CHARACTERIZATION STUDY OF PLATINUM-DOPED STANNIC OXIDE CERAMICS FOR METHANE SENSING IN AIR

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This thesis is dedicated to my

my beloved wife (Rohanin Ahmad) and my dearest son (Faisal Zuhairi).
Thank you for being with me all along.

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ABSTRACT

Pure SnO_2 and Pt-SnO_2 ceramics were prepared by the dry-pressing method using a pressure of 40 MPa and sintered at various temperatures between 100-000°C from a mixture of powders of (100-x)SnO_2.xPt ($0 \leq x$ wt % ≤ 5). The electrical properties of the ceramics were studied using a home-made Sensor Element Characterization System (SECS) and an Impedance Analyzer. The sensing probe of the SECS was modified so it was much slimmer with most of the electrical connections concealed and could measure either the bulk or surface resistance of the ceramic. The optimum composition for detecting methane in air was 0.5 wt.% Pt-SnO_2 sintered at 1000°C and the optimum operating temperature was at 400°C. The resistance of the 0.5 wt.% Pt-SnO_2 in 25000 ppm methane decreases from ~ 54.0 kΩ to ~ 4.6 kΩ at temperatures of 200°C up to 440°C respectively. The activation energies were between 0.30 eV and 0.45 eV for temperatures between 200°C and 400°C. The corresponding conductance (G) decreased with Pt loading and the gas partial pressure (p) or methane flow rate (χ). As such, it indicates that the doped SnO_2 is an n-type semiconductor. The conductance power law takes the form $G \sim p^{-0.5}$ and this indicates that the chemisorbed ions on the doped ceramics depended only on temperature. The conductance (G)-methane concentration (c) takes the form $G = kc^{0.35}$. A linear relationship $\ln G = 0.35 \ln c - 11.9$ was obtained when plotting $\ln G$ against $\ln c$. The relative conductance change ($\Delta G/G$) and the square root of methane concentrations ($c^{1/2}$) obey the relationship $\Delta G/G = 0.08c^{1/2}$ which indicates the doping with 0.5 wt.% Pt increased the sensitivity of the base material (SnO_2) to methane by a factor of 133. The response and recovery times were affected by the methane flow rate, operational temperature, level of doping with values between 30 s up to 154 s and between 600 s up to 1317 s respectively. The doping of Pt at 0.1 wt.% up to 5 wt.% in SnO_2 produced ceramics with densities of 7.01g/cm^3 up to 7.03 g/cm^3 which exceeds the full density of pure SnO_2 (6.90 g/cm^3). The strength and stability were indicated from the doped SnO_2 measurements of Vickers hardness (10 GPa and up to 19 GPa), Young modulus (20 GPa and up to 55 GPa) and Bulk modulus (20 GPa and up to 80 GPa) for Pt loadings between 0.1wt.% and 2.5 wt.%. High resolution X-ray diffraction showed that the mean crystallite size ranges between 25 nm and 55 nm for Pt loadings from 1 wt% up to 5 wt.% in SnO_2. The strain in doped samples could not be eradicated by either sintering at high temperature (1000°C) or high Pt loading (5 wt.%). X-ray photoemissions spectroscopy (XPS), Mössbauer and nuclear magnetic resonance (NMR) analysis showed that the doped SnO_2 has additional chemical environment (compared to pure SnO_2) can be attributed to the ease of detecting methane in air via electrical measurements.

