UNIVERSITI PUTRA MALAYSIA

PHYSICAL AND THERMAL CHARACTERIZATION OF PLATINUMTIN DIOXIDE BASED CERAMIC FOR GAS SENSING

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By

AIZA MASYATI BINTI MAS'UT

Thesis Submitted to the School of Graduate Studies Universiti Putra Malaysia, in Fulfillment of the Requirements for the Degree of Doctor of Philosophy

December 2014

This thesis is dedicated to my family especially

to my beloved parents (Rohayati Armia and Mas'ut Awang Samah)
who have sacrificed so much for me..

to my soul mate (Mohd.Taufik Mohd. Tasrip)
for his patience, understandingand emotional support…

and to my dearest children (Inas Zara Sufiya and Muhammad Firas Mifzal)
for their unconditional love..

Thank you for being with me all along.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

PHYSICAL AND THERMAL CHARACTERIZATION OF PLATINUM TIN DIOXIDE BASED CERAMIC FOR GAS SENSING

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December 2014

Chairman: Associate Professor Zaidan Abdul Wahab, PhD
Faculty: Science

Semiconducting metal oxide such as tin dioxide (SnO_2) is widely utilized for sensing reducing gases such as Hydrogen (H_2) and Carbon Monoxide (CO). Gassensor characteristics such as sensitivity, selectivity, response time and recovery time are often reported to be improved for the sensor with Platinum-catalyst than without the Platinum-catalyst. Thus, in this study, Platinum (Pt) up to 10 wt.% is added to SnO_2 via solid state route and sintered at various temperatures. The material will further analyzed for thermal properties such as thermal diffusivity and thermal conductivity, as well as structural properties such as phase and crystallinity, microstructure, density-porosity, mean particle size and specific surface area.

The gas sensor characteristics were studied in air, H_2 and CO, respectively using two-probe method between 150 to 450 °C while the thermal properties of the Pt-SnO_2 ceramic was studied using Laser Flash Analyzer from room temperature up to 400 °C. The microstructure of the sensor element was studied using X-Ray Diffractometer (XRD), Surface Analyzer, Scanning Electron Microscope (SEM) and density-porosity measurements.

The mean particle size and specific surface area of the SnO_2 powder performed by BET method were 0.12 µm and 7.5 m^2g^{-1}, respectively, and those of the Pt powder were 0.8 µm and 3.5 m^2g^{-1}.The density (porosity) of the samples increases (decreases) with sintering temperature and Pt loading. The phase composition analyzed by XRD, pointed out that all samples were tetragonal cassiterite polycrystalline in nature and there was no impurity phases in Pt-SnO_2 system other than SnO_2 and Pt phases. SEM micrographs showed that samples were assembled by lots of small spherical grains with voids and pores among them. Samples sintered at higher temperature yielded larger average grain size. As 0.5 wt.% Pt is introduced to pure SnO_2 sample, the average grain size was decreased but the doped samples grew in grain size as Pt loading was further increased. The thermal diffusivity is increased with the increasing size of grain, at higher sintering temperature and with increasing of Pt loading. Samples with larger grain size also have larger room temperature thermal conductivities. All samples show a decrease in resistance either in air or gases with an increase in operating temperature. The resistance in air for the doped samples showed a higher resistance than the undoped SnO_2 sample over the

operating temperature. The resistance of the doped samples also increased with an increase in Pt doping in SnO_2. The resistance of all samples in both H_2 and CO gases decreases with temperature over the operating temperature. The undoped SnO_2 sample was sensitive to all the test gases but the sensitivity value was very poor. The maximum sensitivity of undoped SnO_2 was obtained at 400 ^oC. It was found that the optimum operating temperature for H_2 and CO sensing in air was 300 and 200 ^oC, respectively, and the optimum composition for both gases was 0.5 wt.% Pt -SnO_2 sample. Sample with 0.5 wt.% Pt loading also show good selectivity to H_2 and CO at different temperature. The response and recovery times were greatly influenced by material composition, H_2 concentration and H_2 flow rate.

