ZnO, WO_3 and TiO_2. The performances of the developed pellet towards various VOCs have been carried out. The results clearly indicated that the thick pellets can be used to detect various VOCs. However, the sensitivity of the developed pellet is still low and requires further improvements (Tan *et al.*, 2010; Ang, *et al.*, 2011; Lim *et al.*, 2011). It has been reported the sensitivity and selectivity of the metal oxide gas sensors could be further enhanced by developing the sensing layer with proper layer coating control. In this method, the metal oxide layer will be deposited on the surface of a substrate such as alumina.

CVD method had been chosen to deposit the SnO_2 film due to its high purity deposition, wide range material deposition, high deposition rate, smoother deposition and industrial applicable (Park and Sudarshan, 2000). On the other hand, it was found that CVD was normally performed by using complicated and costly processes such as dopant incorporation, high vacuum and also laser, ultrasonic, plasma, liquid injection and aerosol assisted process. In order to reduce the process complication and cost, simple CVD method was proposed. Hence, the present work studied the characterisation and performance of SnO_2 film for detection of VOC by using simple CVD method.

1.5 Research Objectives

The objectives of the present work are as follows:

- To develop SnO_2 film as the sensor material by using CVD method.
- To characterise SnO_2 film as the metal oxide sensor for detection of ethanol vapour.
- To determine the optimum value of coating parameters in CVD such as coating temperature, coating time and annealing temperature on the film sensitivity in order to produce reliable gas sensor with good sensitivity.
- To test the performance of the optimised film towards a variety of ethanol concentrations and other VOCs such as acetone and methanol vapour.

1.6 Scope of study

The scope of study of this work consisted of the fabrication of CVD rig, the development of SnO_2 film on alumina, film material characterisation, the effect of coating temperature on the film sensitivity towards 500 ppm ethanol vapour, the effect of coating time on the film thickness and sensitivity towards 500 ppm ethanol vapours, the effect of annealing temperature on the film sensitivity towards 500 ppm ethanol vapour, the effect of ethanol vapour concentrations on the optimised film, the selectivity of the optimised film towards 500 ppm ethanol, acetone and methanol vapour as well as the response and recovery time of the optimised film.

1.7 Organisation of Thesis

The thesis covers a total of five chapters which including the introduction, literature review, material and experimental methods, results and discussion as well as conclusions and recommendations. Each chapter is presented in sequence showing the detail of the research study.

Chapter 1 (Introduction) gives a general background of the research study from the gas sensor types converging to the sensor preparation techniques. Besides, the chapter also shows the problem statement, objectives and scope of study for the present work followed by the thesis organisation which gives clear and simple overview of this thesis.

Chapter 2 (Literature Review) consists of the review of the published works, particularly on the metal oxide prepared by CVD method. This chapter introduces the history and development as well as the gas sensing application of the metal oxide prepared by CVD. It also includes the gas sensing mechanism for metal oxide and the selection of precursor. The chapter winds up with concluding remarks which summarise the required information for the research from the literature reviews.

Chapter 3 (Material and Experimental Methods) comprises the description of the experiment carried out in term of chemicals and materials, CVD rig setup, SnO_2 films preparation and characterisation, sensitivity performance measurement, optimisation techniques as well as parameter studies. The photos of the experimental rig and required calculation for the study are included in this chapter too.

Chapter 4 (Results and Discussion) presented the results and discussion of the synthesised film sensors in term of material characterisations and sensitivity performance for different CVD operating parameters in order to obtain the respective optimum value. By using the optimum operating parameters, the synthesised film was further discussed on its sensing properties towards different ethanol concentration and other VOCs as well as its response and recovery time.

Chapter 5 (Conclusions and Recommendations) summarised and concluded the overall findings of the research study as well as providing some recommendations for future improvement.