ABSTRAK

Seramik Timah Oksida tulen dan timah oksida yang didop dengan Platinum telah disediakan dengan kaedah Tekanan Kering dengan menggunakan tekanan 40 MPa dan disinter pada suhu antara 100-1000^{o}C daripada campuran dalam bentuk bedak berkomposisi (100-x)SnO_2.xPt ($0 \leq x$ %berat ≤ 5). Pencirian elektrik bahan tersebut dilakukan dengan mengunakan alat yang dibina dinamakan Sistem Cirian Elemen Sensor (SECS) and Penganalisa Impedans bagi mengesan gas metana di udara. Prob pengesan Sistem Cirian Elemen Sensor diubah agar ia lebih langsing dengan sambungan elektriknya terlindung dan boleh mengukur rintangan padu atau rintangan permukaan seramik. Adunan optimum untuk mengesan metana di udara adalah 0.5 % berat Pt-SnO_2 dan suhu operasi optimumnya pula ialah 400^{o}C. Rintangan elektrik bagi 0.5 % berat Pt-SnO_2 di dalam 25000 bahagian per juta metana di udara susut dari ~ 54.0 kΩ ke 4.6 kΩ pada suhu 200^{o}C hingga ke 400^{o}C, masing-masing. Konduktans (G) pula susut dengan tambahan Pt dan tambahan tekanan separa gas (p) atau kadar aliran metana (χ). Dengan itu tertunjuk bahawa SnO_2 yang didop ialah semikonduktor jenis-n. Hukum kuasa konduktans dinyatakan dalam bentuk $G \sim p^{-0.5}$ dan ini menunjukkan ion-ion yang diserapkimia pada seramik yang didop hanya bersandar kepada suhu. Hubungan antara konduktans (G) dan kepekatan metana (c) adalah dalam bentuk $G = kc^{0.35}$. Hubungan linear $\ln G = 0.35 \ln c - 11.9$ diperolehi bila memplot $\ln G$ lawan $\ln c$. Perubahan relatif konduktans ($\Delta G/G$) dan punca ganda dua kepekatan metana ($c^{1/2}$) mematuhi hubungan $\Delta G/G = 0.08\, c^{1/2}$, yang menunjukkan 0.5 % berat Pt meningkatkan kepekaan bahan asas (SnO_2) kepada metana dengan faktor sebanyak 133. Masa respons dan masa pemulihan dipengaruhi oleh kadar aliran metana, suhu operasi, amaun dopan dengan nilai- nilai 30 s hingga 154 s dan antara 600 s hingga 1317 s, masing-masing. Mengedop Pt dari 0.1 % berat sehingga 5 % berat dalam SnO_2 menghasilkan seramik dengan ketumpatan 7.01 g/cm^3 hingga 7.03 g/cm^3 yang melebihi ketumpatan penuh SnO_2 (6.90 g/cm^3). Kekuatan dan kesetabilan SnO_2 yang didop ditunjukkan oleh ukuran dari kekerasan Vickers (10 GPa sehingga 19 GPa), Modulus Young (20 GPa sehingga 55 GPa) dan Modulus Pukal (20 GPa sehingga 80 GPa) bagi tambahan Pt dari 1 % berat sehingga 5 % berat dalam SnO_2. Pembelauan sinar-X resolusi tinggi menunjukkan min saiz kristalit berada dalam julat 25 nm sehingga 55 nm untuk tambahan Pt dari 1 % berat sehingga 5 % berat dalam SnO_2. Spektroskopi fotopancaran sinar-X (XPS), Mössbauer dan salunan-magnetik-nuklear (NMR) menunjukkan SnO_2 yang didop memiliki suasana kimia tambahan (berbanding dengan SnO_2 tulen) yang mungkin menjadi atribut mudahnya mengesan metana di udara melalui pengukuran elektrik.

