

UNIVERSITI PUTRA MALAYSIA SENSOR CHARACTERISTIC STUDIES AND THERMAL DIFFUSIVITY MEASUREMENT OF TIN (IV) OXIDE-BASED CERAMIC GAS SENSORS

ROSYAINI AFINDI ZAMAN FS 2004 19



SENSOR CHARACTERISTIC STUDIES AND THERMAL DIFFUSIVITY MEASUREMENT OF TIN (IV) OXIDE-BASED CERAMIC GAS SENSORS

ROSYAINI AFINDI ZAMAN

MASTER OF SCIENCE UNIVERSITI PUTRA MALAYSIA

2004

SENSOR CHARACTERISTIC STUDIES AND THERMAL DIFFUSIVITY MEASUREMENT OF TIN (IV) OXIDE-BASED CERAMIC GAS SENSORS

By

ROSYAINI AFINDI ZAMAN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

December 2004

DEDICATION

Specially Dedicated to My Beloved Family And to My Beloved ONE ... Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

SENSOR CHARACTERISTIC STUDIES AND THERMAL DIFFUSIVITY MEASUREMENT OF TIN (IV) OXIDE-BASED CERAMIC GAS SENSORS

By

ROSYAINI AFINDI ZAMAN

December 2004

Chairman: Professor W. Mahmood Mat Yunus, PhD

Faculty : Science

The atmospheric pollution has lead to the research and development of a variety of sensors using different materials and technologies particularly for low cost and lower operating temperatures. An n-type semiconducting oxide such as tin oxide (SnO_2) is one of the most important and extensively used materials for the detection of gases.

In this project, the I-V characteristic and thermal diffusivity of pure SnO_2 and SnO_2 -CuO was studied. The I-V characteristic was measured using two-probe technique while the thermal diffusivity was measured using a photoflash method. The X-Ray Diffraction was used for identification of the phase in the sample and Scanning Electron Microscopy (SEM) was used to provide supportive evidence for the factor causing the changes of the parameters included. These methods are important to confirm the existence of SnO_2 peaks which is critical to CO_2 gas.

It was found that the I-V characteristics of sensor materials remain linear in a temperature range of 27 0 C – 340 0 C both in air and CO₂ environment. Sensor sensitivity was found to be dependent on temperature. Pure SnO₂ showed maximum

sensitivity (~ 2.5) at operating temperature 300 $^{\circ}$ C. Operating temperature is defined as the temperature that gas sensor give a maximum reaction (sensitivity) with tested gas. With addition of CuO into SnO₂, the gas sensing temperature and electrical conductivity of the sensor was found to decrease. The operating temperature also rapidly decreased from 300 °C (pure SnO₂) to 220 °C (addition of 40 mol% CuO). It is also observed that the annealing process has lowered the operating temperature of the sensor from 220 °C (sample as prepared) to 180 °C (samples annealed 600 °C, 700 °C and 800 °C). The effect of gas pressure on operating temperature did not change with increasing gas pressure but it showed higher sensitivity at higher gas The sensor response time was also studied as a function of SnO₂ pressure. composition and gas pressure. It was found that by increasing the gas pressure, the sensor response time decreased. The addition of CuO also has lowered the response time of SnO_2 from 10 minutes to 6 minutes. We found that 60 mol% SnO_2 - 40 mol% CuO system which annealed at 600 °C, 700 °C and 800 °C has the best sensing properties and lower operating temperature at 180 °C. In this study, thermal diffusivity of SnO₂ - CuO system and 60 mol% SnO₂ - 40 mol% CuO system was in range of 1.4 to 7.8 $\times 10^{-2}$ cm²/s.

Abstrak tesis ini yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

KAJIAN CIRI-CIRI SENSOR DAN PENGUKURAN PENYERAPAN TERMA SENSOR GAS SERAMIK BERASASKAN OKSIDA STANUM (IV)

Oleh

ROSYAINI AFINDI ZAMAN

Disember 2004

Pengerusi: Professor W. Mahmood Mat Yunus, PhD

Fakulti : Sains

Peningkatan pencemaran alam sekitar telah menggalakkan penyelidikan dan pembangunan dalam menghasilkan pelbagai pengesan (sensor) daripada bahan-bahan yang berbeza untuk mengurangkan kos dan menghasilkan pengesan pada suhu operasi yang rendah. Semikonduktor jenis n seperti Oksida Stanum (SnO₂) adalah satu bahan yang selalu digunakan dalam mengesan gas.