CHAPTER TWO

LITERATURE REVIEW

2.1 Metal Oxide Synthesis

The synthesis of metal oxide film can be done through the deposition processes in which the metal oxide will be deposited as films and coatings. These processes are generally categorised into two broad types depending on the process nature, typically chemical deposition and physical deposition. In chemical deposition, this technique is done by chemical means in which the precursor used will undergo chemical reaction at the substrate/solid surface under certain condition. The end product will then form on the substrate surface resulting in a solid layer and, at the same time, producing byproducts in solid, liquid or gaseous form. Meanwhile, physical deposition, involves atom-by-atom, molecule-by-molecule, or ion deposition of various materials on solid substrates in vacuum systems.

2.2 Chemical Vapour Deposition (CVD)

CVD is a process whereby the deposition of required material occurs on the target heated surface in a gaseous phase chemical reaction (Pierson, 1999). This reaction involves the interaction of precursor or dissociated precursor with other gaseous reactants under activated environment by using heat, light or plasma as energy source (Choy, 2003).

The synthesis of the metal oxide by CVD starts with the transformation of precursor into vapour phase. Then, the gas will be flowed into the horizontal or vertical chamber containing heated substrate together with other gases for coating purpose (Park and Sudarshan, 2000). The reaction can take place either near or on the vicinity of a heated surface, leading to the formation of powders or films on substrate (Choy, 2003). At the same time, byproducts and unreacted reactant gases will be vented out of the chamber. The operating conditions of the process are normally ranging from temperature 200-1600 ^{o}C and pressure from vacuum to above-atmosphere pressure with or without carrier gases (Park and Sudarshan, 2000).

There are different types of CVD used in the film coating industry depending on the process condition such as conventional CVD, atmospheric-pressure CVD (APCVD), metal-organic CVD (MOCVD), aerosol assisted CVD (AACVD), high vacuum CVD, atomic layer epitaxy processes, liquid injection MOCVD, plasma assisted MOCVD, plasma-enhanced atomic layer deposition (PEALD), laser-induced CVD (L-CVD) and others. Nowadays, CVD is widely used in film coating industry, however this method has its own pros and cons (Pierson, 1999; Park and Sudarshan, 2000; Choy, 2003; Dobkin and Zuraw, 2003).

One of the advantages is that CVD able to produce conformal thin films. This means that the films able to uniformly coat the complex shaped substrate surface including insides and undersides, and also fulfilling other features such as high aspect ratio holes. In addition, CVD has the capability of producing material with high purity and density. Besides, there are wide variety of materials can be deposited depending on the precursor chosen. For instance, chemical precursors can be halides, hydrides and organometallics. CVD also provides advantage with high deposition rate that enables the feasibility in industrial commercialisation and more economic. Other advantages include clean deposition of film without creating particles as well as ability to control the product characteristic (structure and morphology) with ease.

In contrary, CVD has several drawbacks, primarily the precursors requires the properties of high volatility hence limiting the source of available precursor for CVD. Furthermore, precursors with high vapour pressure are normally hazardous materials which can be toxic ($Ni(CO)_4$, $(CH_3)_4Sn$), explosive (B_2H_6) and corrosive ($SiCl_4$). The byproducts such as CO, CO_2, CH_4, H_2 or HF are also hazardous. On the other hand, the CVD deposition temperature is usually elevated, therefore restricting the option of substrate to be coated due to its thermal instability.

Besides, there are some CVD that utilise the state-of-the-art technology such as low pressure or ultrahigh vacuum CVD, plasma assisted CVD and photo-assisted CVD which may provide high fabrication and production cost. Nevertheless, the problem can be solved by using other CVD alternatives which do not use sophisticated reactor and/or vacuum system.

2.3 Metal Oxide Synthesis by CVD

Since 1960, CVD had been introduced in the fabrication of semiconductors. The development of CVD in coating industry has been growing ever since. Until recent years, researches related to metal oxide film coating is still continuing. In year 2002, research on the iron oxide deposition had been conducted using conventional CVD from iron(III) tert-butoxide and showed that it's possible to control the composition and morphology by varying the right CVD parameters (Mathur *et al*., 2002). Saitoh *et al*. (2002) used titanium tetra-isopropoxide as precursor to grow epitaxial crystalline and whisker TiO_2 thin film with different substrate temperature by using CVD method. Meanwhile, Lee *et al*. (2002) tried to use high vacuum CVD to produce high quality epitaxial MgO film from methylmagnesiumtert-butoxide. This method was found to be effective in establishing epitaxial growth of MgO films.