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A	-	area of cross-section
A'	-	absorbance
Å	-	Angstroms
B	-	bulk modulus
β	-	Full Width Half Maximum
c'	-	velocity of light
c	-	gas concentration
cps	-	count per second
χ	-	flow rate of methane
d_V	-	average length of the Vickers diagonals
δ	-	shifts (Raman, chemical)
δa	-	distortions in the lattice parameter a
δc	-	distortions in the lattice parameter c
e	-	electronic charge
E	-	elastic modulus
E_g	-	forbidden band gap energy
E_C	-	conduction band energy
E_V	-	valence band energy
E_D	-	ionization energy of donors
E_A	-	ionization energy of acceptors
E_a	-	activation energy
E_f	-	Fermi energy
eV_S	-	work function of an electron
ε_o	-	permittivity of free space

ε_r	-	relative permittivity
F	-	force
$F^{/}$	-	structure factor
G	-	conductance in methane
G_o	-	conductance in air
H_V	-	Vickers hardness
hkl	-	Miller indices
h	-	Planck constant
I_o	-	intensity of incident beam
I_T	-	intensity of transmitted beam
K	-	absorption coefficient
k_B	-	Boltzmann constant
ΔL	-	increase in length
L	-	original length
l,z	-	thickness
λ	-	wavelength of X-ray radiation (e.m. radiation)
μ	-	shear modulus
N_i	-	net density of ions in the space charge region
n	-	refractive index of a medium
N_S	-	negative surface charge
ρ	-	bulk density
$p^{/}$	-	porosity
P	-	load
P_o	-	partial pressure of oxygen
p	-	partial pressure
$p^{/}$	-	porosity
$R^{/}$	-	particle size
R	-	electrical resistance
R_X	-	mean crystallite size
RF	-	radio frequency
$S^{/}$	-	sensitivity

$\check{S}$	-	selectivity
S	-	specific surface area
sccm	-	standard cubic centimetre per minute
σ	-	electrical conductivity
θ	-	diffraction angle
θ'	-	phase angle
T	-	transmission
V_C	-	voltage supply
V_L	-	voltage across load resistor
V_S	-	voltage across sensor
v_L	-	longitudinal velocity
v_S	-	shear velocity
W	-	weight loss
W^*	-	Pt loading
W_1	-	weight in air
W_2	-	weight in toluene
Y	-	Young modulus

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CHAPTER 1

INTRODUCTION

1.1 General Introduction to Gas Sensing

A sensor is a form of transducer which converts physical or chemical quantity into an electrical quantity for the purposes of measurement. A transducer is a device which converts one form of energy into another. A gas sensor is then a chemical sensor whose sole purpose is to determine the gas composition and concentration via an electric signal. The use of sensors has increased as it was necessary where environmental, health and safety issues are concerned to improve the quality of life (Brailsford and Logothesis, 1998). For example, low level toxic gases emission from exhaust systems could only be possible if high efficient sensors are realised (Ogita *et al*., 2001).

1.1.1 Methane gas

Methane gas is colourless, odourless and lighter than air. The methane gas is a molecule which is made up of 1 carbon atom and 4 hydrogen atoms. Natural sources of methane include wetlands, grass hydrate, termites, oceans and freshwater bodies. Human related (anthropogenic) activities like fossil fuel production, animal husbandry, rice cultivation, biomass burning and waste management also release methane into the atmosphere and alter the atmospheric composition. Also, almost all (95%) of the methane emissions are from coal in underground mines. This is still the main danger in coal mines all over the world. Methane gas sensing is difficult because it is colourless and odourless. A crude method of methane sensing is by its pungent smell when an additive such as mercaptan is added in low dosage. Mixtures of methane and air between 5 to 15% methane when ignited can burst into flame and explode (Leer, 1992). This will then cause widespread fire and can claim many lives.

