THE EFFECT OF Pd ON ELECTRICAL PROPERTIES OF SnO_2 IN CH_4 DETECTION

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DEDICATION

To my late mother

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ABSTRACT

The effect of Pd on electrical properties of Tin (IV) oxide (SnO_2) as an element for CH_4 detection is investigated for samples prepared from a mixture of powders of $(100\text{-}x)SnO_2.xPd$ ($0 \leq x$ wt % ≤ 15) which were pressed into pellets and sintered at various temperatures ranging from 600°C to 1100°C. In order to achieve the objectives of the study, a Gas Sensor Characterization System (GSCS) was built. The main component of the GSCS is an airtight gas sensor test chamber with a volume of about 405 cm^3. The conductance of a sample is monitored in this chamber at various operating temperatures, flow rate of carrier gas (synthetic air) and applied voltages when the sample was exposed to small concentrations (in ppm) of CH_4 in air. The GSCS is interfaced, via an ADC card, with a computer for data acquisition, storage and analysis. Results show that SnO_2 without Pd cannot detect CH_4 in air up to an operating temperature of 400°C. However, the modification of SnO_2 by the addition of Pd significantly enhances its sensitivity to CH_4 with the highest sensitivity occurring at around 400°C. The general trend is a sharp increase in sensitivity of SnO_2 up to about 3 wt% Pd and thereafter a gentle decrease up to 15 wt% Pd. Fifty percent (50 %) response time of about 20 seconds and recovery time of 7.27 minutes were calculated for samples with 3 wt% Pd sintered at 900°C. The relationship between sensitivity and the concentration of CH_4 in air at the operating temperature of 400°C can be approximated by the logarithmic function. Results on the effect of sintering temperature show that the sensitivity of SnO_2 with Pd as additive is higher for samples sintered at lower temperatures. The flow rate of the carrier gas was found to significantly affect the sensitivity of samples sintered at lower temperatures. The response and recovery times generally decreased with increasing flow rate of the carrier gas. This effect is attributed to increase in the oxygen partial pressure of the carrier gas in the test chamber with increasing flow rate. On the other hand, it was observed that the sensitivity depends on the applied voltage especially for samples sintered at lower temperatures. Measurements on ethane (C_2H_6) and hydrogen sulfide (H_2S) in air were carried out in order to test the selectivity of some samples to other gases. It was found that sensitivity to C_2H_6 is higher than sensitivity to CH_4 but in the same operating temperature range with a selectivity of about 1.69 at 400°C. H_2S was detectable in air with the highest sensitivity at 100°C and decreased to a minimum at 200°C. SEM micrographs of the samples indicate that the SnO_2 crystallites are of sub-micron sizes. The Pd concentration in SnO_2 determined by AAS was shown to increase with increasing nominal composition of Pd added to SnO_2. It was possible to detect Pd in samples with 15 wt% Pd using EDAX but not for samples with nominal composition of ≤ 10 wt% Pd.

