DEVELOPMENT OF SnO_2-BASED THICK-FILM GAS SENSOR USING SCREEN-PRINTING TECHNIQUE FOR DETECTION OF ETHANOL GAS

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by

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LIST OF SYMBOLS

C	Concentration of target gas
e^-	Electron
eV	Energy barrieer
I	Current
M	Concentration of solution
P	Pressure
P/P_o	Relative pressure
R	Resistance
R_A	Resistance in air
R_G	Resistance in target gas
S	Sensitivity
T	Temperature
V	Voltage
wt%	Weight percent
°C	Degree celcius
λ	Wavelength of CuKα
β	Full width of half maximum (FWHM)
θ	Bragg angle

LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
a.u	Arbitrary unit
BET	Brunauer-Emmett-Teller
D	Diameter
DC	Direct Current
E_g	Band Gap
EDX	Energy Dispersive X-ray
FID	Flame Ionization Detector
FWHM	Full Width Half Maximum
GC	Gas Chromatography
IUPAC	Chemistry
LPG	Liquified Petroleum Gas
LPE	Liquid Phase Epitaxy
ppm	Parts Per Million
rpm	Revolution Per Minute
SEM	Scanning Electron Microscope
SERC	Science and Engineering Research Centre
STP	Standard Temperature Pressure
TEM	Transmission Electron Microscopy
TGA	Thermal Gravimetric Analysis
USA	United State of America
VOCs	Volatile Organic Compounds
XRD	X-ray diffraction

PEMBANGUNAN GAS SENSOR FILEM TEBAL BERASASKAN SnO_2 DENGAN MENGGUNAKAN TEKNIK SKRIN-PERCETAKAN BAGI PENGESANAN GAS ETANOL

ABSTRAK

SnO_2 berliang-meso telah disintesis melalui kaedah pencontoh-lembut dengan menggunakan surfaktan kationik (sitiltrimetilammonium bromida: CTAB) sebagai pencontoh dan klorida timah terhidrat ($SnCl_4.5H_2O$) sebagai pelopor bukan organik yang akan digunakan sebagai bahan pengesanan gas. Prestasi sensor filem tebal yang dipilih di bawah pelbagai keadaan operasi telah dikaji lagi dengan kepekatan gas etanol yang berbeza antara 100 ppm hingga 1000 ppm. Berdasarkan keputusan prestasi pengesanan dan pencirian kajian, keputusan yang terbaik diperolehi apabila pengkalsinan SnO_2 dilakukan pada suhu 400 °C dengan 5 lapisan pendepositan. Manakala rumusan pes terbaik adalah pes B dengan komposisi 40 wt% SnO_2 berliang-meso bercampur 60 wt% hidroksilpropil sellulos dan etilena glikol. Prestasi sensor filem-tebal yang terbaik (Sn-400-40-5) mencatatkan nilai kepekaan, S = 84.6 pada suhu operasi 300 °C dibawah 1000 ppm kepekatan ethanol. Masa tindak balas dan pemulihan yang direkodkan adalah 36 saat dan 300 saat.

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ABSTRACT

Mesoporous SnO_2 were synthesized via soft-template method by using cationic surfactant (cetyltrimethylammonium bromide: CTAB) as template and hydrated tin chloride ($SnCl_4.5H_2O$) as inorganic precursor to be used as gas sensing materials. The performance of selected thick-film sensor under various operating conditions was studied with different concentrations of ethanol gas between 100 ppm and 1000 ppm. Based on the detection performance and characterization study, the best result was obtained when as-prepared SnO_2 was calcined at 400 °C with 5 depositing layers while the best formulation was paste B when 40 wt% of mesoporous SnO_2 mixed with 60 wt% of hydroxypropyl cellulose and ethylene glycol were used. The performance of selected thick-film sensor (Sn-400-B-40-5) under various operating conditions was at the optimum when operating temperature was at 300 °C with the highest sensitivity of 84.6 for 1000 ppm of ethanol gas detection. The response and recovery times were recorded to be 36 s and 300 s respectively.

