STANUM DIOXIDE (SnO_2) DOPED POLYANILINE ($n\text{-}C_6H_5NH_2$) THIN FILM AS THE MATERIALS FOR LIQUEFIED PETROLEUM GAS (LPG) AND HYDROGEN (H_2) GAS SENSOR

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Submitted to the Faculty of Chemical & Natural Resources Engineering in partially fulfillment of the requirements for the degree of Bachelor of Chemical Engineering (Gas Technology)

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APRIL 2009

AKNOWLEDGEMENT

First of all, I would like to express my heartily gratitude to my research supervisor, Mr. Azizan Bin Ramli for his guidance, advices, efforts, supervision and enthusiasm given throughout for the progress of this research.

In preparing this thesis, I was in contact with many people, lecturers, and training engineers. They have contributed towards my understanding and thoughts. Without their continued support and interest, this thesis would not have been the same as presented here.

I would like to express my sincere appreciation to my parents for their support to me all this year. Without them, I would not be able to complete this research. Besides that, I would like to thank my course mates and my friends especially my housemate E32 for their help, assistance and support and encouragement.

ABSTRACT

Gas sensor is a device which detects the presence of gas. The choice in selecting gas sensor was based on their sensitivity, selectivity and stability. The objectives of this research are to study stanum dioxide (SnO_2) doped polyaniline (n-$C_6H_5NH_2$) as new sensing materials for LPG and H_2 gas sensor at room temperature and to study the gas (LPG and H_2) sensing characteristic to the sensor at room temperature. This research focused on the effect of doping ratio of sensor material, gas flow time to the gas response and response time of the sensor. Sensors are prepared using two deposition methods which are chemical bath deposition (CBD) for fabrication of SnO_2 and electrodeposition (ED) for fabrication of polyaniline. In this experimental work 3 sensors with different doping ratio (polyaniline: SnO2) were prepared which is 70:30, 50:50 and 30:70. The gas response most influenced by the doping ratio. From the result the highest gas response (55%) achieved by sensor with doping ratio 70:30 for LPG contrast with highest gas response (50%) for H_2 achieved by sensor with doping ratio 30:70. The response time most influenced by gas flow time. High flow time means the concentration is high. Based on experimental result at range 10s to 40s of gas flow time, the 40s gas flow time show the short time response for all sensor.

ABSTRAK

Pengesan gas adalah sebuah alat yang mengesan kehadiran gas. Pilihan dalam pemilihan pengesan gas telah didasarkan kepekaan mereka, pemilihan terhadap sesetengah gas dan kestabilan. Objektif bagi penyelidikan ini adalah mengkaji stanum dioksida (SnO_2) 'doped' polyaniline (n-$C_6H_5NH_2$) sebagai satu komposisi baru bagi alat pengesan gas untuk gas LPG dan H_2 pada suhu bilik dan untuk mengkaji sifat-sifat pengesan gas terhadap (LPG Dan H_2) pada suhu bilik. Kajian ini memfokuskan pada kesan nisbah campuran atau 'doping' antara SnO_2 dan polyaniline dan masa aliran gas terhadap respon gas dan masa respon oleh pengesan tersebut. Pengesan disediakan pada tiga nisbah campuran iaitu (polyaniline: SnO_2) 70:30, 50:50 dan 30:70. Kaedah yang digunakan adalah kaedah pemendakan iaitu 'chemical bath deposition'(CBD) dan 'electrodeposition'(ED). Daripada eksperimen, respon gas sangat dipengaruhi oleh nisbah campuran atau 'doping' antara SnO_2 dan polyaniline (polyaniline: SnO_2). Pengesan dengan nisbah 70:30 mencapai respon tertinggi (55%) bagi gas LPG berlainan pula bagi gas H_2 yang mana pengesan dengan nisbah 30:70 mencapai respon tertinggi (50%). Masa respon gas pula dipengaruhi oleh masa aliran gas. semakin tinggi masa aliran gas bermakna kepekatan gas juga semakin tinggi. Ini dibuktikan dari keputusan eksperimen yang mana daripada julat 10s hingga 40s aliran gas, masa respon pada 40s aliran gas memberikan masa respon yang paling pantas untuk semua pengesan.

