DEVELOPMENT OF ZINC OXIDE NANORODS FOR HYDROGEN GAS OPTICAL SENSOR

BY

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A thesis submitted in fulfillment of the requirement for the degree of Master of Science (Communication Engineering)

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ABSTRACT

Hydrogen (H_2) gas is widely used as a clean fuel in various applications. The properties of H_2 gas such as colourless, odourless and highly explosive gas require a practical and robust sensor to minimize the risk of explosion due to its volatile properties. The need to monitor H_2 leakage detection at early stage to avoid accident is very important as it has a wide range of flammability in air (4-75%) by volume. H_2 gas sensor was developed using etched-optical fiber coated with Zinc Oxide (ZnO). Single mode fiber has been used and it was etched by using hydrofluoric acid (HF) to enhance the evanescent field of the light propagates in the fiber core. The etched fiber was coated with ZnO nanorods via hydrothermal process by using seeding and growth solution. The sensing layer was characterized through Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray (EDX) and X-Ray Diffraction (XRD) to verify the properties of ZnO. The sensing layer thickness is measured to approximately 1.5 micrometer. It is reported that the structural of nanorods can be controlled in terms of density, diameter, and length through a different growth duration which these parameters are important to the sensing mechanism of gas sensor. In this thesis, the developed sensor operating temperature was found to be 150°C that produces 6.36 dBm increase in response towards the 1% concentration of H_2 in synthetic air. It is shown that the etching-optical fiber has increasing in the light-intensity output power with the increment of H_2 concentration at 150 °C operating temperature. The sensor response and recovery times are 7 min and 3 min respectively for 0.25% of H_2 concentrations at 150 °C. The etching optical fiber coated with semiconductor material has given significant impact on the optical-based application gas sensor. This work successfully contributes to the enhancement of sensitivity in a development of optical gas sensor compare to other previous work.

نبذة مختصرة

الهيدروجين (H2) غاز واسع الاستخدام كوقود نظيف في العديد من التطبيقات. وخصائص هذا الغاز انه عديم اللون والرائحة وشديد الانفجار لذلك يحتاج هذا الغاز الى مستشعر شديد الحساسية لتقليل خطورة انفجاره لان من خصائصه انه غاز متطاير في الهواء. ظرورة الكشف المبكرعن تسريبات الغاز لتفادي وقوع حوادث امر مهم جدا. حيث أنه يحتوي على قابلية عالية للاشتعال في الهواء (4_75٪) من حيث الحجم. تم تطوير مستشعر الغاز باستخدام الالياف البصرية مغلفة بالزنك اوكسيد
ZnO.
تم استخدام الالياف البصرية الاحادية وتم تحفيزه باستخدام حمض الهيدروفلوريك (HF) لتحسين الفقد الذي يحدث اثناء انتقال الضوء في مركز الفايبر. الفايبر المحفور غلفه بمادة ZNO باستخدام العملية الحرارية الغرس والنمو. طبقة الاستشعار عرفت خصائصها باستخدام ماسح ميكروا الكترونى SEM و اشعة صينية مشتته للطاقة (EDX) و (XRD) للتحقق من خصائص (ZNO) . وقد تم قياس سمك طبقة المستشعر وكانت تقريبا 1.5 سنتمتر. ذكر ان تركيب
(ZON) يمكن التحكم فيه من ناحية الكثافة و القطر وكذلك الطول خلال فترات نمو مختلفة وهده تكون مهمة لألية الاستشعار. في هذه الاطروحة تم تطوير درجة الحرارة الخاصة بتشغيل الحساس الي 150 درجة مؤية والتي تنتج 6.36 ديسبل والتي ساهمة بشكل واضح في زيادة الاستجابة بنسبة 1 % من تركيز الهيدروجين في الهواء الاصطناعي.
تبين أن الألياف البصرية المحفزة لها زيادة خطية قليلة في قدرة خرج الهيدروجين عند درجة حرارة التشغيل 150 درجة مئوية. الضوء مع زيادة تركيز تبلغ مدة استجابة أجهزة الاستشعار ووقت استعادتها 7 دقائق و3 دقائق علي التوالي لاجل 25 % من الهيدروجين المركز في درجة حرارة 150 درجة مؤية. الالياف البصرية المحفزة والمطلية بعناصر اشباه الموصلات والتي تعطي تطبيق عالي الفاعلية وخصوصا في طبيقات استشعار الغاز. هدا المشروع ساهم بنجاح في تحسين حساسية استشعار الغاز مقارنة للبحوث السابقة في نفس المجال.