CHAPTER ONE

INTRODUCTION

1.1 Research Background

Gas sensor plays an important role in monitoring and controlling the safety in the domestic and industrial environments. Since the first metal oxide sensor developed by the Taguchi in year 1971, a lot of efforts have been invested to further optimize the sensor performance towards various gases. A high performance gas sensor would possess high sensitivity, good selectivity, low detection limit, and short response and recovery time towards target gas. Among the sensors, ethanol sensor has always been in great demands for various applications including biomedical and chemical industries, breath analysis and environmental monitoring (Guo et al., 2011).

1.1.1 Ethanol

Ethanol (C_2H_5OH), also commonly called ethyl alcohol is classified as one of the volatile organic compounds (VOCs). It is a colourless liquid with a slight odour (like wine) and easily soluble in water, methanol, diethyl ether and acetone. It is volatile and tends to evaporate easily when left in an open container. Ethanol is also hygroscopic which can absorb water from its surrounding. It has boiling and melting point of 78.5 °C and -114.1 °C, respectively.

1.1.2 Importance of Ethanol Gas Sensor

It is extremely harmful and dangerous for human health if the emission of ethanol gas is not controlled. Inhalation of high concentrations of ethanol gas can cause headaches, balance disorders, nausea, dizziness and confusion. In addition, when contacted with human skin, it may result in eye and mucous membrane irritation, dissolve skin oils and interface with physiological functions (Liao et al., 2013).

Ethanol sensor is also used to monitor fermentation and other processes in chemical industries. In winemaking production, ethanol sensor is used to monitor wine quality as well as to detect leakage of ethanol gas for safety purpose. Ethanol is also a by-product of the decomposition of foodstuffs as a result of bacterial growth and fermentation. Being able to detect the presence of ethanol can therefore assist in preventing or detecting the onset of food spoilage (Ivanov et al., 2004).

Moreover, ethanol sensor can also be used as an Ethanol Breath Analyzer to reduce road car accident (Comini et al., 2000; Ivanov et al., 2004). The ethanol breath analyser is designed to detect ethanol in breath of drivers in order to reduce the number of road accidents caused by excessive alcohol consumption. It can be also fixed on vehicle steering wheels to monitor drunken driver (Ho et al., 1998). It can be also integrated in the ignition system of the car to prevent the vehicle from starting if the driver's breath indicates an over the limit blood-alcohol content.

On top of that, environmental pollution is one of the global highly-concerned issues in 21st century. Detecting and monitoring the emission of ethanol vapor is important as ethanol has been identified as one of the organic pollutants which cause severe harmful effects on environment and human health due to its toxicity, carcinogenicity and hazardous properties. Hence, ethanol gas sensors are developed to detect and quantify this organic pollutant and to help in reducing environmental pollutions (Khan et al., 2012). Thus, it is highly important to be able to detect the presence of ethanol in a variety of applications and situations.

1.1.3 SnO_2-Based Thick-Film Gas Sensor

Recently, thick-film sensors based on semiconductor material are widely used for different applications in gas sensing. It is because of their low cost and flexibility associated to their production; small size; better mechanical strength and thermal stability; and compatibility with electronic systems (Brignell et al., 1988; Prudenziati, 1994; Shimizu and Egashira, 1999). There are many fabricating techniques to produce thick-film sensor but the most common one is screen-printing. Specially formulated paste is required during screen-printing process and this paste plays a major role in enhancing or reducing the sensor performance. Detailed review regarding this issue will be discussed in the next chapter.

The performance of thick-film sensor also depends on the sensing material used as well as its microstructural features. Sensing powder which has a high surface area and porosity, high crystallinity, small crystallite and grain size is crucial to being synthesized. Among the available semiconductor metal oxides, tin dioxide, SnO_2 is considered as the most attractive material in fabricating ethanol gas sensor due to their high sensitivity, quick response and resistance to corrosion as a sensor material (Singh et al., 2009). Mesoporous SnO_2 based gas sensors have given a new dimension for research studies and it has been found as a promising gas sensor for ethanol gas detection (Guo et al., 2011).

