DEVELOPMENT OF WO_3 CATALYTIC FILM FOR DETECTION OF ETHANOL

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DEVELOPMENT OF WO_3 CATALYTIC FILM FOR DETECTION OF ETHANOL

By

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LIST OF ABBREVIATIONS

AACVD	Aerosol assisted chemical vapor deposition
AFM	Atomic force microscope
Al_2O_3	Aluminium oxide or alumina
APCVD	Atmospheric-pressure chemical vapor deposition
Ar	Argon gas
Au/Pd	Gold/palladium
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
CVD	Chemical vapor deposition
E_g	Band gap
EDX	Energy dispersive X-ray spectroscopy
Fe_2O_3	Iron (III) oxide
FID	Flame ionization detector
FESEM	Field emission scanning electron microscope
FWHM	Full width at half maximum
GC	Gas chromatography
GPIB	General purpose interface bus
H_2S	Hydrogen sulfide
ICDD	International Centre for Diffraction Data
ICSD	Inorganic Crystal Structure Database
In_2O_3	Indium oxide
LPCVD	Low pressure chemical vapor deposition
MOCVD	Metallorganic chemical vapor deposition
MOD	Metal organic deposition
NH_3	Ammonia
NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
NO_x	Nitrogen oxides
O_2	Oxygen gas
O_3	Ozone

OFAT	One-factor-at-a-time
PECVD	Plasma enhanced chemical vapor deposition
PID	Photoionization detector
ppb	Parts per billion
ppm	Parts per million
rms	Root mean square
RSM	Response surface methodology
SiO_2	Silicon dioxide
TEAM	Total exposure assessment methodology
TiO_2	Titanium oxide
U. S. EPA	United State Environment Protection Agency
UV	Ultraviolet
VOC	Volatile organic compound
VOCs	Volatile organic compounds
WCl_6	Tungsten hexachloride
$W(CO)_6$	Tungsten hexacarbonyl
$WOCl_4$	Tungsten (VI) oxytetrachloride
WO_3	Tungsten oxide
XRD	X-ray diffraction
ZnO	Zinc oxide

LIST OF SYMBOLS

SYMBOL	MEANING	UNIT
D	Average crystallite size	Å or nm
e^-	Electron	Dimensionless
eV	Energy barrier	kJ/mole
k	Bolztmann constant	Dimensionless
R	Resistance	Ohm (Ω)
R_a	Resistance in air	Ohm (Ω)
R_g	Resistance in VOC	Ohm (Ω)
S	Sensitivity	Dimensionless
T	Temperature	^oC
β	Full width at half maximum	Dimensionless
λ	Wavelength of the x-ray source	Å
θ	Bragg's angle	Dimensionless

PEMBANGUNAN FILEM BERMANGKIN WO_3 BAGI PENGESANAN ETANOL

ABSTRAK

Filem tungsten oksida (WO_3) yang diendapkan atas substrat alumina telah disediakan melalui pengendapan wap kimia (CVD) dengan menggunakan serbuk hexacarbonyl tungsten ($W(CO)_6$) sebagai prapenanda. Pencirian struktur dilakukan dengan menggunakan pembelauan sinar-X (XRD), pengimbasan mikroskop elektron (FESEM) dan mikroskop daya atom (AFM). Respon filem WO_3 terhadap pengesanan 500 ppm wap etanol telah dikaji pada suhu operasi antara 150 hingga 550^oC. Pengoptimuman terhadap parameter persediaan telah dilakukan dengan menggunakan teknik satu faktor-pada-satu-masa. Keputusan menunjukkan kepekaan filem WO_3 berubah mengikut keadaan persediaan termasuk suhu pengendapan (200^oC-350^oC), suhu penyepuhlindapan (500 hingga 700^oC) dan nisbah $Ar(W(CO)_6)/O_2$ (1/6 hingga 1/3).

Keputusan menunjukkan bahawa filem WO_3 yang diendapkan pada suhu 350^oC dengan suhu penyepuhlindapan 600^oC dan nisbah gas aliran $Ar(W(CO)_6)/O_2$ 1/6 adalah filem sensor yang terbaik dengan suhu operasi optimum 450^oC. Filem sensor ini dikaji dengan lanjut di bawah pelbagai keadaan operasi seperti suhu operasi (150^oC-550^oC) dan kepekatan wap etanol (500 ppm-3000 ppm) masa respon dan pemulihan, kememilihan dan akhir sekali kestabilan sensor gas. Didapati bahawa sensor filem WO_3 ini lebih memilih terhadap wap etanol daripada metanol dan aseton. Ianya juga menunjukkan masa respon yang pendek iaitu 12 saat dan masa

pemulihan yang singkat iaitu 134 saat. Kepekaan filem sensor meningkat dengan kepekatan wap etanol sehingga 2500 ppm dan kemudiannya kekal pada tahap kepekaan tersebut. Sensor tersebut juga mempamerkan kualiti kebolehulangan dan kebolehharapan yang tinggi selepas digunakan berulang-ulang selama 35 hari. Kajian ini telah menunjukkan filem WO_3 adalah sensor yang berpotensi bagi untuk pegesanan VOC.

