

**UNIVERSITI TEKNOLOGI MARA**

**ETHANOL SENSING BEHAVIOUR  
OF TIN DOPED ZINC OXIDE/TIN  
OXIDE COMPOSITED NANOROD  
ARRAYS ON MAGNESIUM-  
ALUMINIUM CO-DOPED ZINC  
OXIDE SEEDED LAYER**

**RUZIANA MOHAMED**

Thesis submitted in fulfillment  
of the requirements for the degree of  
**Doctor of Philosophy**

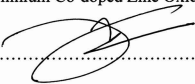
**Faculty of Electrical Engineering**

January 2018

## **AUTHOR'S DECLARATION**

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the result of my work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any other degree or qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

Name of Student	:	Ruziana Binti Mohamed
Student ID No.	:	2013231558
Programme	:	Doctor of Philosophy (Electrical Engineering) – EE950
Faculty	:	Electrical Engineering
Thesis Title	:	Ethanol Sensing Behavior of Tin Doped Zinc Oxide/Tin Oxide Compositied Nanorod Arrays On Magnesium- Aluminium Co-doped Zinc Oxide Seeded Layer
Signature of Student	:	 .....
Date	:	January 2018

## ABSTRACT

The ethanol sensor device fabrication was carried out using undoped zinc oxide nanorod (ZnO NR) arrays, tin doped zinc oxide nanorod (Sn:ZnO NR) arrays and novel nanostructured tin doped zinc oxide/ tin oxide nanorod (Sn: ZnO/SnO<sub>2</sub> NR) arrays film. The sensor consists of a thin film nanostructured deposited on the novel seed layer magnesium-aluminium co-doped zinc oxide (MAZO) coated glass using solution immersion technique. The thin film nanostructures were investigated using X-ray diffraction analysis, energy-dispersive X-ray spectroscopy, field emission scanning electron microscopy, atomic force microscopy, photoluminescence spectrometry, ultraviolet-visible-near-infrared spectrometry, thickness profilometry and two-probe current-voltage measurement system. The sensor performance was analysed based on the change in electrical conductivity upon gas adsorption when ethanol gas was exposed to nanorod arrays film that act as sensing materials. The growth of ZnO NR arrays film was influenced by many factors. In this study, some parameters have been done for ethanol sensor application such as doping process (undoped, single doped and co-doped ZnO seed layer), the variation of coating seed layers (one to nine coating layers), the effect of ZnO NR arrays growth on variation coating layers (one to nine coating layers), the effect of ZnO NR arrays growth at different immersion time (15-90 min), the effect of doping process for ZnO NR arrays (undoped and Sn doped) and the effect of pH of SnO<sub>2</sub> solution to the growth of Sn:ZnO/SnO<sub>2</sub> NR arrays. The conductometric sensor system was set up to study the sensing sensitivity, response and recovery time and selectivity properties towards ethanol gas. The sensor response for Sn:ZnO/SnO<sub>2</sub> NR arrays was 20. It was observed that the Sn:ZnO/SnO<sub>2</sub> NR arrays film showed the highest response to the presence of ethanol gas compared ZnO and Sn: ZnO NR arrays. The Sn:ZnO/SnO<sub>2</sub> NR arrays showed the shorter of response and recovery time which was around 81 and 63 s, respectively. The sensing sensitivity of Sn:ZnO/SnO<sub>2</sub> NR arrays prepared at pH 5.5 of SnO<sub>2</sub> solution was increased from 2.4 to 5.2 with an increase of ethanol concentration range 60 to 300 ppm. The Sn:ZnO/SnO<sub>2</sub> NR arrays prepared at pH 5.5 of SnO<sub>2</sub> solution also showed the increasing of sensing sensitivity value range 2.5 to 8.0 when the working temperature is increased from 60 to 140 °C. It also was observed that the Sn:ZnO/SnO<sub>2</sub> NR arrays have good selectivity properties towards ethanol vapor as compared to acetone and propanol vapor.

## 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>	xi
<b>LIST OF FIGURES</b>	xv
<b>LIST SYMBOLS</b>	xxiii
<b>LIST OF ABBREVIATIONS</b>	xxvi
<b>CHAPTER ONE: INTRODUCTION</b>	1
1.1 Sensor	1
1.2 Ethanol Sensor	1
1.3 Sensing Materials	3-
1.4 Problem Statement	5
1.5 Research Objectives	6
1.6 Research Scope	7
1.7 Research Contributions	8
1.8 Thesis Organisation	8
<b>CHAPTER TWO: LITERATURE REVIEW</b>	10
2.1 Introduction	10
2.2 Zinc Oxide as Functional Material	10
2.3 Electrical Devices and Detection Mechanism	12
2.4 The Role Zinc Oxide as a Seed Layer	14
2.5 Zinc Oxide Nanostructures	26
2.5.1 Growth of Zinc Oxide Nanorods	26
2.5.2 Zinc Oxide Nanostructures Based Ethanol Sensor	38
2.6 Chapter Summary	46

# **CHAPTER ONE**

## **INTRODUCTION**

### **1.1 SENSOR**

Until now, a wide range of gas sensors has been developed. Development of sensor era has already begun since 1970s in which the semiconductor combustible gas sensor, an oxygen sensor of solid electrolyte and humidity sensor were commercialized [1]. During these two decades, considerable effort has been made not only to advance on these sensors but also to develop a range of gas sensors that were in prodigious request for making safety, health, environment controlling, automotive application and security [2, 3]. Due to numerous requests for the development of gas sensors, research which focuses on development of small, compatible, inexpensive with low energy consumption has expanded over the years and sparked a major research around the world to improve the metal oxide sensor mainly in sensitivity, speedy response, selectivity and stability properties.

Currently, semiconductors, electrolytes or catalytic combustion gas sensor have been used to detect various kinds of gases such as reducing gas; methane, propane, carbon monoxide, ammonia, hydrogen sulfide and adsorptive gas; oxygen, nitrogen dioxide and ozone. Up to now, there are many new demands for gas sensor which includes detection of Volatile Organic Compounds (VOC) to find new innovations for better sensing performances, lower power consumption and more compact device structures. To meet these demands, semiconductor gas sensors are considered to be the best suited because they have advantageous features such as simplicity in device structure and circuitry, high sensitivity, versatility and robustness.

### **1.2 ETHANOL SENSOR**

The growing interest on the development of alcohol sensors for food quality control, industrial areas, breath analysis and environment control [3-9] has created a great demands on seeking the gas sensor with high sensitivity, stability and wide selectivity. Presently, the analytical instruments such as gas chromatography, high