Dalam projek ini, ciri-ciri arus-voltan dan penyerapan terma ke atas SnO₂ and CuO-SnO₂ telah dikaji. Ciri-ciri arus-voltan ini dikaji menggunakan kaedah dua penduga sementara penyerapan terma dikaji menggunakan kaedah sinaran flash kamera. Belaun sinar-X telah digunakan untuk mengenal pasti fasa-fasa bahan di dalam sampel dan Elektron Mikroskop (SEM) telah digunakan bagi menyokong faktor perubahan parameter yang diukur. Kaedah-kaedah ini penting untuk memastikan kewujudan SnO₂ di mana ia penting di dalam tindak balas gas CO₂.

Didapati bahawa ciri-ciri arus voltan adalah lurus dalam julat suhu 27 $^{0}C - 340 ~^{0}C$ sama ada di udara atau CO₂. Tindak balas sensor didapati bergantung kepada suhu.

 SnO_2 menunjukkan tindak balas maksimun (~2.5) pada suhu 300 ⁰C. Suhu tindak balas di definisikan sebagai suhu di mana sensor gas bertindak balas secara maksimum (sensitiviti) dengan gas yang diuji. Penambahan CuO ke dalam SnO₂ mengurangkan suhu tindak balas dan kekonduksian elektrik. Suhu tindak balas berkurang daripada 300 °C (SnO₂) kepada 220 °C (dengan penambahan 40 mol% CuO). Proses rawatan haba juga mengurangkan suhu tindak balas daripada 220 °C (sampel yang disediakan) kepada 180 ^oC (sampel yang melalui perawatan haba pada suhu 600 °C, 700 °C and 800 °C). Masa tindak balas oleh SnO₂ berubah dengan komposisi bahan dan tekanan gas. Dengan meningkatnya tekanan gas, masa bagi sensor bertindak balas dengan gas berkurang. Penambahan CuO kepada SnO₂ telah mengurangkan tindak balas masa SnO2 daripada 10 minit kepada 6 minit. Didapati bahawa sistem 60 mol% SnO2 - 40 mol% CuO yang melalui perawatan haba pada suhu 600 °C, 700 °C and 800 °C mempunyai ciri-ciri pengesan terbaik dan suhu tindak balas paling rendah pada 180 °C. Dalam kajian ini kadar serapan terma bagi sistem SnO₂ - CuO dan sistem 60 mol% SnO₂ - 40 mol% CuO ialah dalam julat 1.4 to 7.8 x 10^{-2} cm²/s.

ACKNOWLEDGEMENTS

Bismillahirrahmanirrahim ...

First and foremost, I would like to extend my praise to Allah s.w.t. that gives me the patience, strength, determination, and courage to produce this thesis.

It is a great pleasure to acknowledge my supervisor, Prof. Dr. W. Mahmood Mat Yunus for his guidance, suggestion, assistance, patient, tremendous support and invaluable advice throughout the duration of this project. I would like also like to extend my sincere appreciation to my co-supervisor Assoc. Prof. Dr. Zainal Abidin Talib and Assoc. Prof. Dr. Mansor Hashim for their advice and helpful discussion during this period of study.

Special thanks to Assoc. Prof. Dr. Zaidan Abdul Wahab, Prof. Dr. Abdul Halim Shaari for their advice on setup arrangement and sample preparation. I would also like to thank all the staff in the Physics Department especially En. Roslim and En. Nordin for their help and co-operation given throughout my work.