DEVELOPMENT OF WO_3 CATALYTIC FILM FOR DETECTION OF ETHANOL

ABSTRACT

Tungsten oxide (WO_3) films deposited on alumina substrate were prepared by chemical vapor deposition (CVD) using tungsten hexacarbonyl ($W(CO)_6$) powder as precursor. The structural characterization was performed using X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and atomic force microscope (AFM). The responses of WO_3 films towards 500 ppm of ethanol vapor were investigated at operating temperatures of 150 to 550^oC. Optimization on the preparation condition parameters was performed using one-factor-at-a-time technique. The results showed that sensitivity of the developed WO_3 film varied according to its preparation condition which included deposition temperature (200 to 350^oC), annealing temperature (500 to 700^oC) and ratio $Ar(W(CO)_6)/O_2$ (1/6 to 1/3).

The results indicated that WO_3 film deposited at 350^oC with annealing temperature of 600^oC and gas flow ratio of $Ar(W(CO)_6)/O_2$ of 1/6 was the best sensor with the optimum working temperature of 450^oC. This sensor film was further investigated under various conditions such as operating temperature (150 to 550^oC) and concentrations of ethanol vapor (500 to 3000 ppm), response and recovery time, selectivity and lastly stability of gas sensor. It was found that the WO_3 sensor film was more selective to ethanol vapor than methanol and acetone. It also showed a short response time of 12 seconds and recovery time of 134 seconds. The sensitivity of the sensor film increased with concentration up to 2500ppm of ethanol vapor and

then it leveled off. It also exhibited high repeatability, reliable sensitivity after being used for up to 35 days. This study demonstrated the WO_3 films were potential sensors for the detection of VOCs.

CHAPTER ONE

INTRODUCTION

Air pollution caused by volatile organic compounds (VOCs) is major global environmental issue and this problem is now receiving much publicity from government and anti-air pollution groups. Dispersion of VOCs in atmosphere can cause harmful effects to human body, plantation and global environment. VOCs are primary contributors to indoor air pollution and have adverse impacts on health of peoples exposed (Luo et al., 2007). Most notable are the strong correlations between VOCs emissions and diversiform cancers (Boeglin et al., 2006).

Governments in many countries had tightened the environmental and safety regulations on VOCs as their toxic and hazardous nature make them dangerous to environment and humans. United State Environment Protection Agency (U. S. EPA) enlists VOCs as priority pollutants. The Clean Air Act and subsequent amendments are also designed to limit the use of chemicals which contained VOCs and setting limits for allowable VOCs emission for different industries (Scheiner, 2004). Therefore, it is necessary to detect and control VOCs around human beings especially in the indoor environment as most people spend more than 80% of the daytime in the indoor environment (Jiang et al., 2006).

1.1 Volatile Organic Compounds (VOCs)

1.1.1 Definition

The general definition of VOCs in the scientific literature is organic compounds which composition makes them to possible to evaporate under atmospheric conditions (EPA, 2010). Original definition of VOCs defined by U.S EPA is organic compounds in which its vapor pressure greater than 0.1 millimeter of mercury (EPA, 2010). Until December 29, 2009, U. S. EPA redefines the VOCs as any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions (EPA, 2010).

1.1.2 Emission Source

The emission sources of VOCs are originated from human-related (anthropogenic) and natural sources. Natural sources give rise to considerable ambient concentrations of organic compounds. Forests are the primary natural sources of VOC emissions and tropical forests are estimated to produce about half of all global natural VOC emissions (Ignatova, 2008). Another natural source included emission from plants, trees, wild animals, volcanoes and natural forest fire.

On the other hand, anthropogenic sources included solvent usage, transportation, industrial process, oil refining, agricultural, food manufacture and land filled wastes. The common consumer and commercial product that related to VOC emissions are paints, varnishes, wood preservatives, cleansers, disinfectants, air fresheners, pesticides, correction fluids, glues, permanent markers and so on. All of these products can release VOCs whenever be used or stored.

Figure 1.1 shows the estimation of VOCs emission by source sector in Canada in 2010. It has indicated that solvent use (32%) and transportation (25%) are the predominant sector contributors. They contributed 57% of total VOC emission for Canada. After that, residential/commercial fuel/wood combustion (17%) is the third largest contributors, followed by industrial sources (16%), fuel marketing (7%), others (3%) and electric power (<1%) (Figure 1.1).

