UNIVERSITI PUTRA MALAYSIA

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

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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

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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 CO_2 environment. Sensor sensitivity was found to be dependent on temperature. Pure SnO_2 showed maximum sensitivity (~2.5) at operating temperature 300 ^{0}C. Operating temperature is defined as the temperature that gas sensor give a maximum reaction (sensitivity) with tested gas. With addition of CuO into SnO_2, the gas sensing temperature and electrical conductivity of the sensor was found to decrease. The operating temperature also rapidly decreased from 300 ^{0}C (pure SnO_2) to 220 ^{0}C (addition of 40 mol% CuO). It is also observed that the annealing process has lowered the operating temperature of the sensor from 220 ^{0}C (sample as prepared) to 180 ^{0}C (samples annealed 600 ^{0}C, 700 ^{0}C and 800 ^{0}C). The effect of gas pressure on operating temperature did not change with increasing gas pressure but it showed higher sensitivity at higher gas pressure. The sensor response time was also studied as a function of SnO_2 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 ^{0}C, 700 ^{0}C and 800 ^{0}C has the best sensing properties and lower operating temperature at 180 ^{0}C. In this study, thermal diffusivity of SnO_2 - CuO system and 60 mol% SnO_2 - 40 mol% CuO system was in range of 1.4 to 7.8 x10^{-2} cm^2/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

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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 (SnO_2) adalah satu bahan yang selalu digunakan dalam mengesan gas.

Dalam projek ini, ciri-ciri arus-voltan dan penyerapan terma ke atas SnO_2 and CuO-SnO_2 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 SnO_2 di mana ia penting di dalam tindak balas gas CO_2.

Didapati bahawa ciri-ciri arus voltan adalah lurus dalam julat suhu 27 ^{0}C – 340 ^{0}C sama ada di udara atau CO_2. Tindak balas sensor didapati bergantung kepada suhu.

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

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

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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:

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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:

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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:

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LIST OF ABBREVIATION

CO	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
α_c	Corrected value of thermal diffusivity
2θ	Scanning angle
A	Cross sectional area the current flows through
I	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
T	Temperature
t	Time
$t_{0.25}$	Time to reach 25% of the maximum
$t_{0.75}$	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, CO_2 or H_2. 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).

Table 1.1: Material gas response and response temperature

Materials	Gas responses	Operating temperature (^0C)
SnO_2	O_2, CH_4, CO, H_2, NH_3, C_3H_8, SO_2, Cl_2	300 350
ZnO	CO, H_2, NO_2 Benzene, acetone, alcohol	400 380
TiO_2	O_2, CO, H_2, SO_2, H_2S	500 450
WO_3	O_2, CO, H_2, C_3H_8, NH_3	500
$TiNb_2O_7$	CO, H_2, C_3H_8, NH_3	380
$CuTa_2O_6$	CO, H_2, C_3H_8	380
$BaTi_7Nb_4O_{25}$	CO, H_2, C_3H_8, NH_3 O_2	520 720
CeO_2	O_2 CO_2	700-1100 842
Ga_2O_3	O_2, H_2, CH_4, NH_3	550

1.2 Tin Oxide (SnO_2)

n-type semiconducting oxides such as SnO_2, ZnO or Fe_2O_3 have been known for the detection of inflammable or toxic gases (Yu and Choi, 1998). Tin oxide (SnO_2) 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 SnO_2 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, SnO_2 shows very high sensitivity to many reducing gas such H_2, CH_4, C_2H_5OH 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 SnO_2 crystals, namely O_2, O_2^-, O^- and O^{2-}. In the last three types of adsorption state, electrons have to be transferred from SnO_2 to oxygen atoms or molecules to form the ions. The electrons are supplied from the conduction band of the SnO_2 crystal, and it follows that the conductance of SnO_2 crystal will change as the adsorption state of oxygen changes (Zhang et al., 1998). Generally, the increase of conductance (or decrease of resistance) of SnO_2 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 SnO_2 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 SnO_2 to increase the sensitivity and lower the operating temperature of the sensor.

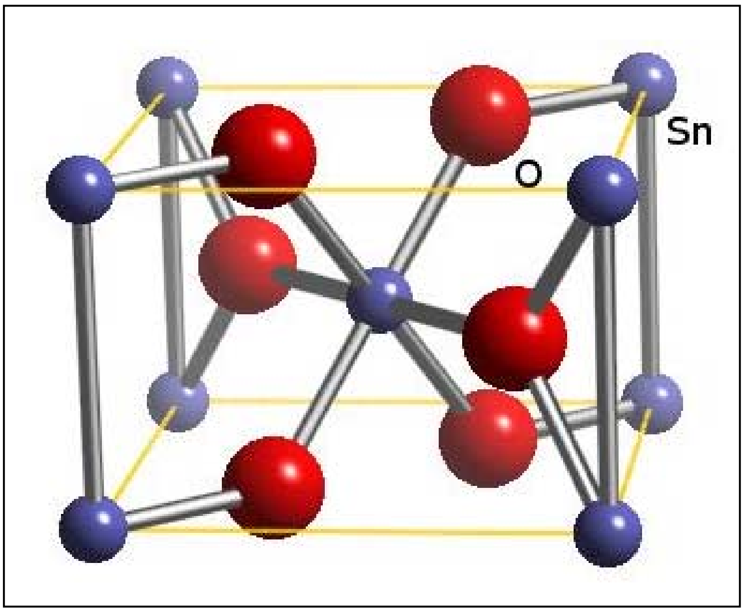

Figure 1.1: The structure of SnO_2

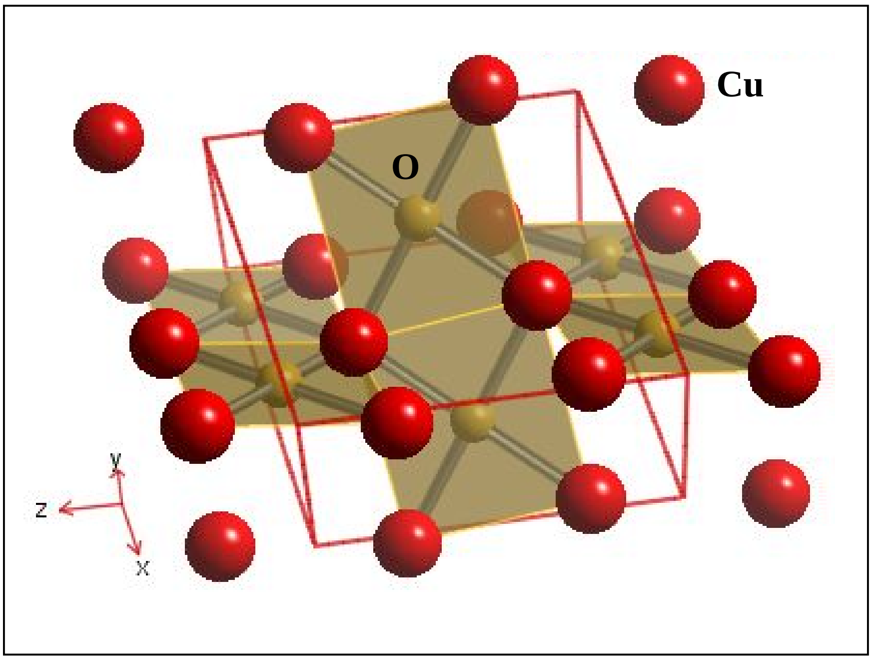

Figure 1.2: The structure of CuO

1.3 Carbon Dioxide (CO_2)

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