In another works by Loo *et al.* (2004) and Aspinall *et al.* (2004), they investigated liquid injection MOCVD on the rare earth metal neodymium and gadolinium in order to produce neodymium and gadolinium oxide thin films. Precursors such as neodymium alkoxide with tetraglyme in toluene and gadolinium alkoxide were used in the process for respective films. Both groups indicated the films deposited were grown over a wide range of substrate temperatures. Another research based on plasma-enhanced CVD (Seman and Wolden , 2004) were done to produce tungsten oxide thin film by using tungsten hexafluoride which provides the thin film good diffusion and absorption coefficients that enables successfully reproduced transient optical performance.

From year 2005-2007, plasma incorporated with CVD or MOCVD method was further developed. By utilising plasma in the process, a few cases such as silicon oxide, vanadium oxide, titanium oxide and aluminium oxide thin film were explored (Alexandrov *et al.*, 2005; Seman *et al.*, 2005; Yang *et al.*, 2006; Yang and Wolden, 2006; Arockiasamy *et al.*, 2007; Szymanskia *et al.*, 2007). Among these cases, Yang *et al.* (2006) concentrated on the impact of annealing temperature on titanium oxide dielectric performance by using plasma-enhanced CVD. The optimal annealing temperature was 600 ℃, which maximised both the dielectric constant and minimised the leakage current density. This was superior to the SiO_2 performance of equivalent oxide thickness. Another typical case showed the apparent dielectric constant of the TiO_2 thin films increased with film thickness as well (Yang and Wolden, 2006). The dielectric performance was suspected applicable for being gas sensing materials. In the same year, Sousa *et al.* (2006) reported highly oriented a-axis CrO_2 films were successfully fabricated via atmospheric pressure CVD (APCVD) at temperatures as low as 330 ℃. Film surface microstructures depended on film thickness, whereas for deposition rates the dependence was mainly on the substrate temperature.

Recently, Rowlette *et al.* (2009) had investigated the deposition of ZnO by using plasma-enhanced atomic layer deposition (PEALD) from precursor dimethyl zinc (DMZ, $Zn(CH_3)_2$) at temperature ranging from 25 to 120 ^oC. The saturated growth rate of the films increased from 1.6 to 2.9 Å per cycle within temperature 25-85 ^oC. From temperature 85-120 ^oC, the saturated growth rate will remain constant. It was found that substrate temperature able to affect the film structure and properties. The research showed that the crystal orientation evolved from the (100) direction at room temperature to (002) at 120 ^oC. This film exhibited semiconductor quality, displaying band edge photoluminescence and containing negligible impurities as measured by FTIR and XPS. Meanwhile, the film purity, refractive index, and electrical conductivity increased as the substrate temperature increased. It was observed that strong bandage emission only existed in the films deposited at 120 ^oC. Hence, higher temperature may be preferred for applications where optical emission is desired.

2.4 SnO_2 as Gas Sensor by CVD Method

Several researches (Seiyama *et al.*, 1962; Morrison, 1982; Ihokura and Watson, 1994; Zhao *et al.*, 2006; Paraguay-Delgado *et al.*, 2008) show that sensing effect existed in metal oxides and is affected by the reactive gas in the environment. SnO_2-based sensors have emerged as the choice of materials for solid-state gas detection alarms in domestic, commercial and industrial premises on account of their sensitivity to detect VOCs gases in low concentrations and their ability to operate at low temperatures. The gas sensors based on SnO_2 have its advantages of cheapness, simplicity and high sensitivity.