In summary, the gas sensing process is strongly related to the surface reactions. Doped samples showed better gas response than the undoped sample due to the "spill over effect". High surface areas (small grain size) with mesoporous structure produced by 0.5wt.%Pt-SnO_2 sample provides large reaction contact area between gas sensing materials and target gases, thus contribute to the enhancement of the gas sensor characteristics. As for the thermal diffusivity and thermal conductivity of the SnO_2-based samples, grain size and density-porosity effects play a major role in determining the properties where the values were in the range of 2.78 - 3.22 $\times 10^{-6}$ $m^2s^{-1}$and 3.93 - 4.87 $Wm^{-1}K^{-1}$, respectively.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysiasebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENCIRIAN FIZIKAL DAN TERMA SERAMIK BERASASKAN PLATINUM TIMAH OKSIDA UNTUK PENDERIAAN GAS

Oleh

AIZA MASYATI BINTI MAS'UT

Disember 2014

Pengerusi: Profesor Madya Dr. Zaidan Abdul Wahab, PhD
Fakulti: Sains

Semikonduktor logam oksida seperti timah dioksida (SnO_2) digunakan secara meluas untuk mengesan gas yang berkurang seperti hidrogen (H_2) dan Karbon Monoksida (CO). Ciri-ciri penderia gas seperti sensitiviti, pemilihan, masa tindak balas dan masa pemulihan sering dilaporkan lebih baik bagi penderia dengan pemangkin Platinum jika dibandingkan dengan penderia tanpa pemangkin Platinum. Oleh itu, dalam kajian ini, Platinum (Pt) sehingga 10% berat ditambah kepada SnO_2 melalui kaedah tindak balas dalam keadaan pepejal dan dibakar pada pelbagai suhu. Bahan ini akan seterusnya dianalisis untuk sifat terma seperti keresapan terma dan kekonduksian terma, dan juga sifat-sifat struktur seperti fasa dan penghabluran, struktur mikro, ketumpatan-keliangan, purata saiz zarah dan keluasan permukaan tertentu.

Ciri-ciri penderia gas telah dikaji di dalam udara, H_2 dan CO, masing-masing, menggunakan kaedah penduga dua titik antara 150 hingga 450 °C manakala ciri terma seramik Pt-SnO_2 dikaji menggunakan Penganalisis Kilat Laser daripada suhu bilik sehingga 400 °C. Struktur mikro elemen penderia dikaji menggunakan Pembelau Sinar-X (XRD), Penganalisis Permukaan, Mikroskop Imbasan Elektron (SEM) dan pengukuran ketumpatan-keliangan.

Purata saiz zarah dan luas permukaan tertentu bagi serbuk SnO_2 yang dilakukan oleh kaedah BET, masing-masing adalah 0.12 μm dan 7.5 m^2g^{-1} dan bagi serbuk Pt ialah 0.8 μm dan 3.5 m^2g^{-1}. Ketumpatan (keliangan) sampel meningkat (berkurang) dengan suhu pembakaran dan kemasukan Pt. Komposisi fasa yang dianalisis oleh XRD menunjukkan bahawa semua sampel secara semula jadinya adalah polihablur kasiterit tetragon dan tiada fasa bendasing dalam sistem Pt-SnO_2 selain daripada fasa-fasa SnO_2 dan Pt. Mikrograf SEM menunjukkan bahawa sampel terdiri daripada banyak butiran sfera kecil dengan lompang dan liang di kalangan mereka. Sampel tersinter pada suhu yang lebih tinggi menghasilkan saiz purata butiran yang lebih besar. Apabila 0.5% berat Pt diperkenalkan kepada sampel SnO_2 tulen, purata saiz butiran telah menurun tetapi saiz butiran sampel yang didop berkembang apabila kemasukan Pt dipertingkatkan. Keresapan terma meningkat dengan bertambahnya saiz butiran, pada suhu pensinteran yang lebih tinggi dan dengan peningkatan kemasukan Pt. Sampel-sampel dengan saiz butiran yang lebih besar juga mempunyai nilai-nilai kekonduksian haba pada suhu bilik yang lebih besar. Semua sampel menunjukkan pengurangan rintangan sama ada di dalam udara atau gas dengan

