

# Chapter I

## Introduction



### 1.1 Why Gas Sensors?

We are now living in a continuously changing world with science and technology developments. Since the days of the industrial revolution, most of technological developments have been desired to respond the economical demands of human society. However, in today's world, two additional factors appear in defining the state of technology development: *health and environment*. As a result, new and powerful research areas have emerged in the awareness of health and environmental monitoring. To fulfill these requirements, the field of chemical sensors continues to be a topic of interest. The extensive pollution problems, especially in air, have been pushed a great effort in the developments of solid state gas sensors.

In recent years, many solid-state gas sensors have been developed to detect gaseous components. These devices have grown to support our civil life in various aspects. The applications of these devices are now not only concentrated in industrial applications but also extended to the area of environmental control and monitoring. Ever-increasing industrialization dramatically increases the number of gases to be covered by gas sensors. Some applications of gas sensors are summarized in Table 1.1. From the above reasons, it has become important to develop highly sensitive and selective gas sensors. The following lists give both constraints and requirements for an ideal gas sensors[1,2].

- high sensitivity
- chemical selectivity
- quick response
- small size (portability)

- simple operation
- simple fabrication
- high degree of linearity
- low power consumption
- long term stability
- microelectronics compatibility
- low cost

Table 1.1 Applications of gas sensors[3,60].

Application	Example
Gas detection	<ul style="list-style-type: none"> <li>-Measurements of CH<sub>4</sub> and CO in coal mining</li> <li>-Measurements of the content of inflammable or poisonous gases in air</li> <li>-Examination of exhaust gases from industrial factories and automobiles such as NO<sub>x</sub>, SO<sub>x</sub>, and CO<sub>x</sub></li> <li>-Control of air/fuel ratio in automobiles by monitoring O<sub>2</sub></li> <li>-Odor checkers</li> <li>-Alcohol checkers</li> </ul>
Gas alarm	-Gas leak detector for LPG, H <sub>2</sub> , freon, CH <sub>4</sub> and CO <sub>2</sub>
Home application	<ul style="list-style-type: none"> <li>-Automatic cooking control for microwave oven</li> <li>-Detection of the various volatile gases or smells generated from foods or food materials</li> <li>-Air purifier system in air conditioner</li> </ul>
Industrial application	<ul style="list-style-type: none"> <li>-Monitor of oxygen content in molten steel</li> <li>-Monitor of exhaust gases from refineries</li> <li>-Measurement of odor in liquor and perfume industry</li> <li>-Monitor freshness of meat, fish and fruit</li> </ul>

## 1.2 Chemical Gas Sensors

In general, a chemical sensor is a broad term used to call a sensor whose electrical properties are affected by the presence of chemical substances in gas-phase or liquid-phase, the change in electrical properties is observed and then used to detect the chemical substances[4]. Gas sensors are also classified into this type of sensors. Chemical sensors are very different from physical sensors in many aspects[5]. First, the number of chemical species to be detected is very high. Second, in a real situation, chemical sensors must be *open* to the medium which is to be measured.

This means that they are exposed to undesirable effects or interference such as light or corrosion.

The major advantages of chemical sensors are their simplicity in function, small size and projected low cost. The simplicity in function is in sharp contrast to the classical analysis techniques such as gas chromatography and mass spectroscopy, which require complex equipment and a skilled operator to perform an analysis. The projected cost is low because the size of sensor is small (typical measured in centimeters to micrometers). Moreover, the cost is further reduced by using the batch processes or microelectronics fabrication technology. However, comparing to the physical sensors, the chemical sensors still have some weak points such as lack of stability, lack of reproducibility, low selectivity (cross sensitivity) and insufficient sensitivity for certain applications.

As a chemical sensor, a gas sensor must have two basic functions: *receptor and transducer functions*[6-8]. The receptor function recognizes a particular gas species by using a chemical reaction between the gas species and the sensor material. The transducer function changes the gas recognition into an electrical or physical sensing signal. In general, the gas recognition is performed through gas-solid interactions such as adsorption, ion exchange and chemical reactions[9]. In contrast, the transducer function depends heavily on the materials utilized in the fabrication of gas sensors. For example, the gas recognition by semiconductor gas sensors are conveniently transduced into a sensing signal through the electrical resistance changes of the sensor elements, while electromotive force, resonant frequency, optical absorption or emission etc. can also be used as sensing signals for other type of sensor materials. The basic configuration of a chemical sensor is shown in Fig. 1.1. Table 1.2 summarized a classification of gas sensors. This table also shows physical gas sensors which can detect gas species by monitoring the physical properties of the interest gases. Table 1.3 shows comparisons of performance of various chemical gas sensors.