I gratefully acknowledge the award of the PASCA Scholarship from Universiti Putra Malaysia, which enable me to undertake this work. Last but not least, my sincere thanks to all my friends, seniors and lecturers, especially to Yap, Linda, Yus, Josephine, Chia, Sabrina, Maznaliza, Liaw and Dr. Lim, who have directly or indirectly contributed towards the success of this study. Thank you for making my study of Master Science at UPM a memorable and enjoyable one.

May Allah bless and take care of you. In truth, Only Allah can reciprocate all the kindness.

Rosyaini Afindi Zaman, Physics Department, Faculty of Science, UPM. I certify that an Examination Committee met on 22nd December 2004 to conduct the final examination of Rosyaini Afindi Zaman on her Master of Science thesis entitled "Sensor Characteristic Studies and Thermal Diffusivity Measurement of Tin (IV) Oxide-Based Ceramic Gas Sensors" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

Mohd Maarof Mokhsin, PhD

Professor Faculty of Science Universiti Putra Malaysia (Chairperson)

Ibrahim Abdul Talib, PhD

Professor Faculty of Science and Technology Universiti Kebangsaan Malaysia (External Examiner)

Azmi Zakaria, PhD

Associate Professor Faculty of Science Universiti Putra Malaysia (Internal Examiner)

Jumiah Hassan, PhD

Faculty of Science Universiti Putra Malaysia (Internal Examiner)

> **GULAM RUSUL RAHMAT ALI, PhD** Professor/Deputy Dean

School of Graduate Studies Universiti Putra Malaysia

Date:

This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as partial fulfilment of the requirements for the degree of Master of Science. The members of the Supervisory Committee are follows:

W. Mahmood Mat Yunus, PhD Professor

Faculty of Science Universiti Putra Malaysia (Chairman)

Zainal Abidin Talib, PhD

Associate Professor Faculty of Science Universiti Putra Malaysia (Member)

Mansor Hashim, PhD

Associate Professor Faculty of Science Universiti Putra Malaysia (Member)

AINI IDERIS, PhD

Professor/ Dean School of Graduate Studies Universiti Putra Malaysia

Date:

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

ROSYAINI AFINDI ZAMAN

Date:

TABLE OF CONTENTS

Page

DEDICATION	ii
ABSTRACT	iii
ABSTRAK	v
ACKNOWLEDGMENTS	vii
APPROVAL	viii
DECLARATION	Х
LISTS OF TABLES	xiii
LISTS OF FIGURES	xiv
LISTS OF ABBREVIATIONS	xvi
LISTS OF SYMBOLS	xvii

CHAPTERS

1	INTR	TRODUCTION		
	1.1	Introduction	1.1	
	1.2	Tin Oxide (SnO ₂)	1.3	
	1.3	Carbon Dioxide (CO ₂)	1.5	
	1.4	Background of Electrical Properties Measurement	1.6	
	1.5	Thermal Diffusivity	1.7	
	1.6	The Objective of Study	1.8	
2	LITE	RATURE REVIEW		
	2.1	Introduction	2.1	
	2.2	The History of Gas Sensor	2.1	
	2.3	Sensing Characterization	2.2	
	2.4	SnO ₂ Gas Sensor	2.3	
	2.5	Measurement of Thermal Diffusivity Using Photoflash		
		Technique	2.8	
3	THE	ORY		
	3.1	Semiconductor Material	3.1	
	3.2	Ohmic Contact	3.2	
	3.3	Sensing Properties of SnO ₂ Ceramic Gas Sensor	3.3	
	3.4	Photoflash Technique	3.5	
4	MET	HODOLOGY		
	4.1	Sample Preparation	4.1	
	4.2	X-ray Diffraction Analysis	4.5	
	4.3	Microstructure Analysis	4.5	
	4.4	Sensing Characteristics System (SCS)	4.6	
		4.4.1 Experimental Procedure of Sensing Characteristic		
		System	4.13	
	4.5	Photoflash Technique	4.14	
		4.5.1 Experimental Procedure of Photoflash Technique	4.16	