peningkatan dalam suhu operasi. Rintangan di dalam udara bagi sampel yang didop menunjukkan rintangan yang lebih tinggi berbanding sampel SnO_2 yang tidak didop pada suhu operasi. Rintangan sampel yang didop juga meningkat dengan meningkatnya kemasukan Pt dalam SnO_2. Rintangan semua sampel dalam kedua-dua gas H_2 dan CO berkurangan dengan suhu pada semua suhu operasi. Sampel SnO_2 yang tidak didop adalah peka terhadap semua gas ujian tetapi nilai kepekaan tersebut sangat lemah. Kepekaan maksimum SnO_2 yang tidak didop telah diperolehi pada 400 °C. Didapati bahawa suhu operasi optimum untuk penderiaan H_2 dan CO di udara masing-masing adalah 300 dan 200 °C, dan komposisi optimum bagi kedua-dua gas adalah sampel SnO_2 dengan 0.5% berat Pt. Sampel dengan kemasukan 0.5% berat Pt juga menunjukkan pemilihan yang baik untuk H_2 dan CO pada suhu yang berbeza. Masa tindak balas dan pemulihan kuat dipengaruhi oleh komposisi bahan, kepekatan H_2 dan kadar aliran H_2.

Secara ringkasnya, proses penderiaan gas adalah sangat berkaitan dengan tindak balas permukaan. Sampel yang didop menunjukkan tindak balas gas yang lebih baik berbanding sampel yang tidak didop disebabkan oleh "kesan limpahan". Luas permukaan yang tinggi (saiz butiran kecil) dengan struktur liang meso yang dihasilkan oleh sampel 0.5% berat Pt-SnO_2 memberikan reaksi kawasan sentuhan yang besar antara bahan penderiaan gas dan gas sasaran, sekali gus menyumbang kepada peningkatan ciri-ciri penderia gas. Bagi keresapan terma dan kekonduksian terma sampel berasaskan SnO_2, saiz butiran dan kesan kepadatan-keliangan memainkan peranan utama dalam menentukan sifat-sifat tersebut di mana nilai-nilainya masing-masing adalah dalam julat 2.78-3.22 $\times 10^{-6}$ m^2s^{-1} dan 3.93 - 4.87 $Wm^{-1}K^{-1}$.

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I certify that a Thesis Examination Committee has met on 19 December 2014 to conduct the final examination of Aiza Masyati Binti Mas'ut on her thesis entitled "Physical and Thermal Characterization of Platinum Tin Dioxide Based Ceramic for Gas Sensing" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia[P.U.(A)106] 15 March 1998. The Committee recommends that the student be awarded the Doctor of Philosophy.

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LIST OF ABBREVIATIONS

AFM	Atomic Force microscope
Ave	Average
BET	Brunauer, Emmett and Teller
BJH	Barrett-Joyner-Halenda
C_2H_5OH	Ethanol
dc	Direct current
EPR	Electron paramagnetic resonance
eV	Electron volt
FET	Field-effect transistor
FWHM	Full Width at Half Maximum
GSCS	Gas Sensing Characterization System
IR	Infrared
ISFET	Ion sensitive field-effect transistor
ITO	Indium Tin Oxide
I-V	Current–voltage
JCPDS	Joint Committee on Powder Diffraction Standards
LFA	Laser Flash Analyzer
MCT	Mercury Cadmium Telluride
$MgAl_2O_4$	spinel magnesium aluminate
MOS	Metal Oxide Semiconductor
MOSFET	Metal-oxide-semiconductor field-effect transistors
n_a	Electron concentration in air
Nd-YAG	Neodymium-Yttrium Aluminium Garnet
n_g	Electron concentration in gas
N_2H_4	Hydrazine
$N_2H_4.H_2O$	Hydrazine monohydrate
NTC	Negative temperature coefficient
ppm	Part per million
R_a	Resistance in air
Rec	Recovery
Resp	Response
RF	Radio frequency
R_g	Resistance in gas
RGTO	Rheotaxial growth thermal oxidation
R&D	Research and Development
S	Sensitivity
Sel_{CO}	selectivity of the sensors towards CO
Sel_{H2}	selectivity of the sensors towards H_2
SEM	Scanning Electron Microscope
S_{max}	Maximum Sensitivity
STM	Scanning tunneling microscope
T_{crit}	Critical Temperature
T_{Max}	Temperatures at maximum sensitivity
TPD	Temperature programmed desorption
wt.%	Weight percentage
XPS	X-ray photoelectron spectroscopy
XRD	X Ray Diffractometer