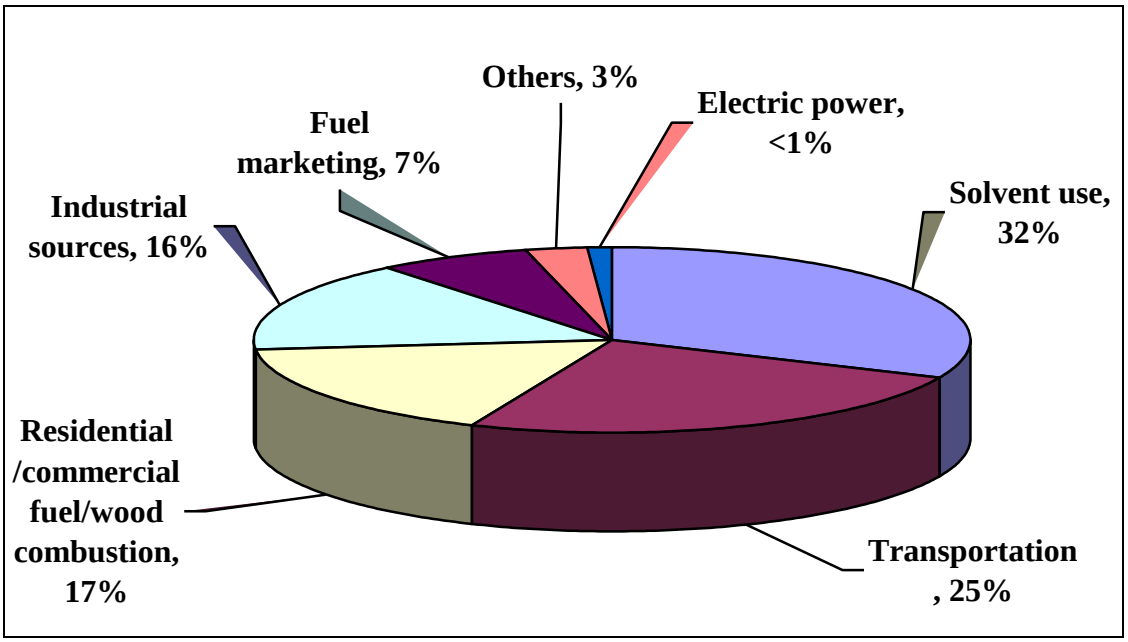


Figure 1.1: VOC emissions in Canada in 2010 (Government of Canada, 2010).

U. S. EPA's Office of Research and Development's Total Exposure Assessment Methodology (TEAM) found that concentrations of VOCs in indoor air are 2 to 5 times greater than in outdoor air (EPA, 2010). TEAM also indicated that people can expose themselves to elevated concentrations of VOCs persisted in the air long after the activity is completed while using products containing organic chemicals (EPA, 2010).

1.1.3 Human Health and Environmental Impact

VOCs such as methane have direct impact as green house gases which enhanced global warming by absorbing the infrared radiation. In addition, VOCs contribute significantly to the formation of ground-level ozone (smog) (EPA, 2010). VOCs react with nitrogen oxides in the presence of sunlight to form ozone. Although, ozone is beneficial in the upper atmosphere for protecting humans, plants, and animals from exposure to dangerous ultraviolet (UV) radiation, it poses a health threat in the lower atmosphere by causing serious respiratory problems (BAMA, 2011). Besides, high concentrations of low level ozone can also damage crops and buildings (BAMA, 2011).

Apart from these, exposure to VOCs can adversely affect to human health. The risk of health effects depends on level of exposure and length of time exposed (EPA, 2010). Short-term exposure to high levels of VOCs can cause eye, nose and throat irritation, headaches, nausea, vomit, dizziness, memory impairment, skin allergic and worsen the respiratory problem such as asthma (MDH, 2010). Long-term exposure to high levels of VOCs can cause cancer, liver damage, kidney damage and central nervous system damage (MDH, 2010). Many VOCs have distinctive odor which becomes a localized nuisance. For instance, pungent odor of formaldehyde (EPA, 2010). However, some of the VOCs with highly odor or annoyance under most circumstance are not necessarily harmful. For example, ethylene gas emitted when fruits reach full maturity (Nimittrakoolchai and Supothina, 2008).

1.2 Gas Sensor Technology

Gas sensor technology is an indispensable tool to create new technologies which are compatible with sustainable society. A variety of gas sensors had been developed so far. Real gas sensor era has started in 1970s where gas sensors were commercialized for non professional usage (Yamazoe, 2005). Over the past 20 years, extensive efforts have been done not only to improve gas sensor but also developed new gas sensor in order to meet market demand (Yamazoe, 2005).

A gas sensor is a device used to detect particular gas molecules and produces an electrical signal with a magnitude proportional to the concentration of the gas (Anuj Kumar and Sud, 2010). Due to the information obtained from this process is useful; gas sensor has found widespread applications in both domestic and industry. Table 1.1 shows examples of applications of gas sensors in various fields. Ideally, gas sensors should exhibit high sensitivity and fast response towards gas of interest. Sensors should also have stable and reproducible signal in order to reduce the time needed for calibrations. Other practical concerns such as minimizing size, weight as well as power consumption also exist.

Table 1.1: Applications of gas sensors (Tong et al., 2001a, Capone et al. 2003, Yamazoe, 2005)

Fields	Functions
Automobiles	• Car ventilation control • Filter control • Gasoline vapor detection
Safety	• Fire detection • Leak detection • Toxic/flammable/explosive gas detectors • Boiler control • Personal gas monitor
Indoor air quality	• Air purifiers • Ventilation control • Cooking control • Odor control
Environmental control	• Weather stations • Pollution monitoring
Food	• Food quality control • Packaging quality control (off-odours) • Fish freshness
Industrial production	• Fermentation control • Process control
Medicine	• Breath analysis • Disease detection

1.3 Types of Gas Sensors

There are five types of gas sensors, which are electrochemical gas sensors, catalytic combustible gas sensors, infrared gas sensors, photoionization gas sensors and solid-state gas sensors (Chou, 2000). These gas sensors are widely used as gas monitors for assessing air quality and safety of certain area. All of the gas sensors are also suitable to be used for detection of toxic and combustible gases. The use of gas sensors is crucial for human and property protection and process control.

1.3.1 Electrochemical Gas Sensors

Electrochemical gas sensors are devices used to detect target gas by react with target gas to produce an electrical signal with a magnitude proportional to the gas concentration. These kinds of gas sensors are able to monitor approximately 20 toxic gases at low concentration in ppm ranges. The best electrochemical sensors are for detection of O_2, which has good selectivity, reliable and long life expectancy (Chou, 2000). However, the cost of replacement of sensors is high, especially when the number of instruments in use is large (Chou, 2000).