Among the method of SnO_2 deposition, CVD has played an important role. In order to increase the capability of SnO_2 based sensor, doping has been considered in the research of CVD deposition. For instance, Salehi and Gholizade (2003) investigated the sensing properties of the indium-doped SnO_2 sensors using $SnCl_4$ as precursor solution and $InCl_3$ as doping solution. It was found that with different doping concentration, different film structure will be produced and hence affecting the sensitivity. The optimum sensitivity of 17% was obtained at 20 wt% $InCl_3$ films towards 1000 ppm hydrogen, methanol and carbon monoxide. The result showed that further increase of $InCl_3$ concentration will decrease the sensitivity due to the substitution of Sn^{2+} with In^{3+}.

In the following years, a lot of researches have been concentrating on the surface morphology, structure and size of the SnO_2. For example, Ge *et al.* (2006) had successfully produced polycrystalline SnO_2 microspheres which can have high sensitivity towards ethanol. This study showed that the reason for the highly sensitive reaction is because of the small grain size and relative large pore diameter of the sample. The polycrystalline SnO_2 microspheres were prepared by two-step vapour phase reaction which is the formation of SnS_2 microspheres from $SnCl_2$ precursor, followed by the second step of oxidising the SnS_2 into SnO_2. This had lead to the new exploration for the SnO_2 nanostructure to be used as gas sensor. Meanwhile, Kwoka *et al.* (2007) used the CVD techniques to produce SnO_2 film in order to determine the detail structure of the grain with surface roughness of 0.5 nm, average grain height of 1 nm and maximum grain height of 2 nm which in turn giving a very smooth thin film layer. This can be very promising gas sensor towards reducing gases like CO and H_2.

In order to further study the effect of grain structure or morphology towards the sensing performance, deposition of films were also conducted using more complicated process including laser, ultrasonic and plasma technology in order to obtain better sensing performance and selectivity. For example, Larciprete *et al.* (1998) and Lancock *et al.* (2005) had utilised laser technology in the film deposition process. The former grew organotin film from tetrametyltin (TMT) by using laser-induced CVD under ultra high vacuum condition (10^2 Pa) at a laser repetition rate of 5 Hz. This sensor gave high sensitivity towards NO_2, ethanol and hydrogen gas with short response time. The prepared Pd-doped SnO_2 thin film by laser-assisted MOCVD technique with TMT and oxygen as precursor. They had successfully grown the thin film with crystalline grain size of 7.5-15 nm at 300 ^oC which gave good sensitivity towards several different target gases like CH_4, SO_2, CO, N_2O, CO_2 and H_2. The best sensitivity of this sensors were achieved at 15.8 for 10 ppm of SO_2 gas at 268 ^oC with TMT:O ratio of 1:50, whereas, for 10 ppm NO_2 gas, best sensitivity were obtained at 274 ^oC with TMT:O ratio of 1:200.

Similarly, years ago, Briand *et al.* (1998) also studied on the Pd-doped tin oxide films but with different technique that assisted ultrasonic spraying CVD was used. This method enabled production of 250 nm thick nanocrystalline structure Pd-doped SnO_2 sensor film deposited at 460-500 ^oC which sensitive towards CO gas in term of electrical conductance with sensitivity of about 230 at sensing temperature of 100 ^oC. The film also showed cross sensitivity towards other reducing gas such as ethanol and methane after annealing under air for 12 hours at temperature of 500 °C. It was said that annealing help to stabilise the film microstructure and increase its resistivity in air which enable the increase in sensitivity.