LIST OF SYMBOLS

α	Thermal diffusivity
A	Surface area
C	Specific heat
C_p	Specific heat at constant pressure
d	Spacing between planes in the atomic lattice
D	Crystallite size
e	Electron
g	Finite thickness
G	Lattice vector
I	Current through the object
l	Sample thickness
l	Mean free path
l_{th}	Mean free path determined by thermal scattering
l_{im}	Mean free path determined by scattering by impurities
L	space-charge layer thickness
L	Lorentz number
m	Mass
N	Number of unit cells in the crystal lattice of solid
θ	Scanning angle
ρ	Resistivity
ρ	Density
ρ_{th}	Theoretical density
q	Lattice vibrations wave number
q	Rate of heat flow
Q	Radiant heat
R	Resistance
T	Temperature
$t_{1/2}$	Half rise time
t_{res}	Response time
t_{rec}	Recovery time
τ	Pulse time
μ	Carrier mobility
μ	micro
v	Average velocity of the phonons
V	Voltage
V	Volume
x	Composition of ceramics
σ	Electrical conductivity
λ	Wavelength of incident wave
λ	Thermal conductivity
λ_c	Thermal conductivity ofcontinuous phase
λ_d	Thermal conductivity of dispersion phase

CHAPTER 1

INTRODUCTION

1.1 Hydrogen Gas

Hydrogen (H_2) is the latest in the succession of fuels with many social, economic, and environmental benefits to its credit (Han *et al.,* 2007). The twenty-first century will be the century of H_2 as the technology is now obtainable to begin transforming a petroleum-based economy to a hydrogen-based one. Hydrogen has widely acknowledged as a green energy source attributable to its cleanliness, recyclability and lavishness (Kim *et al.,* 2011).

Hydrogen is a very gainful gas because it finds many industrial applications such as metal smelting, eliminating friction heat in turbines, electronic fabrication process, medical installation and corrosion prevention in nuclear reactors (Tang *et al.,* 2008). Besides that, H_2 is used as a chemical in industries, as cryogenic-fuel in rockets and as a lift off gas in weather balloons (Ramesh *et al.,* 2004) as well as applied in Nickel Hydrogen batteries used in satellites (Velayutham *et al.,* 2004). However, H_2 has inherent hazards. Low viscosity and small molecular size of H_2 give it a greater tendency to leak than other common gaseous fuels. A gaseous H_2 leakage at concentrations as low as 4% in air at normal conditions may lead to an explosive atmosphere of easy ignition (Han *et al.,* 2007). So, H_2 must be produced, stored, transported and handled carefully.

Based on the fact that H_2 is odourless, colourless, and tasteless, most human senses will not help to detect a leak (Hafeez *et al.,* 2011). For these and other reasons, industry often uses H_2 sensors to help detect H_2 leaks which have stimulated considerable efforts towards developing sensitive, reliable and economical H_2 sensors for the fast detection of H_2 leaks. The first H_2 sensor was developed by Lundstrom *et al.,* (1975) and was a metal oxide semiconductor (MOS) structure using silicon as substrate, silicon dioxide as gate insulator and palladium as gate electrode. Since then, a lot of research on H_2 sensors has been done. Different materials and fabrication methods have been used to make the H_2 sensors (Kim *et al.,* 2000; Spetz *et al.,* 1999; Lundstrom *et al.,* 1989). Types of H_2 sensors available include electrochemical, catalytic, semiconductor and resistivity sensors (Velayutham *et al.,* 2004). The most commonly used H_2 sensors in industries or research are the semiconductor type and the catalytic combustion type (Han *et al.,* 2007).