ABSTRAK

Kesan palladium (Pd) terhadap sifat elektrik Stanum (IV) oksida (SnO_2) sebagai elemen pengesan gas metana (CH_4) yang disediakan daripada campuran serbuk berdasarkan komposisi (100-x)SnO_2.xPd, dengan peratus berat x dalam julat 0% hingga 15% telah dijalankan. Sampel elemen pengesan berbentuk pelet disediakan dengan pencetak tekanan dan disinter pada suhu antara 600°C hingga 1100°C. Untuk mencapai objektif kajian, satu sistem peralatan dinamai sistem pencirian pengesan gas (*Gas Sensor Characterization System* –GSCS) telah direkabina. Komponen utama GSCS ialah sebuah kebuk kedap udara berisipadu 405 cm^3, dipanggil "*gas sensor test chamber*". Di dalam kebuk ini sampel ditempatkan dan dipantau perubahan konduktans sampel terhadap suhu pemanasan, kadar aliran gas pembawa (udara sintetik) dan voltan kenaan apabila didedahkan kepada kepekatan rendah (ppm – part per million) gas CH_4 di udara. Kad ADC digunakan untuk mengantaramukakan GSCS dengan komputer yang boleh mengambil, menyimpan dan menganalisa data. Hasil kajian menunjukkan sampel SnO_2 tanpa Pd tidak dapat mengesan CH_4 di udara walaupun suhu operasi dinaikkan sehingga 400°C. Tetapi apabila Pd dicampurkan kepada SnO_2, sampel menjadi sangat peka kepada kehadiran gas CH_4 di udara dan kepekaan tertinggi dicapai pada suhu operasi disekitar 400°C. Umumnya, kepekaan terhadap gas CH_4 meningkat tinggi sehingga komposisi 3% berat Pd dan kemudian turun dengan perlahan sehingga ke 15% berat Pd. Masa respons 50% sekitar 20 saat dan masa pemulihan 7.27 minit diperolehi untuk sampel 3% berat Pd yang disinter pada suhu 900°C. Hubungan antara kepekaan dan kepekatan CH_4 pada suhu operasi 400°C adalah bersifat logaritma. Umumnya kepekaan adalah tinggi bagi sampel yang disinter pada suhu rendah. Kepekaan sampel yang disinter pada suhu rendah sangat bergantung kepada kadar aliran gas pembawa. Kesan ini adalah disebabkan oleh penambahan tekanan separa oksigen dalam kebuk *"gas sensor test chamber"*. Kepekaan bergantung juga kepada voltan kenaan terutama sekali bagi sampel-sampel yang disinter pada suhu rendah. Untuk menguji kepilihan (selectivity) terhadap beberapa gas lain, pengukuran kepekaan terhadap gas etana (C_2H_6) dan gas hidrogen sulfida (H_2S) di udara telah dibuat. Keputusan menunjukkan kepekaan kepada gas C_2H_6 adalah lebih tinggi daripada gas CH_4 tetapi pada julat suhu operasi yang sama dengan nilai kepilihan 1.69 pada suhu 400°C. Gas H_2S juga dapat dikesan di udara dengan kepekaan tertinggi pada suhu 100°C dan menurun ke nilai minimum pada 200°C. Analisis SEM menunjukkan saiz butiran sampel seramik yang dihasilkan berukuran sub-mikron. Analisis AAS menunjukkan kepekatan Pd dalam SnO_2 meningkat sejajar dengan pertambahan nominal Pd kepada SnO_2. Dengan menggunakan EDAX, unsur Pd hanya dapat dikesan dalam sampel SnO_2 dengan 15% berat Pd. Dengan kaedah yang sama, Pd tidak dapat dikesan untuk sampel-sampel dengan $\leq$ 10% berat Pd kerana kepekatan Pd adalah dibawah had pengesan EDAX.

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LIST OF SYMBOLS

$\hbar$	-	Planck's constant
k	-	Boltzmann constant
R	-	Gas constant
E_F	-	Energy of the Fermi level
E_G	-	Forbidden energy band
E_C	-	Bottom of the conduction band
E_V	-	Ceiling of the valence band
E_D	-	Ionization energy of donors
E_A	-	Ionization energy of acceptors
I_H	-	Ionization energy of hydrogen atom
N_D	-	Donor concentration of free current carriers
N_A	-	Acceptor concentration of free current carriers
$N_{D,ef}$	-	The effective donor concentration of free current carriers
$N_{A,ef}$	-	The effective acceptor concentration of free current carriers
ε_0	-	Permittivity of free space
ε	-	Pemittivity of a material
ε_r	-	Relative permittivity
m_n^*	-	Effective mass of an electron
m_0	-	Mass of an electron in vacuum
σ	-	Electrical conductivity

P_{O_2}	-	Partial pressure of oxygen
e	-	Electronic charge
ΔH^0	-	Enthalpy changes of a reaction
j	-	Current density
n	-	Concentration of electrons
v_D	-	Drift velocity of electrons
$\vec{F}$	-	Force on a electron
$\vec{a}$	-	Acceleration
μ_n	-	Mobility of current carriers
E_a	-	Activation energy
l	-	Mean free path of an electron
L	-	Diameter of a crystal
L_D	-	Debye shielding length
a, c	-	Dimensions of the unit cell in a crystal (lattice constant)
E_p	-	Energy level of a polaron
Å	-	Angstroms
E_{VAC}	-	Energy of the vacuum level
E_{CS}	-	Bottom of the conduction band at the semiconductor surface
E_{VS}	-	Ceiling of the valence band at the semiconductor surface
E_t		Energy position of chemisorbed particles
E_S	-	Surface barrier energy caused by surface charging
χ	-	Value of affinity to electron of a semiconductor surface
$e\varphi$	-	The work function of an electron
∂	-	The dope parameter of a semiconductor
E_{CD}	-	Donor levels below the bottom of the conduction band
n_b		Concentration of electrons in the bulk of grains
p_b	-	Concentration of holes in the bulk of grains
Q_S	-	Charge on surface states