On the other hand, modified PECVD with post-plasma treatment was done by Lee *et al.* (2008) in order to develop the undoped SnO_2 and Pd-SnO_2 nanorod film. The undoped SnO_2 exhibited lower sensitivity than the Pd-SnO_2 with a value of 2.5 and 6 times lower for 1000 ppm H_2 and ethanol respectively. Such sensitivity improvement from the Pd-doped was due to the increase of the semiconductor work function in which the resistance in air increases (Yamazoe *et al.*, 2003). Upon further investigation on the sensitivity in lower gas concentration, Pd-SnO_2 showed maximum sensitivity of around 33 and 15 towards 50 ppm of H_2 and ethanol respectively at 300 ^oC. In year 2009, another research (Huang *et al.*, 2009) was carried out to produce SnO_2 nanocolumn with crystalline and uniform structure by using liquid injection plasma-enhanced chemical vapour deposition (LI-PECVD). In this study, they improved the sensitivity by using post O_2 plasma treatment in which the sensitivity towards 1000 ppm H_2 increased from 17 to 160 after the plasma treatment at 400 ^oC. Similarly, sensitivity towards 1000 ppm CO also increased from 4 to 33. It was said that the increase in sensitivity was caused by the increased chemisorbed oxygen after plasma treatment. The fact that post O_2 plasma treatment enhance SnO_2 sensitivity also was supported by Pan *et al.* (2010) such that the treatment change the morphology and increased the oxygen vacancies concentration on the synthesised SnO_2 nanowires. This resulted in the sensitivity improvement, for instance, it lowered the sensing temperature but showing higher sensitivity towards ethanol.

Additionally, aerosol assisted chemical vapour deposition (AACVD) also has been studied till now. Zhao *et al.* (2010) produced all SnO_2 and Cu-SnO_2 film at 400 ^oC and annealed at 600 ^oC for 2 h. The SnO_2 showed maximum sensitivity of 136 at 25 ^oC towards 50 ppm H_2S at deposition time 3 h. It was explained that the sensitivity change in volcano shape towards the deposition time was caused by the change in film thickness. Meanwhile, Cu-SnO_2 with uniform spherical grains exhibited maximum sensitivity of 382.9 at 25 ^oC towards 50 ppm H_2S at deposition time 2 h. Stoycheva *et al.* (2011) also used AACVD to deposit tetragonal SnO_2 film from a complex precursor but the sensitivity towards 10 ppm NO_2 is rather low. The maximum sensitivity shown was 1.70 at sensing temperature of 300 ^oC for the film deposited at 400 ^oC. Other than AACVD, it is very interesting to find that SnO_2 film was deposited on carbon nanotubes at 375 ^oC through CVD method in order to produce nanostructure SnO_2 (Parthangal *et al.*, 2011). The carbon nanotubes were removed easily by annealing the film at temperature not less than 450 ^{o}C. Such method enables the production of any metal oxide in nanotube structure.

2.5 Gas Sensing Mechanism

The gas sensing mechanism of semiconducting oxides is a modulation of surface charge resulting in a modulation of conductivity as shown in Figure 2.1. In clean air, oxygen will trap free electrons by its electron affinity on the surface of metal oxide layer. Whenever the gas sensor is exposed to target gases, the surface adsorbs the gases and some of the oxygen is removed by reacting with oxygen at the surface. This lowers the potential barrier, thereby reducing the electric resistance (Graf, 2006). The change in the electrical resistance is from a level in air (R_a) to a steady level (R_g) on the exposure of target gas. One of the main gas sensor properties is called sensitivity which is defined as R_a/R_g is much dependant on the operating temperature, concentration of the target gas and other conditions (Yamazoe, 2003). The conduction mechanism in crystalline metal oxides gas sensor is also depending to the grain size distribution, local doping, grain boundaries and surface states (Korotcenkov, 2005). Therefore the preparation technique of the sensing medium of the metal oxide layer is highly important.

