

**UNIVERSITI TEKNOLOGI MARA**

**SENSITIVITY BEHAVIOR OF  
NANOSTRUCTURED ZINC OXIDE  
BASED GAS SENSOR FABRICATED  
BY IMMERSION METHOD**

**SITI SHAFURA BINTI A KARIM**

Thesis submitted in fulfillment  
of the requirements for the degree of  
**Master of Science**

**Faculty of Electrical Engineering**

March 2018

## ABSTRACT

This study aimed to fabricate nanostructured zinc oxide (ZnO) based metal-semiconductor-metal (MSM) gas sensor by immersion method. Three stages of method were employed to fabricate nanostructured ZnO based MSM gas sensor which are: (1) preparation of ZnO nano-template by spin-coating method, (2) preparation of nanostructured ZnO on deposited ZnO nano-template layer by immersion method and (3) fabrication of nanostructured ZnO based MSM gas sensor. For preparation of ZnO nano-template by spin-coating method, both effects of multilayer coating (1 to 9 layers) and annealing temperature (350 to 500°C) of ZnO nano-template were determined. The optimised properties of deposited ZnO nano-template was further employed as a seed layer to grow nanostructured ZnO by immersion method. For preparation of nanostructured ZnO on deposited ZnO nano-template layer by immersion method, effect of molarity (0.02 to 0.10 M) and effect of n-type dopant (Sn) concentration (0.2 to 1.0 at.%) on nanostructured ZnO were evaluated. Field emission scanning electron microscope (FESEM), energy dispersive X-ray (EDS), atomic force microscopy (AFM) and X-ray diffraction (XRD) were employed to characterise the structural properties of deposited samples whereby UV-Vis-NIR spectrophotometer was used for the optical properties determination. The electrical properties were measured using current-voltage (I-V) measurement system (Keithley 2400). Next, gold (Au) was deposited on the nanostructured ZnO as an electrode for the fabrication of nanostructured ZnO based MSM gas sensor. The entire samples were characterised to determine their response and recovery time as well as the sensitivity. The sensitivity behavior of the fabricated samples were determined to detect 20 sccm of methane (CH<sub>4</sub>) gas at operating temperature of 150°C. In preparation of ZnO nano-template by spin-coating method, the results revealed that 5 layers demonstrated a high uniformity with no crack and high electrical conductivity ( $1.1 \times 10^{-3}$  S/cm). Additionally, 500°C has emerged as an optimum temperature upon increment of annealing temperatures. During preparation of nanostructured ZnO on deposited ZnO nano-template layer by immersion method, unique nanostructure (flake-like morphologies) was observed upon the study of molarity effect on nanostructured ZnO (0.02-0.10 M). The electrical conductivity was obtained around  $10^{-3}$  S/cm, which is comparable to previous reported studies. The optimum concentration at 0.06 M has exhibited a good uniformity with low roughness and the highest conductivity of  $3.3 \times 10^{-3}$  S/cm. The effect of n-type dopant (Sn) concentration (0.2-1.0 at.%) has been investigated. The width of flakes have slightly decreased from 64.1 to 41.9 nm as the n-type dopant (Sn) concentration increased. Increasing the n-type dopant (Sn) concentration has greatly enhanced the electrical conductivity from  $6.5 \times 10^{-3}$  to  $12.6 \times 10^{-3}$  S/cm. The highest sensitivity was achieved at 23% with utilisation of 1.0 at.%. The response and recovery time of 1.0 at.% were 46 and 64 s, respectively. Through this research work, the optimum preparation parameters were successfully identified for fabrication of nanostructured ZnO based MSM gas sensor. This work provides an opportunity to explore potential material for the development of gas sensor.

## ACKNOWLEDGEMENT

All praise to Allah S.W.T, for giving me the chance, strength and health to accomplish this study. Special thanks to my main supervisor, Prof. Dr. Mohamad Rusop Mahmood, for his kindness and guidance throughout this journey. Many thanks to my co-supervisors; Dr. Mohamad Hafiz Mamat and Mr. Uzer Mohd Noor, for their knowledge sharing and great encouragement in this study.

I am gratefully acknowledged all staffs in NANO-ElecTronic Centre (NET), Faculty of Electrical Engineering, Universiti Teknologi MARA (UiTM) especially Mr. Mohd Suhaimi Ahmad, Mr. Danial Mohd Johari, Mr. Azwan Roseley and Mr. Asrul Mohamed, for their assistance in the experimental works.