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LIST OF ABBREVIATIONS

LPG	–	Liquefied petroleum gas
H_2	–	Hydrogen
CBD	–	Chemical bath deposition
ED	–	Electrodeposition
SnO_2	–	Stanum dioxide
n- $C_6H_5NH_2$	–	Polyaniline
H_2SO_4	–	Sulphuric acid
HCL	–	Hydrochloric acid
SEM	–	Scanning electron microscopy
p	–	Positive
n	–	Negative

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CHAPTER 1

INTRODUCTION

1.1 Research Background

1.1.1 Gas Sensors

Gas sensor means the device which detects the presence of various gases within an area, usually as part of a system to warn about gases which might be harmful to humans or animals especially the combustible and hazardous gases like liquefied petroleum gas (LPG) and hydrogen (H_2). They are potentially hazardous and combustible because explosion might occur if any leaks of these gases occur accidentally or by mistakes. They also have a potential effect like can cause the respiratory problem to human. Fast detection and location of leakage are important to minimize the emission of these gases and reduce the possibility the explosion occur. The gas sensor must have the ability to detect the gas before their flammability limit. So there is great demand to develop the gas sensor with higher sensitivity to flammable gas like LPG and H_2.

1.1.2 Working Principle

Actually it is same working principle for all type gas sensors. The working principle of the gas sensors is based on conductivity changes produced when the sensing material is exposed to the target gases. Type of gas sensor is miscellaneous based on the sensing material and their selectivity to type of gas. For example the metal oxide gas sensor. This type of sensor based on the ability of the sensing materials like SnO2, ZnO to adsorb the gas which causes the current conductivity across the sensor change. The mechanism for gas sensitivity depends on the chemisorptions characteristics of the oxide surface and on the electronic characteristics of the film. The electronic properties can be influenced by chemical doping and the film microstructure. The metal oxide gas sensor most developed as thin film and thick film sensors. In both, these materials exhibit a fibrous structure with many pores and gaps among the fibers. Due to porous structure the diffusion occur between gas molecules and junction of sensor interface. As the diffusion occurs the resistance of sensor will increase and cause the current over the junction decrease.

Sensitivity or gas response can be measured by from the output voltage that appears across the junction when the gas exposed. So when the gas exposed the resistance in sensor increased, that will cause the current value decrease as the concentration of these gases increase (Dhawale,D.S. et al., 2007; Jinzhong, W. et al., 2002; Mitra,P. et al., 1998)

1.1.3 Material/Composition

The sensing material or composition of sensor is an important part in developing the gas sensors. The good materials must have the good criteria which are gas sensitivity, selectivity and stability. There are two main types of gas sensors which is most developed nowadays which classified namely inorganic like doped or undoped metal oxide like SnO_2 and ZnO and organic material like liquid crystalline cells like nanocrystalline In_2O_3 (Dhawale,D.S et al., 2007Kapse,V.D. et al., 2008; Kiran, J. et al.,2006).

These metal oxides such as SnO_2, ZnO and Fe_2O_3 offer the potential for developing portable and inexpensive gas sensing devices which have the advantages of simplicity, high sensitivity and fast response. SnO_2 serves as an important material for gas sensor applications based on the variation of its resistivity with gas adsorption and desorption. The increased interest in both the application and the fundamental research of this material in the last decade stems from its remarkable optical and electronic properties.

Recently, conducting polymers have been widely investigated as effective material for room temperature chemical sensors. Polyaniline is one of the most attractive among variety of conducting polymers due to its unique electrical properties, environmental stability and easy fabrication process. Due to its interesting properties polyaniline has been a potential candidate in sensor application. However the problems with this conducting polymer are their low processing ability, poor chemical stability and mechanical strength (Dhawale,D.S. et al., 2007; www.azom.com, 2008).