1.3.2 Catalytic Combustible Gas Sensors

Catalytic combustible gas sensors are primarily used to detect combustible gas by causing an actual combustion of gases within sensor chamber (IST, 2008). The gas sensor will give an electrical signal with a magnitude proportional to the gas concentration as temperature changed. These sensors can last a long time because they are not used continuously (Chou, 2000). Catalytic sensors are also quite simple in design, easy to manufacture and inexpensive (IST, 2008). Yet, catalytic combustible gas sensor may deteriorate when exposed to excessive concentration of gases and extreme temperatures (IST, 2008). This sensor may lose its sensitivity or deactivate whenever exposed to certain chemicals such as sulphur, chlorine and heavy metal.

1.3.3 Infrared Gas Sensors

Infrared gas sensors measure trace gases by determining the absorption of an emitted infrared light through air sample. Infrared sensors often used to detect corrosive and reactive gases (IST, 2008). The major advantages of infrared gas sensors are the detector doesn't directly interact with the gas to be detected (Chou, 2000). Besides, the sensors have life expectancy on the order of 3 to 5 years. However, the numbers of gases which can be detected are limited. Moreover, it can be easily affected by humidity and water (IST, 2008). The dust and dirt can coat on the optics and impair the response of infrared sensor.

1.3.4 Photoionization Gas Sensors

The photoionization detector (PID) utilizes ultraviolet light to ionize the gas molecules. The ionized molecules are detected by applying high voltage and the current generated indicates the concentration of analyzed gases (Chasteen, 2009). PID offers fast response, high accuracy and good sensitivity towards low VOCs concentrations (IST, 2008). However, lamp window of PID requires frequent cleaning since the condition of the lamp window is critical to provide accurate reading (IST, 2008). In addition, the presence of high humidity can cause lamp fogging and decrease the sensor sensitivity (IST, 2008). Rapid variations in temperature at the detector, strong electrical fields, and naturally occurring compounds, such as terpenes in wooded areas, may affect instrument response.

1.3.5 Solid-state Gas Sensors

Solid-state gas sensors are also known as semiconductor gas sensors or metal oxide gas sensors. A solid-state gas sensor consists of one or more metal oxide from transition metals, such as tungsten oxide (WO_3), zinc oxide (ZnO) and so on (IST, 2008). The gas sensors can give electrical signal by the change of conductivity resulting from interaction between gas molecules and metal oxide surface. A heating element is always needed to heat up metal oxide to its operation temperature range that is optimal for gas to be detected (Chou, 2000). The main strength of the solid-state sensor is its long life expectancy (lasts 10 years or more) and versatility (monitoring of many different gases and ranges) (IST, 2008).

1.4 Problem Statement

Exposure to VOCs remains a public health issue despite of efforts to reduce the emission of these hazardous substances from many sources. Excessive exposure to VOCs can cause dizziness, irritation, skin allergy, nausea and even cancer. Development of novel VOCs detection devices are not popular until recently, when the devices have been studied intensively for domestic and industrial usage.

Numerous materials have been reported to be usable as metal oxide sensors such as tin oxide (SnO_2), titanium oxide (TiO_2), iron (III) oxide (Fe_2O_3), indium oxide (In_2O_3), ZnO and WO_3. Among these oxides, WO_3 has been proven to be attractive metal oxide owing to its high catalytic behaviour in redox reactions and promising electrical properties which enable it to be used for gas sensing applications (Eranna et al., 2004).

Gas sensors in the form of films seem to be more promising detectors over the pellet form, because they are potentially of low cost, rugged, and have low consumption of electric power (Eranna et al., 2004). Various synthetic approaches had been used to fabricate WO_3 films such as chemical vapor deposition (CVD) (Ashraf et al., 2008), screen printing (Khadayate et al., 2007a) and sputtering (Kim et al., 2000).

Among the above techniques, CVD method is preferred most due to its special features of good adhesion, flexibility according to shape of substrate, able to produce conformal and high purity films (Park and Sudarshan, 2001, Bessergenev et al., 2006). However, further researches on the utilization of CVD on the development of films sensor are still needed. The effects of several CVD parameters need to be researched since they can affect the microstructure of the films which in turn affect the sensitivity of the deposited films.

In present work, ethanol vapor was used as pollutants to be detected. In fact, detection of ethanol vapor is an important feature to monitor ethanol vapor in human breath or even to detect leaks in industrial distribution lines (Khadayate et al., 2007a). Furthermore, it have been reported that WO_3 is sensitive to mainly nitrogen oxide, however detection of ethanol vapor has not been extensively studied in WO_3 gas sensors. Hence, the aim of the present work is to develop and conduct detailed studies on WO_3 films for detection of ethanol vapor. CVD technique for preparation of WO_3 films was adopted.

1.5 Research Objectives

The objectives of the present work are as follow:

- To fabricate the CVD experimental rig for the deposition of WO_3 catalytic film on alumina as substrate.
- To develop WO_3 based catalytic films that can be used to effectively detect ethanol vapor.
- To characterize the WO_3 catalytic films in order to elucidate the physicochemical properties for better performance in VOCs detection.
- To determine optimum value of CVD parameters during preparation of WO_3 catalytic film in order to produce high sensitivity and reliable gas sensor.