Table 1.2 Classification of gas sensors[4,6,10,11]

Type	Name	Detection quantities	Principle	Applications
Chemical gas sensors	Catalytic gas sensor	Resistance	Inflammable gas contact combustion reaction heat	Inflammable gas
	Semiconductor gas sensor (surface conductivity)	Resistance	Migration of charge due to adsorption and desorption of gas from an oxidized semiconductor	CO <sub>2</sub> , H <sub>2</sub> , NH <sub>3</sub> , NO <sub>x</sub> , SO <sub>2</sub> , C <sub>2</sub> H <sub>5</sub> OH
	Semiconductor gas sensor (bulk conductivity)	Resistance	Vacancy control of metal oxide semiconductor by oxygen partial pressure	Automobile exhaust gas or O <sub>2</sub> content in air/fuel ratio
	Electrochemical sensor	Electromotive force	Charge induction or charge transfer by a chemical reaction of a specific gas and electrode	Dissolved gas in liquid, Exhaust gas, oxygen content in molten steel
	GasFET	Current	induced dipole or structural change by adsorbed mass species	CO <sub>2</sub> , NH <sub>3</sub> , C <sub>2</sub> H <sub>5</sub> OH
	QCM & SAW gas sensor	Resonant frequency	Mass loading effect by adsorbed molecular species	Odorants
	Optical gas sensor	Optical absorption or emission	Modulation of optical intensity by chemical reactions	NO <sub>x</sub> , H <sub>2</sub> , CO <sub>2</sub> , organic compound
	Non-dispersive IR analyzer	IR absorption	Absorption of infrared radiation by diatomic molecules	CO <sub>2</sub> , CO, NO, SO <sub>2</sub>
	Magnetic wind or paramagnetic oxygen meter	magnetic susceptibility	Alignment of magnetic moment under an applied magnetic field	O <sub>2</sub> , NO, NO <sub>2</sub>
	Capacitance meter	Capacitance	Change of dielectric constant by partial pressure at constant temperature	O <sub>2</sub> , N <sub>2</sub> , CO <sub>2</sub>
Physical gas sensors	Flame ionization detector	Amount of electricity	Ionization of hydrocarbon molecules in hydrogen flame	Hydrocarbon compound
	Thermal conductivity detector	Resistance	Temperature changes in a thermister or a heating wire due to thermal conductivity of gas	High-density gas

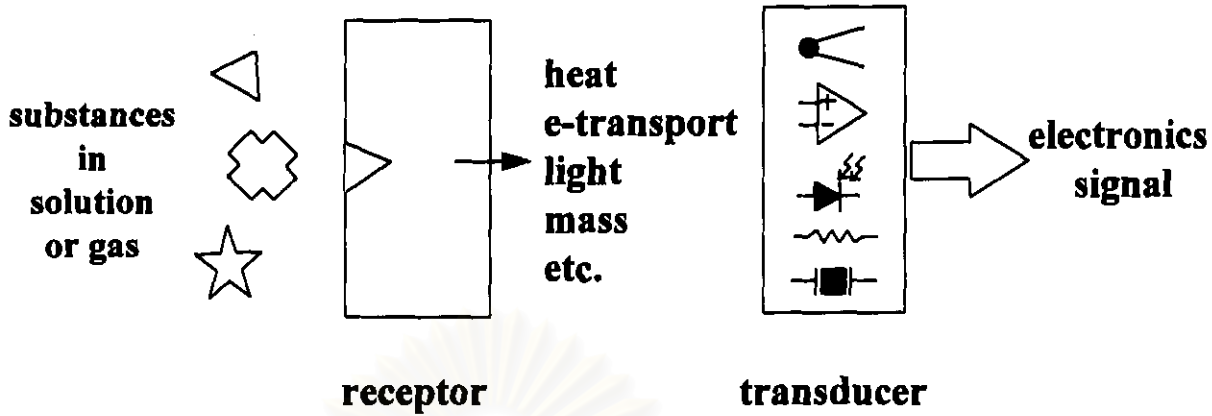


Fig. 1.1 Principle and Structure of chemical sensor.

Table 1.3 Performance of various chemical gas sensors.

Name	Sensor structure	Sensitivity	Selectivity	stability	cost	power consumption
Catalytic gas sensor	O	O	X	Δ	Δ	X
Semiconductor gas sensor	O	O	Δ	Δ	O	X
Electrochemical gas sensor	Δ	Δ	O	Δ	Δ	Δ
GasFET	Δ	Δ	Δ	Δ	O	Δ
QCM & SAW gas sensor	O	O	X	X	Δ	O
Optical gas sensor	X	O	O	Δ	X	Δ

O : good, Δ : fair and X : poor.