1.2 Problem Statement

The main objectives of research work of gas sensors in nowadays are centered on developing new sensing materials/compositions to improve sensitivity, selectivity and stability. Semiconductor inorganic gas sensors like doped or undoped, ZnO or Fe_2O_3 have been well studied to detect most of reducing gases and they are considered interesting for their low cost and simple sensing method. Nevertheless there are some problems with them for example high working temperature like 423 K to 623 K for Fe_2O_3 and 673K to 723 K for ZnO. Hazardous gases specifically liquefied petroleum gas (LPG) and H_2 have been widely used for industries and domestic application. But at certain low concentration of the gases these metal oxides sensor poor performances with respect to sensitivity, long term stability and selectivity. Recently, conducting polymers have been widely investigated as effective material for room temperature chemical sensors. The good polymers must have properties like unique electrical properties, environmental stabilities and easy fabrication process. Due to its interesting properties polymers has been a potential candidate in sensor application. However the problems with this conducting polymer are their low processing ability, poor chemical stability and mechanical strength.

1.3 Objectives

The objectives of this research are:

1. To study stanum dioxide (SnO_2) doped polyaniline (n-$C_6H_5NH_2$) as new sensing materials for LPG and H_2 gas sensor at room temperature.
2. To study the gas (LPG and H_2) sensing characteristic to the sensor at room temperature.

1.4 Scope of Study

The scopes of the study for this research are:

1. To investigate the sensing properties of sensor with respect to; doping ratio of sensor material, flow time of gases and their effect to gas response and response time of the sensor at room temperature.
2. To fabricate potential of deposition method (CBD and ED) for sensor preparation.

CHAPTER 2

LITERATURE REVIEW

2.1 Gas Sensor

Gas sensor is the device which used in the environmental monitoring field for detection of the different ingredient of in natural and artificial mixtures of substances like LPG gas. Gas sensors have been used for industrial process controls for the detection of toxic environmental pollutants, in human health and for prevention of hazardous gas leaks. LPG and H_2 are the combustible gases. They are potentially hazardous because explosion accident might be caused when they leak out accidentally or by mistake (Nazarava, K.V. et al., 2005). So the detection of them in all gas appliances must be no false or missing alarm during work.. In 20th century, when researchers were doing research work related to semiconductor positive-negative (*p-n)* junctions, they discovered that these junctions were sensitive to environmental background gases. During this time, such behaviors were considered a problem and were solved by utilize the semiconductor chip so that it was no longer exposed to the outside environment.

The solving way are introducing of commercial solid state gas sensors based on semiconducting metal oxides. From that invention the semiconducting metal oxide sensor was commercialized based on their properties that detect gas by change of electrical conductivity of junction caused by carrier concentration of semiconductor. Figure 2.1 show the example of gas sensor which have marketed and using nowadays. The choice of gas sensor is based on their selectivity to types of gas and their sensing material and composition. Metal oxide sensor, quartz crystal microbalance sensors, surface acoustic wave sensors and polymeric sensors are among the most popular types of sensors used for detection of gases (Nicola, U. et al., 2006). But some of gas sensors have generally disadvantages which is poor selectivity and low sensitivity to the very low concentration of gases. Therefore several different approaches have been explored in order to overcome these issues.

Figure 2.1: Example of gas Sensor in market

Recently some research work reported that sensor performance can be improve by doping or addition some element to the sensor composition. The gas sensitivity of gas sensor was improved by the addition of Al,Pd, Pt, Ir or Rh. The promoting effects of noble metals have since been confirmed to appear in many combinations of metals and semiconductors and have been utilized extensively in the fabrication of practical gas sensing devices. Conducting polymers also have been investigated as new sensing material. Some of the polymers have the unique electrical properties which contribute in sensor development. They also have the porous structure which also the advantages for sensor making.