1.2 Introduction to SnO_2- based Hydrogen Gas Sensor

Semiconducting gas sensors using tin dioxide (SnO_2) have been studied extensively since it was first proposed in 1962 (Seiyama *et al.,* 1962). This sensor has been widely used as a convenient tool for detecting inflammable or toxic gases diluted in air (Kocemba *et al.,* 2001; Angelis and Riva, 1995; Devi *et al.,* 1995). As an n-type semiconductor, SnO_2 shows a very high sensitivity to many reducing gas such as H_2, CH_4, C_2H_5OH or CO (Kocemba *et al.,* 2001; Moon *et al.,* 2001; Egashira *et al.,* 1996a).The mechanism of this metal-oxide sensor is based on the change of electrical conductance in response to the introduction of a small concentration of

reducing gas, which reacts with the oxygen species at the oxide surface (Seal and Shukla, 2002; Sberveglieri, 1992).

Doped and undoped SnO_2 gas sensors come in different forms such as pellets of pressed powder, thick films and thin films (Garje and Aiyer, 2008). Fabrication techniques such as sintering (Moon *et al.*, 2001), chemical vapour deposition (CVD) (Panchapakesan *et al.*, (1999), evaporation (Tamaki, (1998)), sputtering (Kissine *et al.*, (1999)) and sol-gel (Park and Mackenzie, (1996)) are used.

It has been reported that the principal advantages of using SnO_2 gas sensors are their high sensitivity at temperature ranging from 250~400 ^oC, low cost, fast response and high mechanical strength (Cha *et al.*, 2004). Unfortunately, the gas sensors that are currently commercially available have several problems whereby they are sensitive to partial pressure of too many gases, consume high power and often are not reversible or reproducible (Seal and Shukla, 2002; Morrison, 1982). Other problems, such as the speed of response, stability and lifetime of the devices are also of major concern. Two major methods are used to solve these problems:

i) A mixture with noble metal catalysts, dopants or composites like other metal oxides preferably incorporated during the preparation stage prior to sintering or film fabrication to cultivate the sensitivity to specific components (Hetznecker *et al.*,2002). The addition of Ru, Pt, Pd, Au, Al and Cu in SnO_2 enhances selectivity towards a specific gas, lowers the operating temperature, increases the sensitivity of the sensor as well as reducing the response time and recovery times (Niranjan *et al.*,2003; Mizsei *et al.*, 1998). Moreover, at higher operating temperatures (>100 ^oC), the H_2 sensitivity is often reported to be higher for the sensor with the Pt-catalyst than without the Pt-catalyst (Dieguez *et al.*, 2000). Noble metal additives such as Pd and Pt are dispersed on the oxide as activators or sensitizers to improve the gas selectivity and to lower the operating temperature (Ivanov *et al.*, 2004). However, the actual distribution of the additives mostly depends on the method used to introduce them and on the subsequent thermal treatments performed (Bitteencourt *et al.*, 2004). Addition of a noble metal layer effects in the change in the electronic states of the active layer, modifies the microstructure of the base material and the grain size. The contact of the noble metal additive with the semiconducting oxide changes the depletion region at the semiconductor and modifies surface barrier height. This barrier is fully characterized by electron affinity. The work function values and the density of surface states found inside the energy gap, strongly influence the sensor performance (Zhang and Liu, 2000). The catalytic role of the additive on the sensor characteristics is usually associated with the distribution of additive particles through the whole sensing material surface. The additives alter the microstructure of the base material, control the grain growth mechanism and introduce donor or acceptor levels, thus varying the metal oxide resistivity. This powerful approach unfortunately suffers from several drawbacks such as poor cross sensitivity, use of a large amount of expensive noble metals, ageing and humidity effects resulting in inferior device performance (Chaudhary *et al.*, 1997).

ii) Periodic variation of the sensor operation temperature, different geometry of the sensing layers or application of sensor arrays and numerical analysis of the response data by e.g. neural networks are applied to improve identification and analysis capability (Hetznecker *et al.*,2002). The sensing properties of a sensor are affected

by many factors including operating temperature, target gases, sensor geometry, surface geometry, sensor enclosure, films texture, thickness, grain size, porosity, grain faceting, agglomeration, surface disordering, bulk stoichiometry, grain network, surface area and size of necks (Singh *et al.,* 2013). It has been previously reported that the sensitivity of SnO_2 sensors can be enhanced by reducing grain size of the sensing element, which is related to calcining temperature (Cha *et al.,* 2004).