Among of chemical gas sensors, semiconductor gas sensors seem to be the most attractive one. Because, sensors in this form have many advantages[12,13] include small size, convenient operation using low-voltage power supplies, very high sensitivity in most applications, low cost, fast response and simple electronics interface. The disadvantages are continuous power loss for sensor heating, high operating temperature, sensitive to ambient temperature and the presence of long term drift. Semiconductor gas sensors now have been commercially available for many years. The dominant manufacturer is Figaro Engineering in Japan, the form of sensors

is sintered ceramic powder. In recent years, Motorola has launched a thin film type gas sensor using micromachining processes[14]. These sensors still have several problems, but for many applications, these problems are well compensated by their low cost of the sensors and by their high sensitivities in detection combustion gases (such as hydrogen or hydrocarbon in air).

### 1.3 Semiconductor Gas Sensors

Semiconductor gas sensors detect gas species in air by monitoring the change of electrical conductivity caused by gas adsorption. Indeed, there are many ways which gas ambient can change the conductivity of semiconductor materials. Some of these are unacceptable since they change the surface properties irreversibly, i.e., the growth of an oxide film. Normally the semiconductor gas sensors are designed to operate at the elevated temperature in air, and any non-oxide semiconductor such as silicon or germanium which is not a noble metal, tends to convert to the oxide form. To avoid the oxidation reaction, metal oxides such as ZnO and SnO<sub>2</sub> are commonly used[4,15].

Both of *n*-type and *p*-type semiconductor can be used for gas detection. This depends on the target gas to be detected, whether it is a reducing gas or an oxidizing gas. In the case of the reducing gas, *n*-type semiconductor is preferable. Since, the sensor resistance is decreased by the removal of chemisorbed oxygen when reducing gases come into contact with semiconductor surface. This direction of the resistance change is preferred for sensing reducing gases. However, when the interested gas is an oxidizing gas, the resistance change is in the reverse direction, i.e. the increase of the resistance. Thus, *p*-type semiconductor is more suitable for sensing oxidizing gases. However, many *p*-type oxides such as CuO and Ag<sub>2</sub>O are unstable in air at high temperature, since there is a tendency to exchange lattice oxygen easily with the air[4,9]. This mostly prohibits *p*-type semiconductor from the application to gas sensors, however there are some exceptions, for example NiO is a relatively stable *p*-type oxide.

Many oxides of *n*-type semiconductors show promising properties for gas sensing such as SnO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub>. ZnO and SnO<sub>2</sub> are the most extensively studied. But SnO<sub>2</sub> is currently the primary choice for fabrication of gas sensors[16,17], because it is chemically stable[4] and can be operating at moderate temperature (200 - 350°C)[18].

We can classify the structures of gas sensors into three main groups according to the fabrication techniques.

- sintered or ceramic type structure
- thick film type structure
- thin film type structure

Fig 1.2 shows the structures of semiconductor gas sensors. In the sintered type, semiconductor powder is coated on the outside of a ceramic tube. Inside the tube, there is a heating wire to control the operating temperature of the sensor. The electrical signals are measured through the gold electrodes which are deposited on the ceramic tube. The coating of the tube with the semiconductor is done by using the paste of semiconductor material.

A paste approach can be used to form a thick film gas sensor, often with a planar substrate of alumina with a pair of interdigitized electrodes. In this case, the heater element, for example a Pt thin film resistor or a silk screen printed RuO<sub>2</sub>, is normally located on the back-sided of the substrate[19]. With a paste or ink of the semiconductor materials, the thick film gas sensors can be prepared by screen printing[20] as shown in Fig. 1.2(b). This form of sensor now becomes more interested because its cheaper batch processes are possible.

Thin film gas sensors can be prepared by a vacuum evaporation[21-23], reactive sputtering[24], chemical vapor deposition (CVD)[25], spray pyrolysis[26] or sol-gel technique[27,28]. In the vacuum deposition techniques, multilayer structure are performed by deposition of heater, insulator, electrode and sensing membrane on the substrate (Fig. 1.2(c)). In another procedure, the heater is deposited on the back side of the substrate using a thick film RuO<sub>2</sub> heater or a Pt film resistor.