V_S	-	Potential barrier height of band curvature
Φ_0	-	Potential barrier height corresponding to the intergranular layer material
λ_0		The equivalent right-angled barrier thickness in polycrystalline material
N_t	-	Surface charge of trapped electrons per unit area
ϕ	-	The electric potential
ρ	-	Charge density
p	-	Concentration of holes
N_{D+}	-	Ionized donors
N_{A+}	-	Ionized acceptors
N_C	-	Effective density of states at the conduction band edges
θ	-	The fractional coverage (occupancy) of surface states
G	-	The electric conductance of a material

CHAPTER I

INTRODUCTION

1.1 General Background

Development of gas sensors have proceeded rapidly during the last decade, in response, primarily, to a large R & D expenditure commitment in order to enable environmental legislation to be satisfied [1]. There are two significant factors that will stimulate future gas-sensor device development. Firstly, there is the concern to monitor environmental pollution as well as safety in homes and industrial complexes [2]. Secondly, there is a desire for sensors to monitor process and product performance [1].

The utilization of solid state gas sensor devices in practical applications have resulted in dramatic improvements in industrial process control, in the functioning and facilities of domestic devices, and in the control of environmental pollution through, for example, vehicle exhaust emission controls [3]. However, notwithstanding their success for improved environmental protection, improved process operation or improved product performance, these sensors have not been generally considered sufficiently reliable or durable for industrial flammable gas monitoring [1]. Without developing inexpensive but reliable and durable gas sensors, significant advances in control and

instrumentation, which may bring large commercial opportunities and environmental benefits, will not be possible. Unlike the control electronics, the sensor interacts with, and often is exposed to, the environment [4].

A semiconductor chemical sensor may be defined as an electronic device designed to monitor the content of particles of a certain gas in surrounding medium [5]. In a broader sense, chemical sensing involves recording the concentration of particles such as atoms, molecules or ions in gases or liquids using an electric signal [4]. The term 'sensor' and 'transducer' are often used synonymously. According to Ihokura and Watson [6] a 'transducer' is a device that converts one form of energy into another, and a 'sensor' is a form of transducer that converts a physical or chemical quantity into an electrical quantity for purposes of measurement. Terminologically, the active part of a complete gas sensor assembly is called the sensor element, whilst a complete instrument incorporating such a sensor can take the form of a gas monitor, gas detector or gas alarm.

The operational principle of a gas sensor is based on transformation of the value of adsorption of a gas on the surface of the semiconductor directly into an electrical signal [3]. This signal corresponds to the amount of particles adsorbed from surrounding medium or deposited on the surface of operational element of the sensor due to heterogeneous chemical reaction. The high sensitivity of the electrophysical characteristics of these semiconductor materials to adsorption of various gases as well as the capability to control it makes these materials attractive for manufacturing gas sensitive electronic transducers. Gas sensor science and technology draws on various diverse academic fields such as materials science [3], ceramic fabrication [7], solid state physics and surface chemistry [8], electrochemistry [9], catalysis and gas dynamics [8], and solid state ionics [10]. Therefore, the science of chemical sensors generally requires multidisciplinary approach: choosing the physical detection mechanism and the materials; understanding the physical and chemical properties of the interfaces; selecting device technology and eventually studying signal processing.