1.1.1.1 Anthropogenic methane sources

Amongst the anthropogenic sources of methane are landfills, natural gas and oil systems, domesticated livestock, coal mining, livestock manure, rice cultivation, biomass burning and wastewater treatment. Under anaerobic conditions (without oxygen) landfills and open dumps decompose and generate methane. The volume of methane generated depends upon the waste mass and the moisture content. One of the primary component of natural gas is methane which escapes to the environment during the production, processing, storage, transmission and distribution stages. The fact that the gas is found in conjunction with oil means that the production, refinement, transportation and storage of crude oil is also considered as a source of methane. Cattle, buffalo, sheep, goats are amongst the ruminant animals kept as domesticated livestock. These animals produce methane as part of their digestive processes. It is in their large fore-stomach or rumen that microbial fermentation takes place where the feed is converted into products that can be digested by the animal. The byproduct of the microbial fermentation is methane which is eructed or released by the animal. Human too produces methane via their digestive processes but the emissions from this source is insignificant compared to the case of livestock. Methane which is trapped in coal deposits and in the surrounding strata is released during coal mining operations. Methane is also emitted during the combustion of coal. Reducing the emissions of methane from coal mining is environmentally beneficial as it also a greenhouse gas. Liquid manure from ponds, lagoons and holding tanks also promotes methane production as the manure is produced from decomposition of the organic matter in the livestock and poultry manure. A flooded rice field is an ideal environment for methane production as it contains high levels of organic substrates, oxygen-depleted conditions and moisture for anaerobic decompositions. The level of emissions varies with soil conditions and production practices. In countries like Indonesia, biomass is burned as part of their agricultural system as well as for fuel. A small but significant amount of methane is produced - 95% is carbon dioxide and carbon monoxide. Waste water treatment can only produce methane if the organic matter in the waste water is treated anaerobically. If methane is produced, it is directly released to the air.

1.1.1.2 Natural methane sources

The known natural sources of methane are wetlands, fossil, termites and freshwaters. Natural wetlands are a rich anaerobic environment and abundant in organic matter. As such, it is a conducive habitat for methanogenic bacteria (methane producing bacteria) and enhances the decomposition of the organic matter, thus producing methane. Methane was created in the geologic past and found in the earth's crust in the form of gas hydrates and permafrost. Hydrates are solids comprising water molecules that contain methane molecules which are found in both the polar regions and ocean sediments. Permafrost methane originates from biological processes and is trapped in shallow permafrost ice and soil before it reaches the atmosphere. Today, the amount of permafrost is decreasing and more methane is being released to the environment. Cicerone and Oremland (1988) reported the emissions of methane from termites depended on the termite population, amount of organic matter consumed, type of species and the methane-oxidizing bacteria activity. The freshwater environment is an ideal place for the decomposition of wetlands plants which then emits methane. Emissions from these natural sources are dependent on the temperature and rainfall. For example, temperature changes can promote microbial activity, thus enhancing methane production.

1.1.2 Ceramics

The term ceramics is defined as the art and science of making and using solid articles which have their essential component, and are composed in large part of, inorganic non-metallic materials (Kingery *et al*., 1976). This definition is not limited to just pottery, porcelain, refractories, structural clay products, abrasives, porcelain enamels, cements and glass but it also applies to non-metallic magnetic materials, ferroelectrics, single crystals and glass-ceramics. Barsoum (1997) defined ceramics as solid compounds that are formed by the application of heat and sometimes heat and pressure, comprising at least one metal and a non-metallic elemental solid or non-metal, a combination of at least two non-metallic elemental solids, or a combination of at least two non-metallic elemental solids and a non-metal.

Today, ceramics are, in short "solid inorganic non-metallic materials made by firing" (Murata, 2000). The term ceramics is now classified as traditional and fine ceramics. These ceramics have common features; resistance to rust, heat resistance, non-flammability, extreme hardness and ease of forming. These features are meaningful because neither plastics nor metals have all these features. Today's fine ceramics are a new breed or a new kind of material. To distinguish between fine and traditional ceramics, the latter are made of natural materials whilst the former are produced by putting the atomic compositions of various, refined elements together through scientific forming and sintering processes. In other words, fine ceramics are made by scientifically controlling chemical compositions and this brings the realisation of new materials customised to the unlimited amount of purpose they serve. Therefore, fine ceramics can be grouped as functional materials such as electronic ceramics, optical ceramics and catalyst or structural materials such as bio-ceramics, heat resistance structure and artificial jewellery.