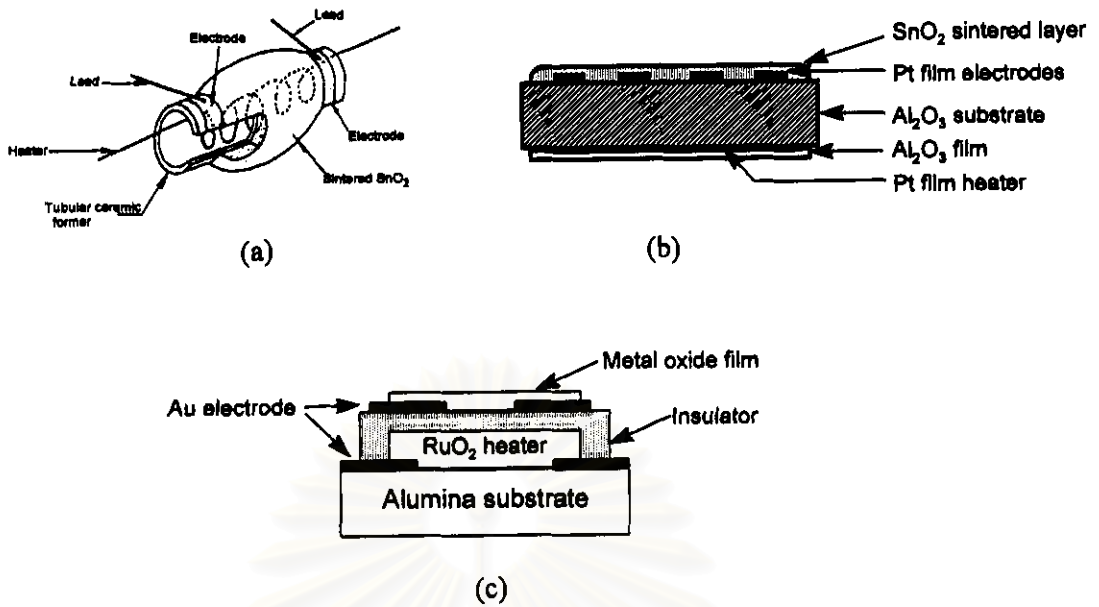


Fig 1.2 structure of semiconductor gas sensors, (a) sintered type, (b) thick film type and (c) thin film type.

In recent years, there is a much interest and a large motivation on fabrication of gas sensors in the thin film form, since there are many advantages such as ease of control process parameters, reproducibility, fast response, microelectronics compatibility and relatively low cost. Table 1.4 shows a comparison of sintered, thick film and thin film type gas sensors.

Table 1.4 Comparison of sintered, thick film, and thin film type gas sensors.[29]

Characteristics	Sintered	Thick film	Thin film
Manufacturing process	$\Delta$	$\Delta$	O
Reproducibility	X	$\Delta$	O
Microelectronics compatibility	X	$\Delta$	O
Sensitivity	O	$\Delta$	X
Power consumption	$\Delta$	$\Delta$	O
Fast response	X	$\Delta$	O
Cost	$\Delta$	$\Delta$	O

O : good,  $\Delta$  : fair and X : poor.



## 1.4 Material Preparations for Gas Sensors

The sensitivity and selectivity of a gas sensor are heavily dependent on the material preparations, the fabrication techniques and the history of heating processes. Thus, the material preparations are the important steps to obtain a high performance gas sensor. In general, there are many techniques which can be employed to prepare special ceramic materials. These special ceramic materials have led to novel applications of gas sensors. We can classify the preparation techniques[30] as in the following lists.

- 1) Chemical solution techniques
  - precipitation techniques
  - solvent evaporation and extraction techniques
  - sol-gel technique
- 2) Vapor phase reactions
- 3) Other techniques

The ceramic materials prepared from the above techniques have some benefit characteristics such as high purity, a precisely controlled and reproducible chemical compositions including dopants, chemical homogeneity on an atomic scale and a precise control of particle size.

In the sintered or thick film type gas sensors, most of semiconductor materials are usually prepared from the precipitation technique[4,15,31]. In this technique, catalysts can be introduced into the semiconductor powder before the final sintering process.

The vapor phase reaction techniques such as CVD are generally used to prepare semiconductor oxide in the thin film form. However, most measurements with these thin film sensors have been done without the addition of a catalyst. Because, it seems to be difficult to deposit both semiconductor and catalyst simultaneously. An alternative approach is to deposit a catalyst layer over an oxide

film and then follow with a thermally drive-in process[24,32] (*surface doped*). However, It is believed that the uniformly distributed catalyst film (*bulk doped*) will have a more improvement in selectivity and stability[33].