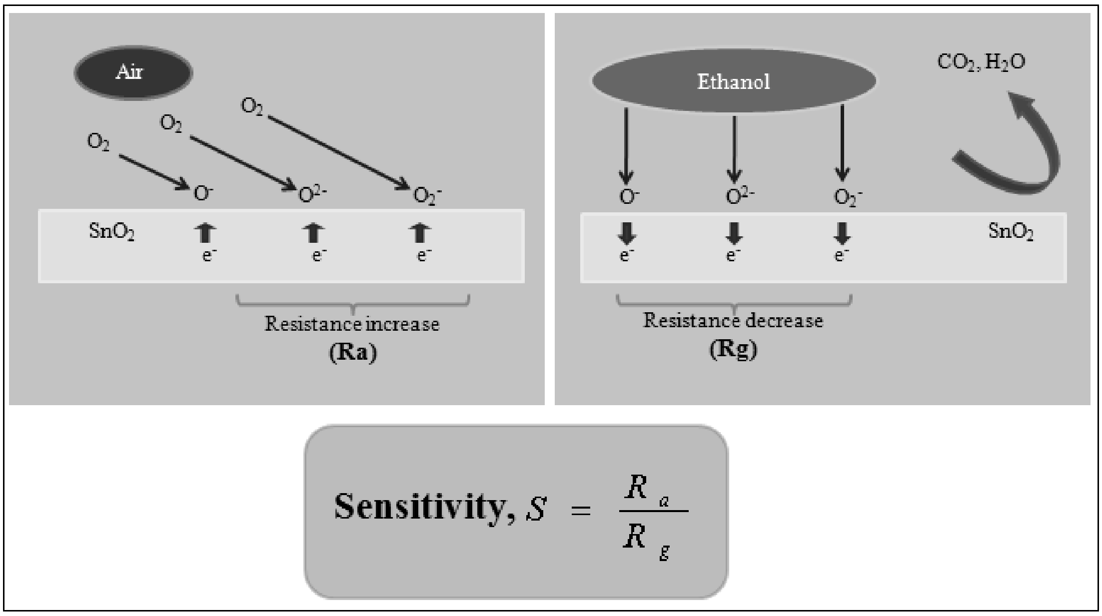

Figure 2.1: Gas sensing mechanism of semiconducting oxides.

2.6 Tetramethyltin (TMT) as Precursor

Tetramethyltin (TMT) was used as the precursor for present CVD works because of its high volatility and stable properties such as simple reaction which reduce complexity, easy to control and handle the operating environment, easily decomposed by heat as well as the coating process has less contaminant compared to complex precursor (Baliga and Ghandhi, 1975; Borman and Gordon, 1989; Wan et al., 1989).

Among the researches of CVD which used TMT as precursor, Baliga and Ghandhi (1975) had successfully deposited SnO_2 films at 450 ^{o}C under atmospheric pressure. This atmospheric pressure chemical vapour deposition (APCVD) was carried out by bubbling 15 ml/min of Ar through TMT reservoir and then reacted with 48 ml/min of oxygen in reactor. The study was mainly concentrated in term of film growth rate, conductivity and transparency. Besides APCVD, Lee and Yoon (1999) investigated the growth of SnO_2 films by using low pressure chemical vapour deposition (LPCVD). They concluded that the deposition rate of SnO_2 from TMT was generally depending on the TMT flow which also mentioned by Baliga and Ghandhi (1975). Other studies relating to the synthesis of SnO_2 films from TMT by CVD without gas sensing application including Ray *et al.* (1997), Tyczkowski *et al.* (1997), Hu *et al.* (2005), Pulpytel *et al.* (2005), Chen *et al.* (2006) and Wavhal *et al.* (2009).

On the other hand, a group of researchers from National Institute of Standards and Technology (Cavicchi *et al.*, 1995; Semancik *et al.*, 1996; DiMeo *et al.*, 1998; Cavicchi *et al.*, 2002) have been investigating and developing SnO_2 microhotplates from precursor TMT by using CVD method. From their characterisation, they concluded that deposition temperature and deposition time did affect the structure and morphology of the deposited SnO_2. For instance, increase of deposition temperature increased the SnO_2 grain size, and also, the SnO_2 grains structure changed from dispersed and unconnected to fully connected across the microhotplates as the deposition time increasing. Besides, they had done many studies on the film conductance under different conditions and found that the conductance change of the deposited films were sensitive enough to be a gas sensor.