1.1.2.1 Electronic ceramics

The secret of the characteristics of fine ceramic is in its microstructure. To a layman it is like an artificially created small piece of stone as shown in Figure 1.1

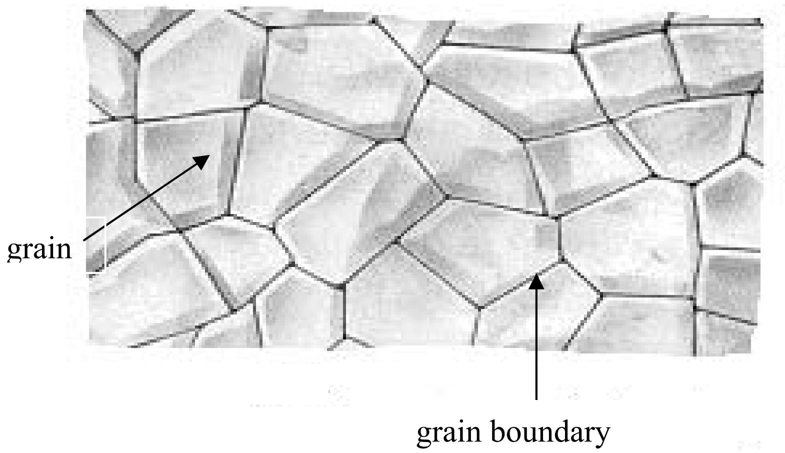

FIGURE 1.1: Microstructure of a fine ceramic showing grain and grain boundary of a typical ceramic.

Technically, they are finely aggregated grains and traditional ceramics are comparatively far more porous and more irregular. The grains and grain boundaries are all scientifically controlled and show specific electrical responses to electrical potential or environmental changes. These specific reactions are utilised for specific purposes. For example, titanium dioxide (TiO_2) ceramics or barium titanate ($BaTiO_3$) ceramics are polarised when voltage is applied to them. On the other hand, other types of ceramics containing different additives, though mainly composed of the same $BaTiO_3$, serve as unique semiconductors which turn an electric flow on and off under a given condition. This is therefore an application of the electrical changes in their grain boundaries. Another example is when the inclusion of a catalyst in semiconductor ceramics such as TiO_2 or SnO_2 affects the conductance of the material which can serve as sensing element in a gas detector. Thus the function of electronic ceramics varies according to their internal microstructure (Saito, 1988).

Most natural stones are insulators. In contrast, fine ceramics can be designed with different conductivities by adjusting their composition; some are conductors and others are insulators. This variation is one of the greatest advantages of electronic ceramics. Electronic ceramics can further sub-divided into magnetic ceramics, transparent ceramics, pyroelectric ceramics, semiconductive ceramics, piezoelectric ceramics, insulating ceramics and dielectric ceramics.

1.2 Justification for Research

In the past, gas sensors were used to control industrial processes and to warn of poisonous gas leakages (Carotta *et al.*, 1991). In Europe, controlling air quality was mandatory by 2001 as stipulated by Council Directives such 96/61/EC and 96/62/EC (Saul Garcia and Fernandez, 1999 and O'Malley 1999). For example, the National Air Quality Standard for CO adopted by the UK government in January 2000 is currently 10 ppm for a running 8 hours mean (Stewart, 2000). It was therefore necessary to focus research on sensors capable of monitoring pollutant gases and controlling combustion processes both at home and in industry (Ruiz *et al.*, 2002). The demands for more accurate and dedicated sensors to monitor and control environmental pollution have led to the development of new sensing materials to improve sensitivity, selectivity and stability of sensors (Sharma *et al.*, 2001).

With reference to an environmental issue, gases like CO_2, methane, water vapour, ozone, nitrous oxide and halocarbons play a significant role in enhancing the greenhouse effect. The greenhouse effect is primarily a function of the concentration of water vapour, carbon dioxide and other trace gases in the atmosphere that absorb the terrestrial radiation leaving the earth surface. The changes in the atmospheric concentration of these greenhouse gases will alter the balance of energy transfers between the atmosphere, space, land and the ocean which will give rise to global warming (Houghton *et al.*, 1996).