To obtain a well-uniform film, sol-gel technique is expected as one of the potential techniques due to its liquid nature. Any additive or dopant in the solution can also be added to the starting precursor and resulting in atomic level mixing. Moreover, the liquid nature makes the sol-gel technique have many unique characteristics[34,35] as follows:

- purity
- homogeneity
- ease of forming a variety of structure
- lower firing temperature
- much finer grain size

This technique also has some disadvantages including the much higher raw-material cost, large volume shrinkage during processing and longer material preparation processing times. The sol-gel technique will be described in more details in the next section.

#### **1.4.1 Sol-Gel Technique**

Sol-gel technique is a new, powderless ceramic processing method. It differs from the traditional forming methods utilizing ceramic powder such as solid-liquid processing (e.g., casting of dispersed suspensions, extrusion of concentrated pastes etc.). This method uses liquid precursors and therefore, avoids uses of powders. With many advantages of the liquid nature described in the previous section, this new method is especially emerging the formation of thin films for the application of high performance electrical and optical ceramics[38-40].

Sol-gel technique is broadly defined as the preparation of ceramic materials by starting from the preparation of a sol, gelation of the sol, and sintering the gel to ceramic[35-37].

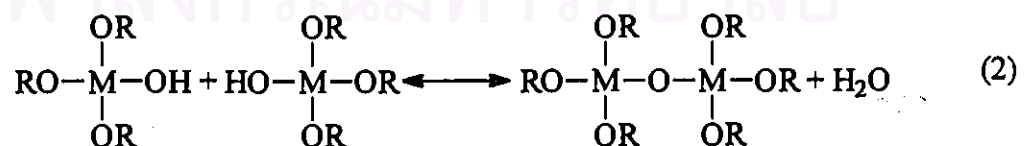
The sol-preparation, in essence, involves the dissolution of the required metal ions, either as alkoxides or other metallo-organic salts in a suitable alcoholic solvent, or as inorganic salts in an aqueous solvent to form the *sol*. The commonly used precursors are metal alkoxides,  $M(OR)_n$ . These compounds consist of a metallic cation bonded to alkyl groups through oxygen atoms. The sol-preparation is followed by the gelation step in which the fluid sol is transformed to a semi-rigid solid, so called *gel*. This process can be done by a number of different routes, resulting in either polymeric or colloidal gels, depending on the particular system. In the case of colloidal systems, gelation is controlled by electrostatic interactions between the colloidal constituents in the sol, while the formation of polymeric gels is determined by the chemical reactions, including hydrolysis, condensation and polymerization. Polymeric gels are almost extensively formed from the metal alkoxide based precursor solutions. A network of metal and oxygen bonds (M-O-M bonds) is formed by hydrolysis and condensation reactions which occur by addition of water to a solution of alkoxide in an anhydrous solvent. The reactions from alkoxide to polymer are schematically illustrated below:

*I) partial hydrolysis*

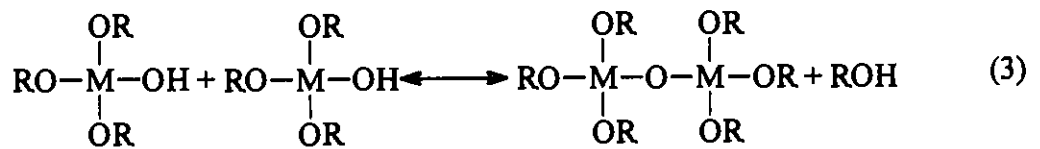


*II) condensation*

a) dehydration



## b) de-alcoholation



The mechanism and rates of the above reactions are very dependent on several factors, including pH, temperature, and water addition.

After forming the gel, conversion to an inorganic oxide structure is accomplished by a heat treatment process. The behavior of a gel under a heating process can be considered in three parts: i) drying and pyrolysis of organic, ii) structural rearrangement and densification, and iii) crystallization. The heat treatment can influence the structure of the ceramics. By suitably controlling the heat treatment, a variety of phase transformation can be obtained ranging from completely amorphous materials and partially crystallized glass-ceramics, to entirely crystalline ceramics.

### 1.5 Research Trends in Semiconductor Gas Sensors

The ultimate objective of the current research in semiconductor gas sensors is to develop ideal sensors which each responds to only one gas species. However, the research and development in this field are rather the combination between art and science. Most of research activities have been done trial and error to optimize sensor characteristics such as sensitivity, selectivity and stability. Few research have been done on the basic science approaches to study the mechanism of chemical reactions at the solid/gas interface[33,64,82]. In this section, a review on the researches in the field of semiconductor gas sensors is given briefly.