1.6 Scope of Study

WO_3 was selected as sensing materials because of its high catalytic behaviour in redox reactions and promising electrical properties which enable them to be used for gas sensing applications (Eranna et al., 2004). The WO_3 films were prepared using tungsten hexacarbonyl ($W(CO)_6$) as precursor via CVD methods. CVD was chosen due to its special features of good adhesion, flexibility according to shape of substrate, able to produce conformal and high purity films (Park and Sudarshan, 2001, Bessergenev et al., 2006).

WO_3 film was prepared at atmospheric pressure by pyrolysis of tungsten hexacarbonyl, $W(CO)_6$ vapor in an O_2 stream. The parameters investigated during preparation of WO_3 films using CVD were effect of deposition temperatures, annealing temperatures and gas flow ratio of $Ar(W(CO)_6)/O_2$ (ratio of argon flow

rate through the $W(CO)_6$ precursor ($Ar(W(CO)_6)$ to O_2 flow rate). Optimization was carried out using one-factor-at-a-time approach in order to obtain the best condition to prepare WO_3 film which can be used to detect ethanol with high sensitivity. The structural characterization was performed using XRD, FESEM and AFM in order to obtain its physiochemical which could be further correlated with sensitivity of the WO_3 films sensor.

The gas sensing behaviors were observed in the existing gas sensor measurement rig. Ethanol was used as model organic pollutants to be detected. The parameters studied for gas sensing performance of the optimum WO_3 film were operating temperatures (150-550^oC), concentrations of ethanol vapor (500-3000 ppm), response and recovery time, selectivity towards different kinds of VOC vapors (ethanol, acetone and methanol) and sensor stability.

1.7 Organization of the Thesis

There are five chapters covered in the thesis and each chapter describes the detail of the research study.

Chapter 1 (Introduction) provides a general overview of thesis. This chapter gives brief introduction, definition of VOCs, emission sources and their impact towards human and environment. Then, the current gas sensor technology to control and monitor the VOCs is also described in detail. The chapter also enclose problem statement, objectives and scopes of study. And finally, organization of the thesis winds up the first chapter.

Chapter 2 (Literature Review) consists of survey of published literature on the theory and work that has been done on the research topic. The brief explanation on metal oxide semiconductor gas sensor provides the lead in to this chapter. This is followed by review on WO_3 among other metal oxide gas sensor. In this section, structural and gas sensing properties of WO_3, sensing mechanism and gas sensor based on WO_3 are briefly reported. Besides, some preparation methods for WO_3 gas sensor which commonly used by other researchers are also covered in this chapter.

Chapter 3 (Materials and Experimental Methods) describes experimental details of the study. It covers the details of chemicals and materials used throughout the experiments. Brief description of CVD experimental rig setup, WO_3 films preparation, WO_3 films characterization, WO_3 films sensing performance measurement, optimization and parameter studies in preparation and detection activity are also reported in this chapter.

Chapter 4 (Results and Discussion) comprises of results and discussions of the study. Effect of parameters on preparation of sensing materials and detection activity are discussed. Besides, the results from materials characterization such as crystallinity, crystal size, surface morphology, grain size, thickness and surface roughness are further discussed correlated with sensing performance.

Chapter 5 (Conclusions and Recommendations) gives the overall conclusions of the results obtained in the present study. Several recommendations for future studies as a continuation to the present one are also included in this chapter.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Gas sensors are used extensively for the purpose of practical applications, such as gas leak detectors and environmental monitoring. Since Taguchi developed metal oxide based sensors (Taguchi-type sensors) into an early industrial product, a lot of technological efforts have been made in this field, aiming at improvements in sensitivity, selectivity, stability and feasibility for practical use (Yamazoe et al., 2003). Due to the fact that the adsorption of gas on metal oxide surface can bring about a significant change in electrical resistance of the material, there has been a sustained and successfully effort to make use of this change for purpose of gas detection. The detection of toxic pollutant gases, combustible gases and organic vapors is a subject of growing importance in both domestic and industrial environments.

The present study is focused on the development of metal oxide semiconductor gas sensor based on WO_3 to detect ethanol. A brief review of metal oxide semiconductor gas sensors is provided in this chapter. It aims to give first vision of metal oxide semiconductor gas sensor. Then, the WO_3 gas sensors are discussed thoroughly with particular focus on their structural and gas sensing properties, gas sensing mechanism and gas sensing application. Next, some preparation methods that are commonly used to prepare WO_3 films as well as precursor used in the CVD method are reported.

2.2 Metal Oxide Semiconductor Gas Sensor

In recent years, much attention has been given to semiconductor gas sensors based on metal oxides in the detection and monitoring toxic pollutants and hazardous gases leakage due to its advantages of reliability, inexpensive, lightweight, long operating life, structural simplicity and easy implementation (Chung et al., 1999, Arshak and Gaidan, 2005, Ruiz et al., 2005, George et al., 2010). Simple metal oxide such as WO_3, SnO_2, ZnO, TiO_2 and In_2O_3 are well known for decades to be good gas sensing materials. The growing number of papers reporting on these successful applications showed their important roles in gas sensor field (Carotta et al., 1999, Lee et al., 2000, Khadayate et al., 2007a, Waugh et al., 2008).

The key factor that makes metal oxide suitable to be used as gas sensor is electro-physical properties (Sofian et al., 2009). Big band gap (E_g) and small activation energy is an optimal combination parameters for the materials designed for semiconductor gas sensors (Korotcenkov, 2007). This correlation of activation energies is necessary to avoid sensor operate in the self-conductance region. Korotcenkov (2007) also reported that for semiconductor gas sensors, the optimal band gap must be higher than 2.5 eV in order to operate at the temperatures exceeding 300^oC. The opportunity to operate at higher temperature is an important advantage since this fact allows reducing the influence of air humidity on gas sensing characteristics (Korotcenkov, 2007). Furthermore, big band gap is also an advantage for metal oxides with ionic conductivity due to the contribution of electron conductivity in sensing material is reduced especially at high operating temperature (Korotcenkov, 2007).