1.2.1 Methane gas and global warming

Methane gas is amongst the greenhouse gases and the atmospheric concentrations of methane have doubled over the last 200 years and continue to rise, although the rate of increase is slowing (Dlugokencky *et al*., 1998). The natural methane emissions to the atmosphere are 30% from wetlands, oceans, termites while the remaining 70% is anthropogenic, from human activities such as agriculture, usage of fossil fuel and waste disposal (Fung *et al*., 1991). When methane enters the atmosphere, it reacts with molecules of oxygen and hydrogen known as OH radicals. The OH radicals combine with methane and they decompose into carbon dioxide and water vapour. Increasing emissions of methane will reduce the concentration of OH radicals, a feedback which may increase methane's atmospheric lifetime. While most greenhouse gas studies focus on CO_2, methane is 20 times more potent as a heat trapping gas in the atmosphere (Houghton, 2001). Thus, methane gas is also a leading contributor to global warming after carbon dioxide.

1.2.2 Methane gas explosions

Methane is the major component (95 %) of natural gas, thus it can be used to produce energy. The lower explosion limit (LEL) is 5% methane in air and the upper explosion limit is 15% methane in air. However, gas explosions are frequently reported in homes, pipelines and coalmines world wide. For example, an explosion at one of the gas pipeline owned by Brunei Shell company in Seria destroyed two homes and hundreds of residents in the vicinity were forced to abandon their homes (Othman, 2000). The cause of the explosion was due to a corroded pipeline which leaked out methane gas (Teo, 2000). Another incident, at a Terengganu gas processing plant in Kertih, owned by Petronas Malaysia caught fire and killed three workers (Alias and Hamidah, 2002). Frequent gas explosions occurred in the 1960s in Japan largely associated with the popular usage of bottled liquid petroleum gas for domestic purposes (some 23 million households use them for cooking requirements and another 18 million used piped gas). In countries like the United Kingdom a similar problem was reported in the Ronan Point disaster. The disaster at Ronan Point in London, England in May 1968 was a gas explosion which led to the collapse of one whole corner of a high rise building and the death of three people. In Malaysia, closed packed condominiums, apartments and flats which utilize bottled or channelled gas pipeline are also prone to disasters like those in Japan.

1.2.3 The importance of methane sensing in Malaysia

There are two main reasons for researching into methane sensing in Malaysia. Malaysia has substantial resources of natural gas from offshore fields such as those based in Terengganu and Sarawak. Its reserves of natural gas ranked 12th in the world (Wu, 2000a). The gas reserves here are dedicated to the Peninsular Gas Utilization Project which provided 37% of the main sources of primary commercial energy for the period 1996 to 2000. By 2005, the contribution is expected to rise to 39.9%. Under the 8th Malaysia Plan (2001-2005), the Government will continue to promote gas usage. Malaysia has the largest natural gas reserves among the Southeast Asian economies and is the third largest amongst the Asia Pacific economies. At the turn of the century, the recoverable gas reserves were 84.4 trillion standard cubic feet, 43% offshore east coast of West Malaysia, 48% located offshore Sarawak and 9% offshore Sabah. This introduces 1753 km of gas pipelines into the network of both domestic and industrial sectors (Balce, 2002). Ambitious constructions of natural gas pipeline in Malaysia like the one from Kuala Terengganu to Segamat and its branches and the 220 miles of gas pipeline from Gulf of Thailand to the northern state of Kedah which will provide natural gas for industries and home would certainly need gas sensors to detect leaks and seepage of gases. It is foreseen that detection and measurement of natural gas leaks such as methane is required on a day-to day basis especially in the natural gas industry such as Petronas, Gas Malaysia and from gas appliances, gas piping inside buildings or buried gas piping.