Lalauze et al.[41] studied the preparation and annealing conditions of SnO<sub>2</sub> compressed powder. Grain size and porosity are measured in term of the annealing

temperatures. The experimental results showed that the sensitivity of SnO<sub>2</sub> to CH<sub>4</sub> and

CO are somewhat affected by the annealing temperature. The another study of the same group[25] reported the effect of growth and annealing conditions in SnO<sub>2</sub> thin film prepared by CVD. A precise control of the deposition parameters, e.g. temperature, and total pressure, as well as appropriate annealing conditions, e.g. duration and temperature, can be done to modify the structural properties of the films such as grain size, thickness and stoichiometry. The correlation between the electrical conduction and the film structure were also discussed.

Many research have been performed to improve sensitivity and selectivity of gas sensors by incorporating additives or dopants into the oxide materials. The additives for catalysts/promoters include noble metals such as Pt and Pd and many oxides, for example transition metal oxide. Since, the catalyst materials must have a high thermal stability and not be changed to oxide upon heating. Table 1.5 summarizes a survey of some typical developments using different fabrication techniques, additives for the detection of different gas components with semiconductor gas sensors. The activity of the catalysts strongly depends on the size of their particles and their dispersion in the ceramic material. Matsushima et al.[49] examined three methods of incorporating Pd into a SnO<sub>2</sub> sensor. These methods were the standard impregnation with an acid solution of PdCl<sub>2</sub>, the deposition from a chloro-complex (the fixation method) and the colloid method. The observations by transmission electron microscope (TEM) revealed that the fixation method gave the finest dispersion of Pd or PdO on the surface of SnO<sub>2</sub>, followed by the colloid method and the impregnation method. The gas sensitivity to H<sub>2</sub> in air was also well correlated with the Pd dispersion.

Table 1.5 Typical fabrication technologies, additives and gas species of semiconductor gas sensors.

Material	Type	Additive	Gas	Reference
ZnO	single crystal	-	CO, CH <sub>4</sub> , H <sub>2</sub> , H <sub>2</sub> O	43
WO <sub>3</sub>	ceramic	-	NO <sub>x</sub>	7
WO <sub>3</sub>	ceramic	Au	NH <sub>3</sub>	7
SnO <sub>2</sub>	ceramic	CuO, SrO	H <sub>2</sub> S, CH <sub>3</sub> SH, (CH <sub>3</sub> ) <sub>2</sub> S, CO, HC, H <sub>2</sub>	42
SnO <sub>2</sub>	ceramic	ZrO <sub>2</sub>	H <sub>2</sub> S, H <sub>2</sub>	44
SnO <sub>2</sub>	ceramic	La <sub>2</sub> O <sub>3</sub> , Pd-La <sub>2</sub> O <sub>3</sub> , Pt-La <sub>2</sub> O <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> OH	45
SnO <sub>2</sub>	ceramic	-	HC	47
SnO <sub>2</sub>	ceramic	Pd	H <sub>2</sub>	49
SnO <sub>2</sub>	ceramic	MgO, CaO, SrO, BaO	C <sub>2</sub> H <sub>5</sub> OH	52
SnO <sub>2</sub>	thick film	BiO <sub>3</sub> , Pd	CO, CH <sub>4</sub> , H <sub>2</sub>	13
SnO <sub>2</sub>	thick film	-	CO, CH <sub>4</sub> , SO <sub>2</sub> , NO	20
SnO <sub>2</sub>	thick film	Pd	CO, CH <sub>4</sub>	46
SnO <sub>2</sub>	thick film	Pd, HP, TM	H <sub>2</sub> S, CO, CH <sub>4</sub>	48
SnO <sub>2</sub>	thick film	-	CCl <sub>4</sub>	50
SnO <sub>2</sub>	thick film	Sb, Pd, MgO, Ni <sub>x</sub> Si <sub>y</sub>	CO, H <sub>2</sub>	51
SnO <sub>2</sub>	thin film	Pd	R-OH, H <sub>2</sub> , CO, HC	21
SnO <sub>2</sub>	thin film	Pt	CO, H <sub>2</sub> , CH <sub>4</sub> , HC	22
SnO <sub>2</sub>	thin film	-	H <sub>2</sub> , CO, CH <sub>4</sub>	23
SnO <sub>2</sub>	thin film	-	CO, R-OH, HC	25
SnO <sub>2</sub>	thin film	CaO, Al	C <sub>2</sub> H <sub>5</sub> OH	32