The Principal types of solid state gas sensors commercially available today are the galvanic oxygen sensors, the catalytic gas detectors and semiconductor oxide sensors [1]. The galvanic and catalytic gas detectors incorporate noble metals such as palladium (Pd) into the device for sensing purposes. Pd is also used as an additive in metal oxide based semiconductor gas sensors in order to improve its sensitivity especially to hydrocarbons. Pd is an element that resists corrosion, dissolves in acids and fused alkalis, readily absorbs hydrogen gas and has a melting point of 1552°C [11]. Semiconductor gas sensors are usually based on the surface properties of the oxides of tin or zinc (SnO_2 or ZnO) [12,13]. These semiconducting oxides could be used for the detection of combustible and toxic gases in air [14]. Their advantages are high sensitivity, simple design, low weight and cost, while, on the other hand, selectivity and stability limit the range of applications. An improvement of these properties cannot be achieved simply by trial and error, but requires a better understanding of the surface processes connected with the conductance changes. In many ways it would be an advantage if the initial studies of the material could be carried out with it in sensor device form [15]. This is not, however, always practicable, since overcoming sensor fabrication problems can be very time consuming. The initial studies, therefore, often involve an investigation of the material properties. Having established the potential of the material as the basis of a gas sensor, device fabrication can then be undertaken in order to establish its feasibility. This is the approached followed in this study.

Tin (IV) oxide (SnO_2) based sensor materials are dominant in research and applications [14,16,17]. Sintered layers and thin films are in practical use. In addition, the surfaces of single crystals are also studied under well-defined conditions to try to achieve a better separation of parameters influencing the properties of gas sensors. Some of the physical properties studied include bulk properties, grain boundary properties and surface properties [18]. In this study, therefore, polycrystalline SnO_2 with Pd as a sensitizing additive is selected as the base material and its electrical properties are analyzed and evaluated with respect to its sensing characteristics to the flammable gas CH_4 in air.

1.2 Scope of the study

Semiconductor gas sensors based on SnO_2 and other metal oxides have not yet attained their projected utility [19]. Although present day sensors respond to part per million (ppm) levels of reducing gases, irreproducibility, drift, and poor selectivity characterize their response. Realizing that any improvement in the gas detection characteristics of metal oxide based semiconductor materials depend on our knowledge of the operating principles of these devices, we embark on an investigation of the characteristics of these devices under controlled environment. In general, the investigation of the sensing properties of metal oxide based semiconductor elements and devices have been of two types. The first, are those researches embracing a wide range of diverse phenomena, and the second are those limited to a thorough study of a particular observation. The flexibility of the first approach prevents the systematic study necessary for a quantitative description of gas sensing characteristics of the materials. The later approach is generally so rigorously limited that it loses sight of the complexity of behavior found in each catalytic material. As a result, there is an insufficient body of quantitative and systematic information concerning the sensing characteristics of metal oxide based semiconductor gas sensors. The scarcity of well-measured electrical response of semiconductor materials to target gases is also another bottleneck limiting the development of descriptive theories of device behavior.

A major concern of this study is, therefore, to acquire a qualitative and quantitative description of the diverse operating characteristic of SnO_2, with Pd as a sensitizing additive, in the detection of CH_4 in air. These operating characteristics include the sintering temperature, operating temperature and the composition of the samples. SnO_2 is chosen as the base material in this study for its proven sensitivity as a gas detector and its chemical stability and durability [13,20]. The behavior of sensor elements and devices based on SnO_2 is characteristic of many sintered and thin film metal oxide semiconductors [20]. What ever has been published in the literature cover limited parameters of the performance of this material in CH_4 detection in a controlled environment. Sensor elements composed only of SnO_2 have a limited sensitivity to

chemically stable gases such as CH_4 [13]. Because the gas sensitivity is closely related to redox reactions of the detected gases on the sensor surface, it is reasonable to suppose that it could be improved by including additives which act as catalyst to these reactions. Noble metals such as Pt, Pd, Rh and Ir are very active for oxidation reactions [8]. Therefore, Pd is used in this study as a sensitizing additive that is added as an impurity to SnO_2 to enhance its sensitivity to CH_4. The research will cover higher composition of Pd (up to 15 wt%). Previous studies have concentrated on lower composition of Pd up to about 5 wt% [6]. It is intended, as one of the major objectives of the study, to design a gas sensor test chamber and build a testing rig by which the parameters of the study can be controlled or varied as required.