In modern, high rise flats, apartments and condominiums in Malaysia, methane gas is supplied via such a network of pipelines. The gas is normally used for domestic cooking or drying clothes. Such areas are enclosed due to the usage of air-conditioning. Therefore, methane leakages in the concealed pipeline network will accumulate in high concentrations in a very short time. This inevitably needs methane monitoring for both public safety and environmental issues. The early warning of methane presence would led to necessary steps that could save lives and preserve the environment.

Malaysia also has large resources of tin and its tin reserves ranked as the world's third largest (Carlin, 2001). Tin is mined by various methods; gravel pump (53.5%), open cast (20.2%), retreatment or Amang plant (12.6%), panning and underground (8.3%) and dredging (5.4%). Malaysia exported 20 614 tons of refined tin and the domestic demand was 5639 tonnes in 2000 (Wu, 2000b). The local consumption are from the Malaysian solder industry (56.3%), pewter industry (14.8%), tin plating industry (10.6%) and other end users (18%) reported by the Wu (2000b).

An oxide of tin known as stannic oxide (SnO_2) is easily obtained from pure tin or tin derivatives in the form of thin, thick film or pellet (ceramic) form. Stannic oxide is a well-known material used for CO and CH_4 gas sensing. Nevertheless, the state of methane gas sensing using stannic oxide needs further investigation as it has not attained its projected capability (Clifford, 1981).

The proposed methane sensing project will contribute to future R&D in methane sensors for Malaysian natural gas pipelines, domestic actuators and an environmental monitoring system to reduce global warming. The usage of tin in the form of stannic oxide will introduce an alternative use of the local tin and promote a diversified Malaysian economy.

1.3 Scope of study

The knowledge of gas sensors has led to high-volume applications which are publicised via periodic international sensor conferences which are devoted to fundamental research, for example Transducers/Eurosensors, Semiconductor Gas Sensors (SGS), Pittsburgh Conference (PITTCON), Electrochemical Gas Sensors and also a book series covering the state of sensor chemistry, physics and technology (Gopel *et al.*, 1990). Much work has been done in the field of methane sensing, for example thick film based on SnO_2 (Carotta *et al.*,1991) in relating the sensitivity to methane. The performance of the sensor material depends strongly on its composition and preparation conditions (de Angelis and Roberto, 1995). It was intended that the material chosen was SnO_2 and takes the form of a sintered pellet. The sensor element that comprised SnO_2 only has limited sensitivity to CH_4 (Williams, 1987). The incorporation of noble metals is to enhance the sensitivity (Yamazoe *et al*., 1983).The use of additives like Pt was also reported to enhance sensitivity and selectivity and to reduce the response time and operating temperature of the sensing material in the form of thin film (Wu *et al.*, 1993; Schierbaum *et al*., 1991; Zakrzewska *et al.*, 1997 and Atashbar *et al.*, 1998). Gélin and Primet (2002) reported that Pt as a catalyst has advantageous over Pd with respect to methane sensing. Firstly, Pd appeared to be more sensitive to poisoning than Pt and secondly Pt could fully and easily restored while the deactivation of Pd was irreversible. Therefore, a great interest in Pt-SnO_2 ceramic to achieve a considerable degree of performance for methane sensing in air was anticipated mainly due to the catalytic behaviour of Pt.