A.1

B.1

5 **RESULTS AND DISCUSSION**

5.1	Introdu	iction	5.1
5.2	I-V Me	easurement Using Two-Probe Technique	5.1
	5.2.1	I-V Characteristic of Pure SnO_2 and SnO_2 - CuO	
		System at Different Temperatures	5.2
	5.2.2	The Effect of Gas Pressure on I-V Characteristic of	
		Pure SnO ₂ and SnO ₂ - CuO System	5.7
	5.2.3	The Influence of Annealing Temperature on I-V	
		Characteristic of 60 mol% SnO_2 - 40 mol% CuO	5.10
	a .	System	- 1 4
5.3	Sensing	g Characteristics	5.14
	5.3.1	Sensing Characteristic of Pure SnO_2 and $(SnO_2 - CuO)$	- 1 -
	5 2 2	System	5.15
	5.3.2	The Effect of Gas Pressure on Sensing Properties of	c 20
	5 2 2	$SnO_2 - CuO System$	5.20
	5.3.3	sensor Sensitivity of (60 mol% SnO ₂ - 40 mol% CuO)	5 24
5 1	Dognor	at Different Annealing Temperature	5.24
3.4	5 4 1	Pagnanga Tima of Dura SnO and SnO CuO System	5.20
	5.4.1	The Influence of G_{23} Prossure on Pospense Time of	3.28
	5.4.2	Pure SnO ₂ and SnO ₂ $-$ CuO System	5 3 1
	5 4 3	Effect of Annealing Temperature on the Sensor	5.51
	5.7.5	Response Time of 60 mol% $SnO_2 = 40$ mol% CuO	5 33
55	Therm	al Diffusivity	5 35
0.0	5 5 1	The Effect of CuO Composition on Thermal	0.50
	0.011	Diffusivity of SnO ₂ - CuO System	5.35
	5.5.2	The Annealing Effect on Thermal Diffusivity of 60	
		mol% SnO ₂ - 40 mol% CuO System	5.39
		- 5	
CON	CLUSIC	DN	
6.1	Conclu	ision	6.1
6.2	I-V Me	easurement Using Two-Probe Technique	6.1
6.3	Sensing	g Characteristics	6.2
6.4	Respor	nse Time Characteristics	6.3
6.5	Therma	al Diffusivity	6.4
6.6	Recom	mendation	6.5
FEREN	CES		R.1

REFERENCES APPENDIXS BIODATA OF THE AUTHOR

6

LIST OF TABLES

Table

1.1	Material gas response and response temperature	1.3
1.2	Material of CO ₂ gas sensors	1.6
2.1	Key solid-state gas sensor R&D Papers	2.7
4.1	Resistance value of the resistor (0.56 k Ω , 1.5 k Ω , 10 k Ω)	4.11
5.1	Response time with different SnO ₂ - CuO composition	5.30
5.2	Response time of 60 mol% ${\rm SnO}_2$ - 40 mol% CuO at different annealing temperature	5.34
5.3	Characteristics rise time and the corrected thermal diffusivity value of SnO_2 - CuO at different composition	5.37
5.4	Characteristics rise time and the corrected thermal diffusivity value of 60 mol% SnO_2 - 40 mol% CuO at different annealing temperature	5.41

Page

LISTS OF FIGURES

Figure		Page
1.1	The structure of SnO ₂	1.4
1.2	The structure of CuO	1.5
3.1	Resistivity scale of materials found in nature	3.2
3.2	Model of n-type semiconductor grains (a) Physical model of three contacting grains are shown to illustrate how depletion region dominates the intergranular contact (b) Band model corresponding to Figure 3.1 (a)	3.5
4.1	Flow chart for sample preparation	4.4
4.2	The front panel of the data acquisition program	4.9
4.3	Block diagram of the data acquisition program	4.10
4.4	The I-V characteristics of resistor (0.56 k Ω , 1.5 k Ω , 10 k Ω)	4.10
4.5	(a) Schematic diagram of chamber	4.12
	(b) Schematic diagram of sample	4.13
4.6	Schematic diagram of the I-V characteristic experiment	4.14
4.7	Schematic diagram of the photoflash experiment	4.15
5.1	I-V characteristics of pure SnO_2 at different temperature in (a) air and (b) CO_2 (gas pressure: 15 Torr)	5.3
5.2	Variation of current at 10 V with addition of CuO into SnO_2 in (a) air (b) CO_2	5.4
5.3	(a) Conductivity of SnO ₂ -CuO system at different temperature (b) Conductivity of SnO ₂ -CuO system measured at 160 0 C, 260 0 C and 320 0 C in CO ₂ environment	5.6
5.4	I-V characteristics at different gas pressure of (a) pure SnO_2 (b) 60 mol% SnO_2 - 40 mol% CuO	5.8
5.5	Resistance and conductivity with different gas pressure of (a) SnO_2 at 300 ^{0}C (b) 60 mol% SnO_2 - 40 mol% CuO at 220 ^{0}C	5.9
5.6	Model illustrating CO ₂ sensing mechanism in SnO ₂ gas sensor	5.10