There are other factors that may influence the sensitivity of gas sensor elements. Some of these factors include the flow rate of the carrier gas and the applied voltage to the sensor elements. The characterization system for this study was designed in such a way that these variables could be controlled or varied as required. Since changes in the partial pressure of oxygen in the carrier gas passing over the sensor element affects its sensitivity [6,8,9,13], it is reasonable to postulate that the flow rate of the carrier gas may affect the oxygen partial pressure and thereby influence the sensitivity of the sensor element. The sensitivity of a sensor element can also be affected by the magnitude of the applied electric field to the sensor element that causes the energy barriers between adjacent grains in the polycrystalline SnO_2 based sensor element to decrease [7].

Another factor that is important in the qualitative and quantitative analysis of gas detection by SnO_2 based sensor elements is the mechanisms underlying the detection of traces of flammable or toxic gases in air. In order to understand these mechanisms it is important to observe the microstructure of the sensor elements. Based on these observed microstructures, it is possible to suggest the most probable mechanisms in the detection process. It is also important to utilize other high precision instruments in determining actual composition of the samples with the view of making samples that are reproducible.

1.3 Statement of hypotheses

The following statements are presented as the major hypotheses of the study:

- The presence of Pd as impurity element in SnO_2 will reduce the temperature at which SnO_2 is operated in order to detect the presence of small quantities of CH_4 (in ppm) in air. Pd is a hydrogen-dissociating catalyst and therefore its presence on the surface of SnO_2 crystallites will lead to the dissociation of CH_4 molecules at lower temperatures compared to pure SnO_2 thus leading to an increased sensitivity to CH_4 in air at these lower temperatures. It is also expected that the temperatures at which the samples are sintered will significantly influence the sensitivity of the sensor elements to CH_4 in air.

- The amount of Pd that is added to SnO_2 in wt% would have a significant influence on its sensitivity to CH_4 in air up to a certain composition level, the optimum composition. However, above the optimum Pd composition in SnO_2, it is expected that the sensitivity to CH_4 in air will drop as a result the hindrance of the gas phase reactions on the SnO_2 semiconductor support by Pd particles. It is further hypothesized that the amount of Pd present will not influence the position of the optimum operating temperature in the detection of CH_4 in air.

1.4 Objectives of the study

- To design and construct an experimental setup for the characterization of the electrical properties of SnO_2 in gas detection.

- To determine the range of operating temperature over which SnO_2 with Pd as additive could detection CH_4 in air and identify the optimum operating temperature.

- To determine the optimum composition of Pd added to SnO_2 in the detection of CH_4 in air and to analyze the effect of sintering temperature of the samples on their sensitivity to CH_4 in air.

- To analyze the sensitivity verses concentration characteristics of SnO_2 with Pd as additive in the detection of CH_4 in air.

1.5 Thesis plan

Following the brief introduction presented in this chapter, a general review of metal oxides is given in Chapter II. This includes a review of the preparation of ceramic materials and the structure and electrical properties of these materials. Chapter III deals with the theory of gas detection using metal oxides. It begins with a review of the quantum mechanical bases of the reactivity of surface state of semiconductor materials in ambient environment. This is followed by an analysis of the theoretical bases of gas detection by metal oxides, and finally the effects of additives on the gas sensing properties of SnO_2 is discussed. Details of the sample preparation, design and construction of the experimental arrangement and the measurement techniques employed are outlined in Chapter IV. Results and discussion of the experimental work carried out on the composition, sintering and operating temperatures on sensitivity, response and recovery times of SnO_2 with Pd as additive in CH_4 detection is presented in Chapter V. The results on the relationship between sensitivity of SnO_2 and the concentration of CH_4 in air (sensitivity-concentration characteristics), cross-sensitivity studies and a comparison of the sensitivity of the sensor elements prepared in this study with those of a commercial gas sensor are given in Chapter VI. Chapter VII is devoted to the evaluation of the results on the microstructural and compositional analysis using SEM, AAS and EDAX. Finally, Chapter VIII presents the major conclusions of the research and suggestions for future studies.