The electrical properties of the ceramic semiconductor Pt-SnO_2 was studied using impedance spectrometer and Sensor Element Characterization System (SECS) which are home-made at the Warwick University, United Kingdom and Universiti Teknologi Malaysia respectively. The measurements made were electrical resistance, conductance and sensitivity of the sensor element. The microstructure of the sensor element was studied using High Resolution X-Ray Diffraction (HRXRD), Energy Dispersive Analysis using X-Ray (EDAX), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM), X-Ray Photoemission Spectroscopy (XPS), Nuclear Magnetic Resonance spectroscopy (NMR), Fourier Transform Infra-red spectroscopy (FTIR), Raman-Shift spectroscopy and Mössbauer spectroscopy. The physical properties of the ceramic was gauged via Vickers hardness, bulk density, porosity and elastic modulus measurements. Brunauer-Emnett-Teller (BET) method was employed to determine the specific surface area and the particle size of the ceramic whilst the Barrett-Joyner-Halenda (BJH) method is for calculating pore size distributions The highlight of the research was to relate where ever possible the sensitivity and the microstructure properties. It is reasonable to expect that if the same microstructure is present in the fabrication of a similar ceramic, then it will show the similar corresponding sensitivity.

1.4 Statements of hypotheses

The hypotheses made are as follows;

1. The usage of Pt-SnO_2 would form a stable and sensitive material for methane sensing in air via the dry pressing method,
2. The amount of Pt in SnO_2 sintered will be minimized in obtaining the optimum composition of the ceramic and the optimum operating temperature of the gas sensor.

1.5 Objectives of the study

The objectives of this study are;

1. To construct and improve a new sensing probe in the acquisition of electrical measurements,
2. To determine the optimum composition and optimum operating temperature of the methane sensing,
3. To determine the sensor resistance, conductance and sensitivity with varying ceramic compositions, operating temperatures of the methane sensor and flow rates of the methane gas,
4. To determine the physical and microstructural properties of the Pt-SnO_2 ceramics.

1.6 Thesis plan

This thesis comprises of nine chapters. In the introduction, the state of gas sensing is briefly mentioned with an emphasis on methane sensing with respect to global warming and perils of gas explosion. The notions of methane sensing as a research project with regards to Malaysian resources are highlighted. The research tools and expectations are stated.

The second chapter deals with methane sensor viewed through the work by researchers in the last four decades, since the birth of the gas sensor in the 1960s. Various methane sensors are mentioned including the stannic oxide based sensors. The introduction of various dopants and their effects on the performance of the gas sensor are also mentioned. The problems that arise from the sensors are also pointed out.

The third chapter mentions the theory of sensing mechanisms known up to the time this thesis was written. These include the well known Spillover and Energy Barrier Model. The role of Pt in SnO_2 in the sensing property is also highlighted.

The fourth chapter states the experimental and measurement techniques which include sample preparation and the apparatus used for both electrical and microstructure analysis. The parameters and physical measurements are defined.

The fifth chapter presents the results of the electrical analysis which are basically the measurement of sensor element resistance, conductance and sensitivity. The variables in the experiments are sintering temperature and the Pt loadings in the SnO_2 ceramics. The effects of methane gas concentration and of methane gas flow rate are also reported. The stability of the methane is viewed via its long term performance.

The sixth chapter highlights two important parameters which will gauge the performance of the methane sensor, namely optimum composition of the ceramics and optimum operating temperature of the sensor with respect to methane sensing in air. These two parameters are then related to the mean crystallite size of the ceramics.

The seventh chapter looks at the response and recovery times of the methane sensor which are influenced by methane gas concentration, operating temperature of the sensor, doping level and the flow rate of the methane gas.

The eighth chapter deals with microstructure analysis of the ceramics. The ceramics analysed using HRXRD, EDAX, SEM, TEM, XPS, NMR, Mössbauer, Raman-Shift and FTIR will lead to the understanding of the microstructure observed. The physical properties in relation to its stability are gauged via DTA, TGA analysis and measurements of density, porosity, BET and elastic modulus.

The ninth or final chapter summarizes the findings and comments on the Pt-SnO_2 ceramics in relation to methane sensing in air. Recommendations for further work are also mentioned.

9.2 Recommendations

It is recommended that the following studies be attempted;

- ✓ perform detection on desired methane concentration using gas blenders,
- ✓ in situ microstructure analysis using built-in heater/temperature controller for temperatures 100-500^{o}C.

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