5.7	I-V characteristics of 60 mol% SnO_2 - 40 mol% CuO at different annealing temperature (a) in air (b) in CO_2	5.12
5.8	Conductivity of 60 mol% SnO_2 - 40 mol% CuO in air and CO_2 environment annealed at (a) 500 0 C and (b) 600 0 C	5.13
5.9	Microscopic structure and sensing mechanism of SnO ₂ gas sensors	5.14
5.10	Sensor sensitivity as a function of temperature (a) pure SnO_2 (b) SnO_2 - CuO system	5.17
5.11	XRD patterns of (a) pure SnO_2 (b) 90 mol% SnO_2 - 10 mol% CuO (c) 80 mol% SnO_2 - 20 mol% CuO (d) 70 mol% SnO_2 - 30 mol% CuO (e) 60 mol% SnO_2 - 40 mol% CuO and (f) 50 mol% SnO_2 - 50 mol% CuO ceramic sensor materials	5.18
5.12	SEM micrograph of fractured surface of (a) pure SnO_2 (b) pure CuO (c) 80 mol% SnO_2 - 20 mol% CuO (d) 70 mol% SnO_2 - 30 mol% CuO (e) 60 mol% SnO_2 - 40 mol% CuO and (f) 50 mol% SnO_2 - 50 mol% CuO	5.19
5.13	(a) Sensitivity of pure SnO_2 at different CO_2 gas pressure (b) Sensitivity/operating temperature of pure SnO_2 as a function of gas pressure	5.21
5.14	a) Sensor sensitivity of 60 mol% $SnO_2 - 40$ mol% CuO at different gas pressure (b) Sensitivity/operating temperature of pure 60 mol% $SnO_2 - 40$ mol% CuO as a function of gas pressure	5.23
5.15	(a) Sensitivity of 60 mol% SnO ₂ - 40 mol% CuO at different annealing temperature (b) Operating temperature of 60 mol% SnO ₂ - 40 mol% CuO at different annealing temperature	5.25
5.16	XRD patterns of 60 mol% SnO_2 - 40 mol% CuO annealed at (a) sample as prepared (b) 500 ^{0}C (c) 700 ^{0}C (d) 900 ^{0}C	5.26
5.17	SEM micrograph of fractured surface of 60 mol% SnO_2 - 40 mol% CuO annealed at (a) 500 ^{0}C (b) 700 ^{0}C (c) 800 ^{0}C (d) 900 ^{0}C	5.27
5.18	Response time at different SnO ₂ - CuO composition	5.30
5.19	The CO ₂ response time of (a) pure SnO ₂ (b) 60 mol% SnO ₂ - 40 mol% CuO	5.32
5.20	Response time to CO ₂ gas at different annealing temperature	5.34
5.21	Thermogram of (a) pure SnO_2 (b) 60 mol% SnO_2 - 40 mol% CuO	5.36
5.22	Thermal diffusivity of SnO ₂ - CuO at Different Composition	5.38

- 5.23 Thermogram of 60 mol% SnO_2 40 mol% CuO annealed at (a) 600 ^{0}C (thickness, L=0.2079 cm) (b) 800 ^{0}C (thickness, L=0.2076 cm) 5.40
- 5.24 Thermal diffusivity of 60 mol% SnO₂ 40 mol% CuO at different annealing temperature 5.41