The mechanism of various catalysts such as Pt, Pd, Ag etc. were investigated by Yamazoe et al.[53]. SnO<sub>2</sub> sensors doped with different substances were set in various atmospheres, and their electrical resistance was measured in term of temperatures. By consider the temperature at which gas sensitivity is maximum and the temperature of the catalytic oxidation of the sample gas, as well as x-ray photoelectron spectroscopy (XPS) measurements, two type of mechanisms, chemical and electronic, were discussed. Based on the XPS results, the catalytic reaction in the Ag-SnO<sub>2</sub> sensor, the electronic interactions appears to be more important than the chemical one, while in the Pd- and Pt-SnO<sub>2</sub> sensors, the chemical interaction (spill over) seemed to be more important.

While catalysts are added to semiconductor to improve the sensitivity and selectivity, binders are also added to provide a mechanically strong layer. Some of these can be tetraethylsilicate, silica sol, alumina or an organic binder. Yasunaga et al.[31] discussed the effect of tetraethylsilicate binders, in term of degree of polymerization (DP), on the long-term stability of SnO<sub>2</sub> sensors. SnO<sub>2</sub> sensor with a large DP exhibited a high gas sensitivity, while sensor with a smaller DP showed a better long-term stability and humidity insensitivity.

The operating temperature is also an another important parameter which can be adjusted to enhance the selectivity of gas sensors. It was observed that a SnO<sub>2</sub> sensor gives selectivity towards CO and alcohol at 300°C but not response to CH<sub>4</sub>, while at temperature of 500°C or above, SnO<sub>2</sub> sensor favors to response with CH<sub>4</sub>[13]. Thus it is possible to detect the certain compounds by the careful selection of operating the temperature of gas sensors as shown in Fig. 1.3.

The another way to improve selectivity of gas sensors is to use filters and membranes which act as diffusion barriers for interfering molecules or as catalytically active preconditioners. There are some reports that a carbon filter reduces interference from NO<sub>x</sub>, a metal membrane can be used to pass CO<sub>2</sub> in the presence of O<sub>2</sub>.

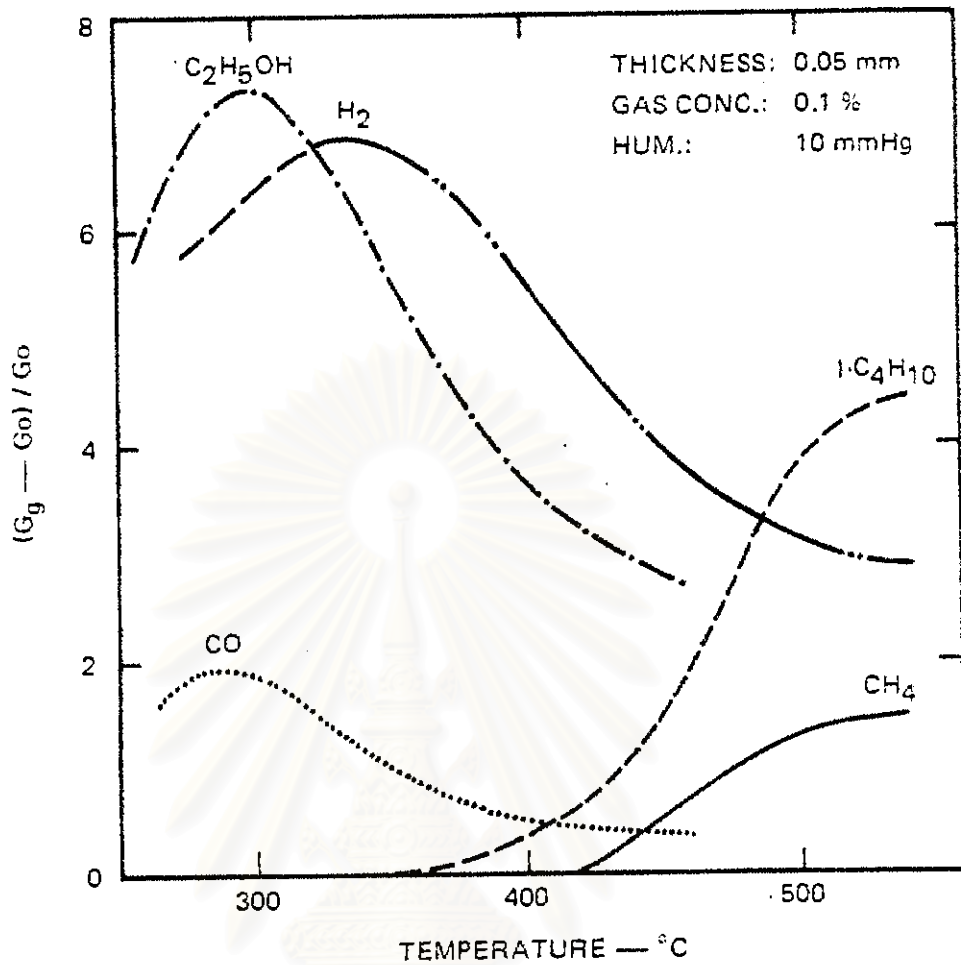


Fig 1.3 Temperature dependence of gas sensitivity for a thin layer sensor.