1.3 Introduction to Thermophysical Properties

Thermophysical properties such as thermal conductivity, thermal diffusivity and specific heat are the most vital physical properties of a material that are needed for heat transfer calculations. These properties are observed when heat is added or removed from a material.

Thermal conductivity, λ assumes a critical role in the performance of materials in high temperature applications. Low thermal conductivity values are required when the purpose is to minimize heat losses while high thermal conductivity values are needed when heat transfer between materials is desirable. So, reliable thermal conductivity values are essential in a selection of a material in order to get the best performance of this material in a specific application. However, predicting the effective thermal conductivity is not a straightforward process. It is difficult to measure because the transfer property is a complex function of many other parameters, such as the thermal conductivities of each phase, their relative proportions, the size of the solid particles, the contact areas and distribution within the medium (Bouguerra *et al.,* 2001). Thermal conductivity involves the movement of energy (heat flux) which is difficult to control or measure directly. Hence, thermal diffusivity is a significant transport property in determining the thermal conductivity of a material.

Thermal diffusivity, α, is a measure of speed of heat propagation through a material. The higher the value of thermal diffusivity of a material, the higher will be the rate of heat propagation in a material (Incropera *et al.,* 2007). For gas sensor application, it is important to first heat up the sensor to its operating temperature (usually at a few hundred degree Celsius) in order to activate the gas sensing. For the sensor to be immediately used, we need the sensor to reach its operating temperature in a short time. Gas sensors with material of higher thermal diffusivity value will give faster initialization time than gas sensors with material of lower thermal diffusivity.

1.4 Scope of Study

Tin (IV) oxide is chosen as the base material in this study for its proven sensitivity as a gas detector and for its chemical stability and durability. It was intended that the material chosen takes the form of a sintered pellet. Pt amount up to 10 wt.% is used in this study as a sensitizing additive that is added as a catalyts to SnO_2 to enhance sensing characteristics (sensitivity, selectivity, operating temperaturem response time and recovery time) to H_2. The gas sensing characteristics of the Pt-SnO_2 ceramic semiconductor, involving electrical properties was studied using two-point probe method in air, H_2 and CO environment from 150 to 450 °C, respectively. The thermal properties of the Pt-SnO_2 ceramic semiconductor was studied using Laser Flash Analyser (LFA) from RT up to 400 °C while the microstructure of the sensor

element was studied using XRD, Surface Analyser, SEM and density-porosity measurements.

1.5 Problem Statement

Semiconducting gas sensors based on SnO_2 have not yet reached their projected value. Although current sensors respond to parts per million (ppm) levels of gases, poor sensitivity and poor selectivity still characterize their response. The sensor element that comprised SnO_2 only, has limited sensitivity to chemically stable gas like H_2, poor selectivity between H_2 and CO, and operates at high temperature up to 600 °C which is very power consuming. Since the gas sensitivity is closely related to redox reactions of the detected gases on the sensor surface, it is reasonable to expect that it could be improved by including noble metal (e.g Pt, Pd, Ag) which act as catalyst to these reactions. Pt which is very active for oxidation reactions, is chosen as an additive via solid state reaction method to improve SnO_2-based gas sensor sensitivity and selectivity, and reduce the operating temperature as well as response time. Pt addition is also expected to improve sensor thermal properties which lead us to the enhancement of gas sensor initialization time.

1.6 Objectives of the Study

The objectives of this study are;

1. to prepare Pt doped SnO_2 pellets from commercial powder via solid state route.
2. to study gas sensing characteristics of Pt doped SnO_2 materials under H_2 and CO gases.
3. to study the thermal diffusivity and thermal conductivity of Pt doped SnO_2 materials.

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