1.2 Problem Statement

Semiconductor based materials have shown a great potential for wide range of application. Metal oxides such as SnO_2, ZnO, WO_3, and TiO_2 have been reportedly applicable as gas sensor. Among these metal oxides, SnO_2 has been proven to be one of the most attractive metal oxides for gas sensor application owing to its chemical stability and sensitivity. It is known that structure and morphology of SnO_2 materials have significant effect on performance of the gas sensors. There have been a lot of approaches to obtain the mesoporous SnO_2 nanopowders materials. However, these approaches present some drawbacks such as less ordered and well-defined structure, more or less random shape and without uniform size morphology. The synthesis of mesoporous SnO_2 nanoparticles with better control of the microstructure still remains a challenge.

Screen-printing is one of the methods for the fabrication of thick-film gas sensors. This method requires specially formulated pastes or inks composed of the sensing powder, inorganic binders and organic vehicles. Using screen-printing machine, paste are being deposited onto insulating substrate (usually alumina) and the film is being annealed in a furnace. The performance of the thick film gas sensor is largely dependent on the parameter related to the paste. Inorganic binder, usually glass frit, is used to enhance mechanical strength and increase adhesion of the thick-film. Organic vehicles, such as the mixture of ethyl cellulose and α-terpinol are needed to adjust the rheological properties required for thick film. For conventional paste, the uses of glass present a negative effect towards sensor performance in terms of reducing sensor sensitivity. For this reason, many researchers have attempted to develop their own special-purpose pastes with enhanced sensing characteristics (Bakrania and Wooldridge, 2009; Riviere et al., 2003; Viricelle et al., 2005).

A number of investigations had been made to remove this inorganic binder (glass frit) and a lot of new formulated paste recipe has been produced. However, the comparison study on the performance of SnO_2 based-thick film sensor by using different paste recipe in detecting ethanol gas is still limited. Besides that, the existing formulated paste composition needs to be optimized to further enhance the performance of the thick-film gas sensor.

1.3 Objectives

The present study has the following objectives:

1. To synthesize the mesoporous SnO_2 via soft-template method that can be effectively used as a sensing material for ethanol gas detection.
2. To fabricate SnO_2-based thick film sensors via screen-printing technique by using synthesized mesoporous SnO_2.
3. To characterize the developed SnO_2-based thick film sensors by using standard methods for the purpose of comparisons and understanding of their properties.
4. To perform ethanol gas detection in order to measure the sensitivity, response time and recovery time of the developed SnO_2-based thick film sensors.

1.4 Scope of Study

The present works attempt to develop an effective and reliable thick-film gas sensor from the mesoporous SnO_2 as sensing materials via screen-printing techniques for ethanol gas detection. The synthesis of mesoporous SnO_2 will be carried out using a soft-template method. Exploration on using screen-printing with different type of paste recipe and its composition will be made in order to further enhance the sensing performance. The gas-sensing performance of the gas sensors towards ethanol will be measured based on electrical resistance by using the existing sensor measurement rig setup. One-factor-at-a-time method will be used to obtain the optimum preparation conditions of SnO_2-based thick-film gas sensor. Last but not least, the optimum sensor will be further investigated to obtain the optimum operating temperature, optimum ethanol concentration and response and recovery time.

1.5 Thesis Outline

This thesis consists of five chapters:

Chapter one (Introduction) discusses briefly about ethanol characteristics and the importance to develop ethanol sensor which can be used in various applications and situations. The SnO_2-based thick-film gas sensor is also explained briefly. This chapter also includes a problem statement that provides some basis and clear direction of research objectives in the current studies. The scope of study covers the research work done to meet these objectives.

Chapter two (Literature Review) compiles all literature reviews conducted on semiconductor gas sensor researches with emphasis on SnO_2 as a sensing material. Methods of synthesizing mesoporous SnO_2 will be described in details. Brief explanations on type of sensor configurations and method to develop thick-film are described. Characterization methods and factors that affect the performance of SnO_2 sensor are covered in this chapter.