However, there are still limited studies on the gas sensing application of the SnO_2 films deposited from precursor TMT by CVD method. Among the researches, Larciprete *et al.* (1998) and Lancock *et al.* (2005) had utilised the laser technology in the CVD. Meanwhile, Wei *et al.* (1999) and Zhao *et al.* (2000) had developed undoped and Th-SnO_2 films from TMT at 400 ^oC by using metallorganic chemical vapour deposition (MOCVD). The maximum sensitivity towards 300 ppm trimethylamine (TMA) was achieved at 330 ^oC for undoped SnO_2 and 290 ^oC for Th-SnO_2 with response value of 5.9 and 142 respectively. For sensing 300 ppm NH_3, the undoped and Th-SnO_2 films showed maximum sensitivity of around 2 at 200 ^oC and 10 at 280 ^oC. The films also exhibited linear relation between thickness and coating time. Similarly, Gao *et al.* (2005) also used MOCVD to develop SnO_2 films by bubbling helium gas through the precursor TMT. The deposition process was carried out at 500 ^oC for 1 hour. After testing with 3000 ppm CO, the film showed highest sensitivity of around 23 at sensing temperature of 200 ^oC, which is relatively lower than the commercial SnO_2 sensor. Besides, Semancik *et al*. (2001) also produced SnO_2 and Pt-SnO_2 films at 480 ^oC under the pressure of 0.8 kPa by LPCVD, in which the films were well responded to H_2 and methanol gas.

There are also other researches used TMT as precursors to deposit SnO_2 based layers by using other methods other than CVD such as plasma polymerisation (Inagaki *et al.*, 1989), flame spray pyrolysis (FSP) (Rellinghaus *et al.*, 2003; Tricoli *et al.*, 2009) and combustion synthesis (Miller *et al.*, 2005; Bakrania *et al.*, 2007;

Bakrania and Wooldridge, 2009; Bakrania and Wooldridge, 2010). Some of them investigated the gas sensing application of the synthesised SnO_2.

Bakrania and Wooldridge (2009) synthesised the SnO_2 powder at temperature range of 227-1127 ^oC from TMT by using combustion synthesis method and then deposited the powder on alumina substrate. The sensors were used to detect 500 ppm CO and exhibited good sensor response value of 4 at sensing temperature of 330 ^oC. The sensors were further improved by doping Au (Bakrania and Wooldridge, 2010) in which the sensitivity increased to 16 for 500 ppm CO at sensing temperature of 330 ^oC. Meanwhile, Tricoli *et al.* (2009) produced SnO_2-TiO_2 films at temperature range of 140-160 ^oC from TMT by FSP method. Pure SnO_2 showed sensitivity of 50 towards 50 ppm of ethanol at 320 ^oC whereas SnO_2 with 3.7% Ti content showed sensitivity increment to 93 at the same sensing environment. Besides, Inagaki *et al.* (1989) also showed the good sensing properties towards CO, ethanol, methane, and propane gases under palladium chloride enhancement.

2.7 Effect of Coating Parameters

In general, in order to investigate the deposition process, three main coating parameters were chosen based own their own influence towards the synthesised films. These coating parameters which affect the film morphology, structure and thickness are coating temperature, coating time and annealing temperature.

2.7.1 Effect of Coating Temperature

Different coating temperature could produce films with different morphology and structure. For example, Dhere *et al.* (1999) who deposited SnO_2 films on substrate borosilicate from TMT precursor reported that the grain size and surface roughness of SnO_2 changed with the coating temperature. As the coating temperature increased from 550 ^{o}C to 600 ^{o}C, the respective grain size increased from 100 m to 120 nm meanwhile the Root-Mean-Square (RMS) surface roughness increased from 11.1 nm to 12.8 nm. Karslıoğlu *et al.* (2010) also reported similar results whereby different coating temperature changed the grain size of SnO_2 under fixed CVD time of 60 min. The grain size increased from 227 nm to 1155 nm as the coating temperature increased from 400 ^{o}C to 600 ^{o}C. Besides, it was also observed that the grains become rougher as the coating temperature increased. Other researches such as Khandelwal *et al.* (2009) showed that the structure of the deposited SnO_2 transformed from amorphous to polycrystalline SnO_2 as the coating temperature increased. Such transformation is sensing favourable. Since the grain size, surface roughness and crystallinity are the important factors to determine the performance of the deposited films, the coating temperature of the deposition process become an important parameter.