2.2 Stanum Dioxide

Stanum or Tin dioxide is the inorganic compound with the formula SnO_2. The mineral form of SnO_2 is called cassiterite, and this is the main ore of tin. This oxide of tin is the most important raw material in tin chemistry. This colorless, diamagnetic solid is amphoteric It crystallizes with the rutile structure, wherein the tin atoms are 6 coordinate and the oxygen atoms three coordinate. Figure 2.2 show the SEM images for SnO_2 structures.

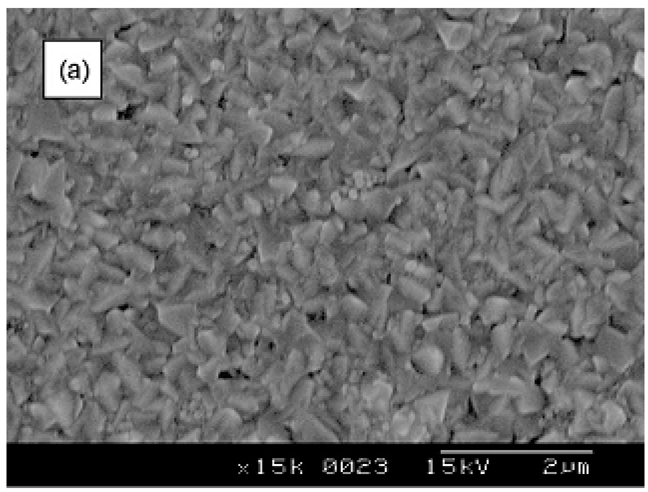

Figure 2.2: SEM image for SnO_2 (B. Thomas et.al. 2008)

SnO_2 is an amphoteric oxide, although cassiterite ore has been described as difficult to dissolve in acids and alkalis. Stannic acid refers to hydrated tin dioxide**,** SnO_2, which is also called stannic hydroxide. Tin oxides dissolve in acids. Halogen acids attack SnO_2 to give hexahalo stannates. The equation below show the reaction occurs.

$$SnO_2 + 6HI \rightarrow H_2SnI_6 + 2H_2O$$

Similarly, SnO_2 dissolves in sulfuric acid to give the sulfate as show in the equation below.

$$SnO_2 + 6H_2SO_4 \rightarrow Sn(SO_4)_2 + 2H_2O$$

SnO_2 dissolves in strong base to give stannates, with the nominal formula Na_2SnO_3. Dissolving the solidified SnO_2/NaOH melt in water gives $Na_2\ [Sn(OH)_6]_2$, the material called" preparing salt," which is used in the dyeing industry.

Table 2.1: Chemical and physical properties of SnO_2

Properties	
Molar mass	150.71 g/mol
Density	6.95g/cm^3
Appearance	White powder
Melting point	1630^{o}C
Boiling point	1800^{o}C-1900^{o}C
Solubility	Insoluble in water, soluble in acid and alkalies
Structure	
Crystal structure	Rutile(tetragonal)
Coordination geometry	Octahedral, trigonal planar

SnO_2 is usually regarded as an oxygen-deficient n-type semiconductor. (Greenwood et al., 1997). Table 2.1 below show the properties of SnO2. SnO2 is used in sensors of combustible gases. In these the sensor area is heated to a constant temperature (low 100s °C) and in the presence of a combustible gas the electrical resistivity drops. SnO_2 is widely used as a gas sensor detecting reducing gases such as H_2, CO and H_2S, based on their resistivity changes with gas adsorption and desorption. The sensor performance such as sensitivity, selectivity, and long term stability is strongly dependent on the particle (grain) size, pore size and grain boundary characteristic and nanoscale crystallites. Additive or surface functionalization and solid solution methods have been employed to improve sensor performance. Recently various SnO_2 nanostructures such as nanotubes, nanoribbons , nanodiskettes and nanocubes are fabricated and applied to gas sensor. It is expected that high surface-to- volume ratio associated with nanostructured materials make their electrical responses extremely sensitive to the species adsorbed to the surface.