There are two types of semiconductors which are n-type and p-type (George et al., 2010). The n-type semiconductor has majority charge carriers are electrons. Interaction with reducing gas results in increase of conductivity whereas interaction with oxidizing gas results in decrease of conductivity (George et al., 2010). In contrary, the p-type semiconductor consist mainly positive charge carriers; hence, the opposite effects are observed during interaction with oxidizing and reducing gas (George et al., 2010). A summary of the response is provided in Table 2.1.

Table 2.1: Sign of resistance change (increase or decrease) according to change in gas atmosphere (George et al., 2010).

Classification	**Oxidizing Gases**	**Reducing Gases**
n-type	Resistance increase	Resistance decrease
p-type	Resistance decrease	Resistance increase

In general, n-type oxides are thermally stable and have possibility to work at lower O_2 partial pressure (Korotcenkov, 2007). On the other hand, p-type oxides are relatively unstable because of their tendency to exchange lattice O_2 easily with air (Korotcenkov, 2007). However, it does not mean that p-type oxides are not applicable for sensor design. For example, there is research based on $SmCoO_3$ (p-type) as O_2 and CO_2 gas sensor design (Michel et al., 2007). $Cr_{2-x}Ti_xO_{3+z}$ (x=0.01-0.45) (CTO) (p-type) gas sensor also showed excellent material for NH_3 detection (Wollenstein et al., 2002). It is able to detect NO_2, CO, and CH_4 as well. Besides, interaction with reducing gas decreases the resistance of n-type oxides is preferred direction contributing to the simpler compatibility with peripheral measuring devices and better reproducibility of output signal (Korotcenkov, 2007).

WO_3 is intrinsically n-type semiconductor because it is typically sub-stoichiometric due to O_2 vacancies. The existence of O_2 vacancies causes electron donor states to be formed, resulting in the presence of charge carriers in the film, thus increasing the conductivity of the film (Godwin, 2005). Most target gases are able to be detected due to their influence on the O_2 stoichiometry of the surface (Godwin, 2005). Figure 2.1 shows physical model and band model of a metal oxide gas sensor. The O_2 molecules in the air are adsorbed onto the surface, forming oxygen ions (O^-) by capture free electrons from conduction band resulting depletion region in the grain boundary as shown in Figure 2.1.

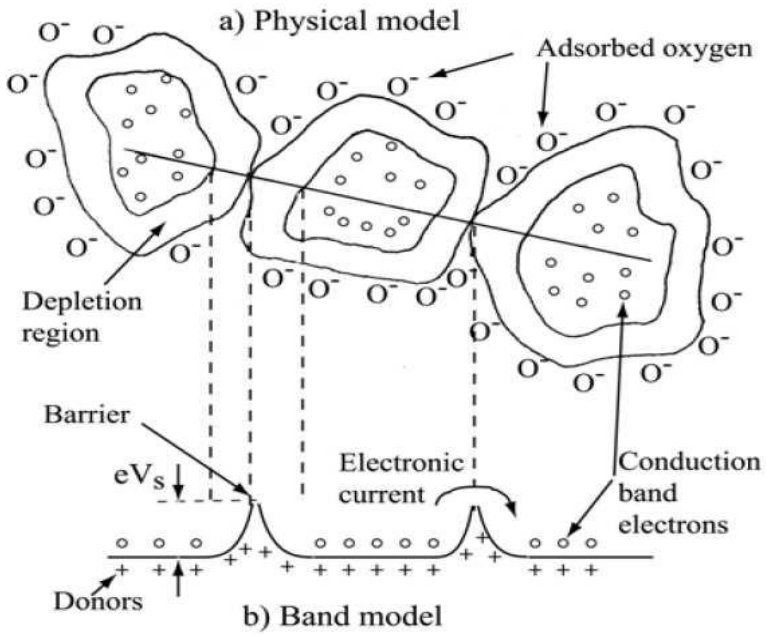


Figure 2.1: Physical model associated with band model of the grains of a metal oxide sensing layer (Godwin, 2005).

2.3 Tungsten Oxide among Metal Oxides for Gas Detection

Since Heiland, Bielanski and Seiyama discovered the gas sensing capabilities of metal oxides (Graf et al., 2006), and since Taguchi developed metal oxide based sensors, a lot of different metal oxides have been proposed for gas detection (Graf et al., 2006). Among these metal oxides, SnO_2 is particular attractive and has received much attention due to its reactivity toward many gaseous species, but this characteristic also revealed that SnO_2 is lack of selectivity, and thus investigation on other metal oxides has been considered necessary (Gallardo, 2003).

Figure 2.2 displays the number of published papers on gas sensors based on SnO_2, WO_3, In_2O_3, TiO_2 and ZnO. It clearly shows that SnO_2 receives most attention than other metal oxides. However, the number of papers for WO_3 has been increasing leading this material to become second most metal oxide semiconductor studied for gas sensing applications.