LIST OF ABBREVIATION

СО	Carbon Monoxide	
CO ₂	Carbon Dioxide	
CuO	Copper Oxide	
E.C	Electrical Conductivity	
H ₂	Hydrogen	
H_2S	Hydrogen Sulfide	
LPG	Liquid Petroleum Gas	
NH ₃	Ammonia	
NO	Nitrogen Monoxide	
O ₂	Oxygen	
Pt	Platinum	
R	Rectification	
SEM	Scanning Electron Microscopy	
S.P	Surface Potential	
SnO ₂	Tin Oxide	
T.V	Threshold Voltage	
TiO ₂	Titanium Oxide	
WO ₃	Tungsten Trioxide	
XRD	X-Ray Diffraction Analysis	
Zn_2SnO_4	Spinel Zinc Stannate	
ZnO	Zinc Oxide	

LIST OF SYMBOLS

ρ	Resistivity
σ	Electrical conductivity
α	Thermal diffusivity
$lpha_c$	Corrected value of thermal diffusivity
20	Scanning angle
A	Cross sectional area the current flows through
Ι	Current through the object
K_R	Correction factor
l	Length of the electric current flowing through the material
L	Thickness of the pellet sample
R	Resistance
Т	Temperature
t	Time
<i>t</i> _{0.25}	Time to reach 25% of the maximum
<i>t</i> _{0.75}	Time to reach 75 % maximum
t_c	Characteristic rise time
V	Potential difference across the object
τ	Pulse time

CHAPTER 1

INTRODUCTION

1.1 Introduction

In recent years, world awareness on environmental problems continue to increase. The continuous release to the atmosphere of chemical pollutants, originating mainly from combustion processes, is the main cause of the deterioration of environmental quality. The development of new methods to monitor polluted gases in the air is of primary concern for the knowledge of the extension of the environmental deterioration. Measurements of gas concentrations in air are being carried out mostly by analytical instruments, which are precise, but also very costly. They often cannot be placed on-site and need long periods for data acquisition. Thus they are not suitable for on-line gas monitoring (Traversa et al., 1998).

Since the demonstration of almost 50 years ago (Zakrzewska, 2001, Sberveglieri, 1995) that the adsorption of gas on the surface of a semiconductor can bring about a significant change in the electrical resistance of the materials, there has been a sustained and successful effort to make use of this change for the purpose of gas detection (Kohl, 1990). From that time, a great amount of research was carried out in order to realize commercial semiconducting devices for gas detection (Sberveglieri, 1995, Brattain and Bardeen, 1953).

Semiconducting gas sensors using SnO_2 have been studied extensively since it was first proposed in 1962 (Seiyama et al., 1962). The development of gas sensors to monitor the toxic and combustible gases is imperative due to the concerns for environmental pollution and the safety requirements for the industry (Chang et al., 2002). The sensors are used as the active part of gas and fire alarm system as well as for measuring or detecting the concentration of combustibles or other gas in the air (Mizsei, 1995).

In general, sensor provides an interface between the electronic equipment and the physical world typically by converting non-electrical physical or chemical quantities into electrical signals. The fundamental sensing principle relies on the change of conductivity of the sensors when they are exposed to certain target gases at moderate temperatures. Ponce et al. in 2003 said that gas sensors based on semiconducting metal oxides are devices which present a change in the resistivity with the gas exposure and the sensing mechanism involves an electrical conductance change caused by gas adsorption on the chemical surface.

It is well accepted that the sensitivity of a semiconductor oxide gas sensors comes from the change of the electrical conductivity of a sensor due to the gas atmosphere surrounding the sensor. The conducting of an n-type semiconductor gas sensor is an oxidizing at atmosphere and when the sensor comes into contact with reducing gas such as CO, CO₂ or H₂. For example, Table 1.1 shows the materials and gas response of each gas sensors. The surface reactions taking place between surface oxygen species and reducing gases are believed to play key roles in increasing the conductivity of the sensors (Li et al., 1999).