In recent years, pattern recognition techniques have been extensively adopted to improve selectivity and drift compensation of semiconductor sensors[59]. This can be achieved by making a system with sensor arrays. Each sensor has its own selectivity and different characteristics from each other. The cross sensitivity of different sensors can be used intentionally to monitor some specific components if suitable pattern recognition procedures are applied subsequently.

To elucidate gas sensing mechanism, various surface analysis techniques have been adopted to clarify gas-semiconductor interaction. Harrison and Willet[54] studied the mechanism which how CO interaction with SnO<sub>2</sub>. The surface species adsorbed onto SnO<sub>2</sub> at different temperatures was monitored by transmission infrared



spectroscopy while simultaneously measuring the electrical change produced in the bulk oxide. This study demonstrated the consistency of model in which conductance is effectively controlled by the population of negatively charged oxygen adsorbates. Ogawa et al.[55] discussed the electrical conduction model of SnO<sub>2</sub> thin film. The model described grain particles in SnO<sub>2</sub> film are melted together, connecting each others with necks, thus they formed a long, thin electrical conduction channel. The electrical channel width was determined by grain size and Debye length. This width could be modulated by the variation of O<sup>-</sup> ions adsorbed on semiconductor surface. Sriyudthsak et al.[56] examined the effect of oxygen content in air on the response characteristics of commercial gas sensors. The percentage of oxygen was varied by adjusting the ratio of oxygen-nitrogen in carrier gas. It was observed that the partial pressure of oxygen in carrier gas enhances sensitivity, dynamic range and reduces recovery time. The results were interpreted that the number of the active sites of gas sensing is controlled by the O<sub>2</sub> partial pressure in air. Clifford and Tuma[57,58] described many parameters of the Figaro sensors. The authors measured these parameters at various concentrations of O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, CO, H<sub>2</sub>O and their mixtures. They also examined how these parameters varied with the measurement temperature. The results indicated that the variation of the sensor conductance with the concentration of the tested gases can be predicted by a power law model ( $G \propto [C]^n$ ).

## 1.6 Purpose and Outline of the Study

The purpose of this thesis is to develop thin film SnO<sub>2</sub> gas sensors having high sensitivity and selectivity by utilizing the sol-gel technique. The study covers the preparation of tin alkoxide by chemical reactions, the deposition of uniform thin films and the characterizations of some important parameters of gas sensing performance such as thickness, operating temperature and additives. In addition, the study also includes the investigation of the effect of the external circuit components on the evaluation of gas sensing performance in the gas measuring circuit. The problems found in the conventional measuring circuit was pointed out and a novel circuit was proposed and developed to eliminate the problems found in the conventional circuit.

This dissertation consists of seven chapters. In chapter I, a brief outline about a classification of gas sensors, semiconductor gas sensors and sol-gel techniques including a short survey on semiconductor gas sensors is described.

Chapter II concerns with fundamental processes occurring at solid/gas interface. This chapter emphasizes on how semiconductor gas sensors can detect gaseous species. The description of the gas measuring system is given in chapter III. The details of each function in this system including gas control system, injector, test chamber and measuring circuit are discussed.

In chapter IV, the effect of external resistance on the calculated sensitivity and recovery time in the conventional measuring circuit is demonstrated. An analysis including a non-linearity of current-voltage characteristics of gas sensors has been carried out to predict the dependence of sensitivity and recovery time on the external circuit components. In order to eliminate these dependencies, a novel measuring circuit having a fixed bias concept is proposed and tested.

Chapter V describes an attempt to synthesize tin alkoxide by chemical reactions. This substance will be used as a starting material for preparing SnO<sub>2</sub> thin films. Many synthesis routes has been tried. In this chapter, the fabrication processes of gas sensors are also exhibited. In Chapter VI, the characterizations of gas sensing performance of the fabricated gas sensors are described. Finally, the conclusions of this dissertation work are given in Chapter VII.

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