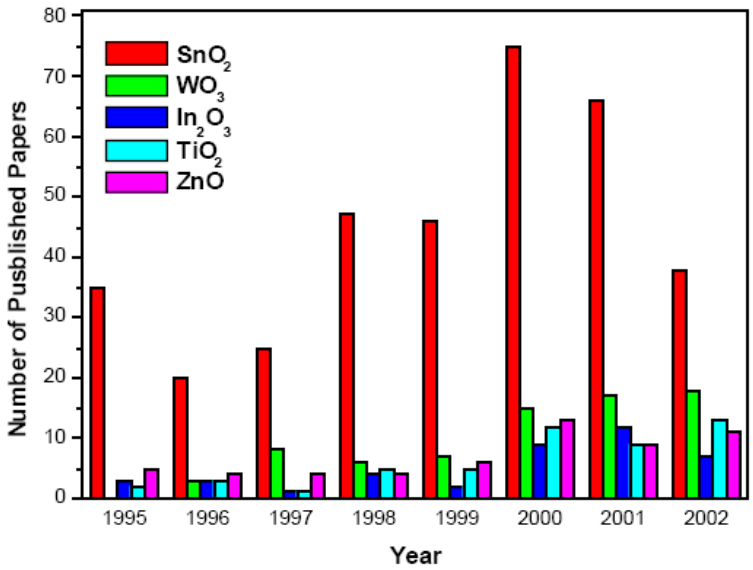


Figure 2.2: Comparison of the published papers on different metal oxide semiconductor gas sensors (Gallardo, 2003).

2.3.1 Structural and Gas Sensor Properties on WO_3

2.3.1(a)Crystalline Structure

WO_3 exhibits a cubic perovskite-like structure based on the corner sharing of WO_6 regular octahedra, with the O atoms (W atoms) at the corner (centre) of each octahedron as shown in Figure 2.3 (Godwin, 2005).

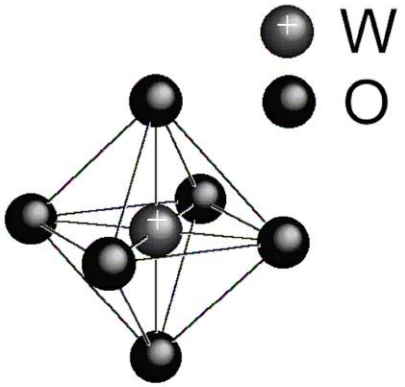


Figure 2.3: Schematic of crystalline WO_3 in the undistorted cubic phase. The unit octahedron presents the tungsten atom at the centre and 6 equivalent O_2 atoms at the corner (Godwin, 2005).

WO_3 adopts 5 structural transformations between absolute zero and its melting point (1700 K). When the temperature is decreased from the melting point, WO_3 undergoes various phase transition which occur in a sequence (i) tetragonal, (ii) orthorhombic, (iii) monoclinic, (iv) triclinic and (v) monoclinic. A summary of these transitions is given in Table 2.2.

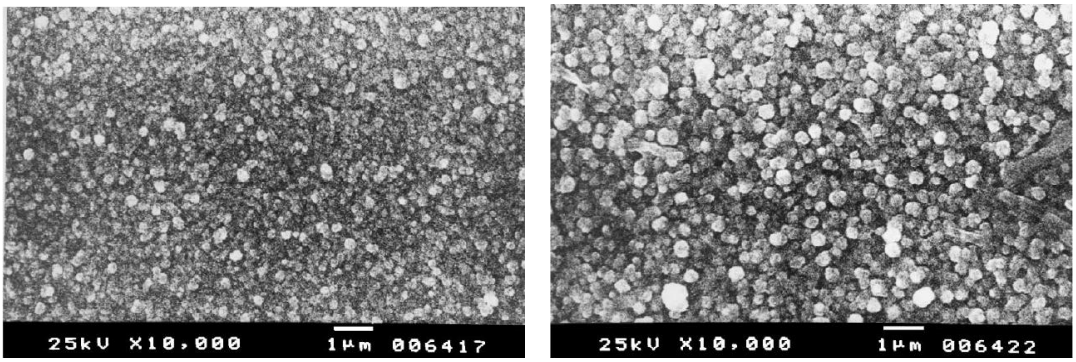
Table 2.2: Known polymorphs of WO_3 (Gallardo, 2003).

Phase	Structure	Temperature range (K)
α- WO_3	Tetragonal	1010-1170
β- WO_3	Orthorombic	600-1170
γ- WO_3	Monoclinic	290-600
δ- WO_3	Triclinic	230-290
ε- WO_3	Monoclinic	0-230

One of the most elementary defects in WO_3 as in most metal oxides is the lattice O_2 vacancy where an O_2 atom is absent from a normal lattice site (Gallardo, 2003). From an electronic point of view, an O_2 vacancy causes an increase in the electronic density on the adjacent metallic tungsten cations, leading to the formation of donor-like states slightly below the edge of the conduction band of the oxide (Godwin, 2005). This results in the oxide acquiring semiconducting properties.