Materials	Gas responses	Operating temperature
		(⁰ C)
SnO ₂	O ₂ , CH ₄ , CO, H ₂ , NH ₃ , C ₃ H ₈ ,	300
	SO_2, Cl_2	350
ZnO	CO, H_2, NO_2	400
	Benzene, acetone, alcohol	380
TiO ₂	O ₂ , CO, H ₂ ,	500
	SO_2, H_2S	450
WO ₃	O ₂ , CO, H ₂ , C ₃ H ₈ , NH ₃	500
TiNb ₂ O ₇	CO, H_2, C_3H_8, NH_3	380
CuTa ₂ O ₆	CO, H_2, C_3H_8	380
BaTi ₇ Nb ₄ O ₂₅	CO, H ₂ , C ₃ H ₈ , NH ₃	520
	O_2	720
CeO ₂	O ₂	700-1100
	CO_2	842
Ga ₂ O ₃	O ₂ , H ₂ , CH ₄ , NH ₃	550

Table 1.1: Material gas response and response temperature

1.2 Tin Oxide (SnO₂)

n-type semiconducting oxides such as SnO₂, ZnO or Fe₂O₃ have been known for the detection of inflammable or toxic gases (Yu and Choi, 1998). Tin oxide (SnO₂) is most used as a material for gas sensor applications and it is the most important material for commercially manufactured gas sensors. The molecular structure of SnO₂ is shown in Figure 1.1. This sensor has been widely used as a convenient tool for detecting inflammable or toxic gases diluted in air (Kocemba et al., 2001, Devi et al., 1995, Angelis and Riva, 1995). As an n-type semiconductor tin oxides, SnO₂ shows very high sensitivity to many reducing gas such H₂, CH₄, C₂H₅OH or CO (Egashira et al., 1996, Kocemba et al., 2001, Moon et al., 2001). It is well known that there are four different adsorption states of oxygen on the surface of SnO₂ crystals, namely O₂, O₂⁻, O⁻ and O²⁻. In the last three types of adsorption state, electrons have to be transferred from SnO₂ to oxygen atoms or molecules to form the

ions. The electrons are supplied from the conduction band of the SnO₂ crystal, and it follows that the conductance of SnO₂ crystal will change as the adsorption state of oxygen changes (Zhang et al., 1998). Generally, the increase of conductance (or decrease of resistance) of SnO₂ caused by the surface reactions between surface oxygen species and target gas molecules are used to detect the reducing gas concentrations (Li and Kawi, 1998, Li et al, 1999). The most commonly accepted model for the operation of n-type semiconductor gas sensor is based on the variation in the potential barrier height at the grain boundary which is induced by the change in the amount of oxygen adsorbates by the reaction of sample with a gas (Shimizu et al., 1998). These devices are mainly manufactured in three groups: ceramic sensor, thin film sensor and thick film sensor (Mukhopadhyay et al., 2000, Kecemba et al., 2001, Jimenez et al., 1999). It is well established that the gas sensors based on SnO₂ offer desirable attributes of cost effectiveness, simplicity and high sensitivity. In this study CuO was chosen as a catalyst (Figure 1.2) and it was added into SnO₂ to increase the sensitivity and lower the operating temperature of the sensor.



Figure 1.1: The structure of SnO₂



Figure 1.2: The structure of CuO

1.3 Carbon Dioxide (CO₂)

In recent years, a great attention has been paid to the development and application of environmental gas CO_2 sensors (Liao et al., 2001, Mutschall and Obermeier, 1995). CO_2 is a typical representative of an acid-base active gas. It is chemically stable and it is difficult to be detected in a sensitive manner by a conventional gas sensor (Ishihara et al., 1995). The increase of CO_2 content in the atmosphere has become a serious problem around the world and the measurement of CO_2 concentration is critical in various advanced technologies, such as air conditioning, agriculture, biological technology and medical services. Furthermore, monitoring of the CO_2 concentration in atmosphere is also important for environmental monitoring since the CO_2 concentration in atmosphere has been increasing for decades and has brought about atmosphere warming (Ishihara et al., 1995, Jio et al., 2002). Infrared