CHAPTER II

GENERAL REVIEW OF METAL OXIDES

2.1 Introduction

This chapter reviews the structure and electrical properties of the oxide of metals. The definition and formation of a ceramic body is discussed in section 2.2. In section 2.3, a discussion on the structure and electrical properties of metal oxides, the influence of impurities and doping impurities, and electrical conductivity and other transport phenomena in ceramic semiconductors is presented. Section 2.4 briefly reviews the structure and properties of SnO_2, which is the base material used in the study. Finally, in section 2.5, a brief summary on the chapter is given.

2.2 The formation of a ceramic body

The word 'ceramics' is not clearly defined but can be taken roughly to mean a substance which is refractory, i.e., resistant to heat and corrosion [21]. It consists of one or more metals (or an element such as silicon) in combination with non-metallic element-usually oxygen. According to Hench and Dove [22], a ceramic crystal could be defined simply as a binary compound of metallic atom with oxygen. Koller [7] defines ceramics as inorganic nonmetallic materials with polycrystalline structure,

prepared by sintering at elevated temperatures. These definitions give a general description of the character of ceramic substances from the viewpoint of traditional approaches to products prepared by ceramics technology. Until recently, it was thought that ceramics are both thermally and electrically nonconductive and that they must necessarily be made of natural raw materials that are subjected to simple treatment, formed and then strengthened by firing. However, as time progressed, ceramics technology began to utilize not only chemically prepared raw materials, but also metal powders (metal ceramics) and powdered glass.

In the production of ceramics from chemically prepared raw materials, the heat treatment is usually divided into two parts. In the first stage, the raw materials are heat treated so that they become suitable for shaping; in the second stage, following the creation of the product, the actual sintering occurs. In the first stage of heat treatment, the raw material is fired to achieve a particular crystal size required for some subsequent shaping operation or, most often, to ensure that chemical reactions and processes occur that would otherwise complicate the subsequent compaction process of sintering during the second firing. The heat treatment of the raw materials is accompanied by the decomposition of carbonates (and thus the first firing stage become known as calcination), dehydration, dehydroxylation and the reaction of oxides to form compounds with higher specific weight. The reactions occur primarily in the solid phase and these reactions are thermally activated.

The second firing in the solid phase then mostly involves only those physical processes that are typical for ceramics technology, denoted as sintering. These processes are typically thermally activated and occur in ovens at high temperatures. The sharp firing involves compaction and strengthening in the process known as sintering. The changes occurring in the ceramics are usually physical in nature, the porosity changes, a glassy phase can be formed, and a mechanically strong, variously dense ceramic body is created. The driving force in sintering is the tendency of the system to attain the state with the lowest free enthalpy. The initial powdered material has a large surface area and is thus also characterized by a large surface energy. During sintering, the surface area of

the system decreases, decreasing the overall surface energy. A growth in the crystal size and a decrease in the overall energy of the boundary surfaces accompany sintering.

Although the production of ceramics is an ancient craft, it was not until the last few decades that theoretical explanations were given for the processes occurring during sintering. On the basis of current knowledge on the sintering of ceramics, four main types of sintering can be distinguished: sintering in the absence of a liquid phase; sintering in the presence of a liquid phase; reactive sintering; and pressure sintering. Here mention is only made of sintering in the absence of a liquid phase, which is relevant to the present study. The mechanism of sintering in the absence of a liquid phase is explained on the basis of a model of two spheres of the same size and identical composition maintained at a constant temperature. This is an ideal model, as such conditions cannot be achieved in practice. In this instance sintering can be theoretically divided into three phases although the individual processes overlap. In the first phase, a neck is formed between the spheres and the material is partly compacted and shrinks by about 5%. The second stage in sintering occurs during compacting of the body down to 5% porosity, where it is assumed that the original material had about 30% porosity. Recrystallization and the growth of larger grains at the expense of smaller ones characterize the final stage of sintering.

2.3 The structure and electrical properties of metal oxides

Metal oxides are an important group of ceramics that are utilized in numerous applications. From the point of view of applications, the electrical properties of metal oxides can be considered from two points of view [7]. In the now traditional utilization of the high electrical resistance of most ceramic materials for insulation of voltages or of the dielectric properties in the construction of ceramic capacitors, materials with practically zero electrical conductivity can be considered as ideal. A decrease in the electrical resistance leads to a deterioration of the insulating or dielectric properties of