B. Thomas et al. in 2008 reported the influence Cs doping in spray deposited SnO_2 thin film for LPG sensor. The SnO_2 thin film was fabricated using spray pyrolysis technique. The electrical resistance change of the films was evaluated in the presence of LPG upon doping with different concentrations of Cs. At different working temperatures in the range 250–400^{o}C. He found that the tin oxide thin film doped with 2% Cs with a mean grain size of 18nm at a deposition temperature of 325oC showed the maximum sensor response (93.4%). At a deposition temperature of 285^{o}C, the film doped with 3% Cs with a mean grain size of 20 nm showed a high response of 90.0% consistently. The sensors showed a rapid response at an operating temperature of 345^{o}C. So from this report it can conclude that sensor response depends on doping of material to the sensor composition and deposition temperature.

2.3 Polyaniline

Polyaniline is one of the conducting polymers which have been widely used in chemical and electronic industries world-wide due to its unique electrical properties, environmental stability and easy fabrication process. Unlike most polymers, conducting polymers have the electrical and optical properties of metals or semiconductors. These materials are of increasing interest in microelectronics because they are inexpensive, flexible and easy to synthesize. The discovery of electrically conductive polymer compositions based on polyaniline provides conductive materials, which are soluble in selected organic solvents. They provide precisely controlled electrical conductivity over a wide range, improve phase compatibility and thus blendability with bulk polymers, provide easier means of processing and forming conductive products and provide low cost solutions for the production of transparent and colored thin films and coatings (www.azom.com, 2008).

Dhawale on 2008 reported the LPG sensing properties of the n-TiO_2/p-polyaniline heterojunction at room temperature. The junction fabricated by a simple electrodeposition technique. The forward biased current-voltage characteristics of the junction showed a considerable shift when exposed to various concentrations of LPG. His observation showed the maximum response up to 60% at room temperature was achieved upon exposure to 0.1 vol% LPG. Depending on the concentration of LPG, the response time was ranged between 140 and 200 s whereas the recovery time was 180 s. From the surface morphological study it is evident that there are many pores on the polyaniline surface, which seem to contribute to the short response and recovery times. Due to the porous structure, LPG diffusion as well as reaction between gas molecules and the interface occurs more easily. The figure 2.3 show the SEM image show that the structures of deposited polyaniline onto stainless steel substrate.

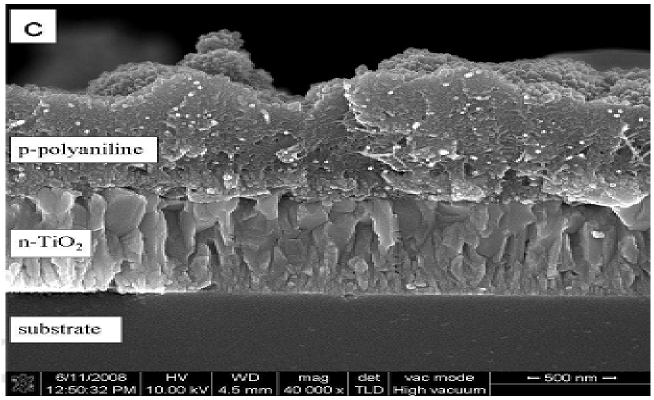

Figure 2.3: SEM image of polyaniline.(Dhawale et.al. 2008)

The electrical currents of a p-polyaniline/n-TiO_2 heterojunction in air (I_a) and in the presence of LPG (I_g) were measured by using the multimeter (EG&G Princeton Applied Research Model 262-A). The gas response was calculated using the following relation

$$S(\%) = \frac{I_a - I_g}{I_a} \times 100 = \frac{\Delta I}{I_a} \times 100$$

Where;

I_a = Current value in air

I_g = Current value in the presence of gas