I also would like to express my sincere appreciation to all staffs in NANO-SciTech Centre (NST), Institute of Science (IOS), UiTM especially Mr. Salifairus Jaafar, Mrs. Nurul Wahida Aziz and Mr. Mohd Azlan Jaafar, who helped me in this project.

Furthermore, I would like to acknowledge UiTM and Ministry of Higher Education Malaysia (MOHE) for their financial support under the Skim Latihan Akademik Bumiputera (SLAB).

To my family, parents; Haji A Karim Jastan and Siti Aishah Ghazali, brothers: Mohamad Shahrim, Mohamad Shafiq and Mohamad Shazwan, thanks for the endless love and support. To my foster family, Ms. Siti Farizah, Ms. Noratiah Dzulkafly and kids, thanks for the love and care. I also dedicated special thanks to my dear friend, Nurhasanah Ismail, Nor Dalila Abd Rahman, Muna Liyana Ahmad Termizi, Nurhafizatul Afifi Mohamud and Ishmah Ahmad, for their time, kindness and support since the first day of my Master study.

Last but not least, million thanks to my friends; Nik Noor Azlin, Raihana, Nurrina, Nur Azwa, Hanis, Nur Nadirah, Suhanis, Maziah, Syamimi, Siti Izzati Husna, Nordiyana, Adillah Nurashikin, Ruziana, Nurbaya, Irma Hidayanti, Najwa Ezira, Nur Amierah, Robaiah, Nurul Hidah, Saurdi, Ishak, Mohd Husairi and Mohd Hannas. May Allah bless our life journey.

# TABLE OF CONTENTS

	<b>Page</b>
<b>CONFIRMATION BY PANEL OF EXAMINERS</b>	ii
<b>AUTHOR'S DECLARATION</b>	iii
<b>ABSTRACT</b>	iv
<b>ACKNOWLEDGEMENT</b>	v
<b>TABLE OF CONTENTS</b>	vi
<b>LIST OF TABLES</b>	ix
<b>LIST OF FIGURES</b>	xi
<b>LIST OF ABBREVIATIONS</b>	xv
<b>CHAPTER ONE: INTRODUCTION</b>	1
1.1 Research Background	1
1.2 Problem Statement	2
1.3 Research Objective	3
1.4 Scope and Limitation	3
1.5 Thesis Organisation	4
<b>CHAPTER TWO: LITERATURE REVIEW</b>	5
2.1 Introduction	5
2.2 Properties of Zinc Oxide	5
2.3 Deposition Method of Zinc Oxide	6
2.4 Development of Gas Sensor	10
2.4 Summary	13
<b>CHAPTER THREE: METHODOLOGY</b>	14
3.1 Introduction	14
3.2 Preparation of ZnO Nano-template by Spin-Coating Method	14
3.2.1 Effect of Multilayer Coating of ZnO Nano-template	15
3.2.2 Effect of Annealing Temperature of ZnO Nano-template	16

# CHAPTER ONE

## INTRODUCTION

### 1.1 RESEARCH BACKGROUND

Nanotechnology is an emerging and exciting area of scientific development. As one of the most active research fields in modern materials science, it offers way to create smaller, lighter and faster devices using fewer raw materials and less energy consumption. The term nanotechnology was first suggested by Norio Taniguchi in 1974 to describe the technology that strives for precision at the level of about one nanometer ( $10^{-9}$  m) [1]. One of the fundamental component and keystone to nanotechnology is nanomaterials that are referred to materials with the grain size of less than 100 nm. The properties of nanomaterials are significantly different from those of atoms and bulk materials. This is mainly due to the surface effects and the quantum size effects. These effects do not only modify the materials structure, but it also produced materials with enhanced and outstanding properties, which can be utilized in various applications.

Methane ( $\text{CH}_4$ ), the main constituent of natural gas, is a colorless, highly volatile, odorless and flammable gas. It is well known that a small spark can trigger violent explosion due to inflammability if the concentration of  $\text{CH}_4$  reaches a critical limit (it has a lower explosion limit (LEL) of 4.9% and an upper explosion limit (UEL) of 15.4%) in the air [2]. Thus, the development of a reliable, low cost methane sensor has gained a great interest, especially to monitor  $\text{CH}_4$  from escaping into the atmosphere during industrial operation in order to protect public health and safe environment [3].

The study on metal-semiconductor-metal (MSM) semiconductor gas sensor has gained numerous attentions since 40 years ago [4, 5]. The MSM gas sensors offer high sensitivity and a real simplicity in function. The surface of sensing material shows a significant change on its electrical conductivity in gas ambient. In today's research, nanomaterials play important role in enhancing its sensing properties; such as the sensitivity, the response time and the recovery time. Nanomaterials offer a high