2.3.1(b)Surface Morphology

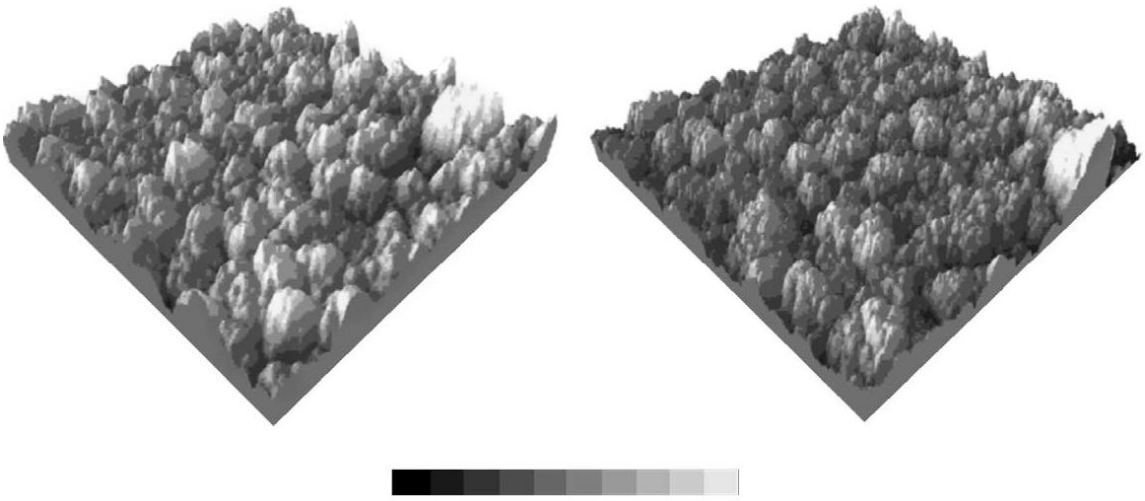
In order to study structure and surface morphology of WO_3 films, SEM and AFM are employed. Since SEM is capable of producing high-resolution image of surface, therefore, grain sizes as well as surface morphology of WO_3 films are able to be judge through SEM image. Figure 2.4 shows top view SEM image of as-deposited and annealed WO_3 films which prepared by CVD method (Tanner et al., 2003). They reported that, average grain sizes of films increase was observed after underwent annealing process. The increment of mean grain size was closely related to annealing process in which induced the grain growth of the sensing layer (Chung et al., 1999). Besides, annealing leads to small degree of additional oxidation increasing slightly the total thickness of the films (Szekeres et al., 1999).



(a) (b)

Figure 2.4: SEM images of WO_3 films: (a) as-deposited at 400^{o}C and (b) following subsequent annealing at 500^{o}C in air for 1 hour (Tanner et al., 2003).

The surface morphology and roughness are able to examined using AFM due to its ability to produce three-dimensional topography of film surface. Figure 2.5 shows the surface topographical images of annealed WO_3 films at (a) 400^{o}C for 1 hour and (b) 470^{o}C for 3 hour in 10^{-1} Pa of O_2 respectively (Tanner et al., 2003). As can be seen from Figure 2.5, the general morphology (irregularly distributed domed crystallites form surface termination with a somewhat lumpy appearance) of the film surface was unchanged (Tanner et al., 2003). The rough surface texture was confirmed by the relatively value of the root mean squared roughness, calculated from Figure 2.5 (a) as 40 nm following long annealing the root mean squared roughness increased by 20-30%, and in Figure 2.5 (b) corresponds to about 50 nm (Tanner et al., 2003).



(a) (b)

Figure 2.5: AFM scans of WO_3 films deposited at 200^{o}C followed by annealing process. The images correspond to a 5 mm x 5 mm area. (a) Image of the film annealed to 400^{o}C for 1 hour (b) Image of film following further annealed to 470^{o}C in 10^{-1} Pa of O_2 for 3 hours (Tanner et al., 2003).

Generally, it is necessary to use minimal grain size (Xu et al., 2000) and rougher surface (Saikaew et al., 2010) in order to maximize sensitivity. This is because increase of the grain size lead to the reduction of effective surface area of the sensor for target gas detection (Chung et al., 1999) while maximized the surface roughness will increase the effective sensor surface (Cricenti et al., 1996). Such behaviours of sensor characteristic led them to the conclusion that grain size and surface roughness plays an important role, but at the same time, it is not always determinative. Therefore, the choice of optimal grain size and surface roughness should be based on detailed consideration of all possible consequences of their influence on the parameters of sensor designed.

2.3.2 Sensing Mechanism

It is necessary to note that the gas sensing mechanism of metal oxide semiconductor gas sensor is complex. The gas sensing mechanism of metal oxide semiconductor gas sensor is generally dominated by bulk processes and surface processes (Rothschild et al., 2000). At high operating temperature (above ~600^{o}C), it involves bulk processes where the oxide defect chemistry equilibrates with the ambient O_2 pressure determining the carrier concentration and bulk electrical conductivity. At low operating temperature (below ~400^{o}C), it involves surface processes where chemisorptions of O_2 captures electrons from the metal oxide producing a depletion region and hence diminishing the surface conductivity.

The gas sensing mechanism is slightly different at different temperature regions. Since the operating temperature of WO_3 film is below 600^{o}C, it could be ensure that the gas sensing mechanism of WO_3 film belongs to surface processes. It is well known that the resistance of WO_3 sensors changed according to environment's reducing gas and amount of chemisorbed O_2 on the surface (Lee et al., 2000). In clean air, O_2 will be adsorbed on the surface of WO_3 when the sensor is activated by increasing temperature (Zhu et al., 2004). The adsorbed O_2 will trap free electrons from conduction band by its electron affinity and remained as O_2^-, O^-, or O^{2-} ions (Wang et al., 2001). These O_2 ion species form potential barrier in the grain boundaries which restricts the flow of electrons and hence increased the electric resistance of WO_3 sensor (Lee et al., 2000).