APPROVAL PAGE

I certify that I have supervised and read this study and that in my opinion, it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science (Communication Engineering).

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I certify that I have supervised and read this study and that in my opinion, it confirms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science (Communication Engineering).

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Erry Yulian T. Adesta
Dean,
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DECLARATION

I hereby declare that this thesis is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently submitted as a whole for any degrees at IIUM or other institutions.

Nur Farahi Binti Idris

Signature ………………………………...   Date……………….

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This thesis is dedicated to my parents for laying the foundation of what I turned to be in life.

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In the name of Allah,
The Most Beneficent, The Most Merciful

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LIST OF SYMBOLS

d_p	Penetration Depth of Amplitude
E_z	Evanescent Field
E_0	Initial Value of Evanescent Field
e	Electron
n_m	Refractive Index of Modified Cladding
n_1	Refractive Index of Core
n_2	Refractive Index of Cladding
E	Light Energy
°C	Degree Celsius
%	Percentage
Cu Kα	Generation of X-Ray Spectrum
Å	Unit of Length Equal To 10^{-10} m
λ_o	Vacuum Wavelength
θ_1	Angle of Incidence to The Normal at The Interface
Eg	Band Gap Energy
L_1	Skip Length
V_o	Oxygen Vacancies
λ_g	Minimum Wavelength
h	Planck's Constant
v	Velocity of Light

LIST OF ABBREVIATIONS

EMI	Electromagnetic Interference
Pd	Paladium
SOF	Silica Optical Fiber
POF	Plastic Optical Fiber
SMO	Semiconductor Metal Oxide
LPG	Liquid Petroleum Gas
ZnO	Zinc Oxide
SMF	Single Mode Fiber
ASE	Amplified Spontaneous Emission
OSA	Optical Spectrum Analyzer
FESEM	Emission Scanning Electron Microscope
EDS	Energy Dispersive Spectroscopy
XRD	X-Ray Power Diffraction
MMF	Multi-Mode Fiber
TIR	Total Internal Reflection
HF	Hydrofluoric Acid
RI	Refractive Index
SMOs	Semiconductor Metal Oxides
ZAH	Zinc Acetate Hydrate
TMAH	Tetra Methyl Ammonium Hydroxide
HMT	Hexamethylenetetramine/Hexamine
SAW	Surface Acoustic Wave
CBD	Chemical Bath Deposition
DI	Deionized
IPA	Isopropyl Alcohol
mM	Milimole
C	Carbon
FOS	Fiber Optic Based Sensor
LD	Laser Diode
EDF	Erbium-Doped Fiber

sccm	Standard Cubic Centimetre Per Minute
Pt	Platinum
Au	Gold
Ag	Silver
Cu	Copper
Co	Cobalt
F	Fluorine
nm	Nanometre
µm	Micrometre
meV	Milli-electron Voltage
ppm	Parts per million
mmHg	Millimetre of Mercury

CHAPTER 1

INTRODUCTION

1.1 RESEARCH BACKGROUND

There are various kind of gases that have been radiated from different sources and many of them are hazardous. The properties of these kind of gases are mostly flammable, colourless and odourless. Most of the surrounding gases exist at a very low concentration, therefore a highly sensitive sensor is vital for monitoring. One of the most promising gas sensor candidate is semiconductor metal oxide (SMO) integrated with optical sensor due to the superior advantages such as immune to electromagnetic interference (EMI), lightweight, small size, high sensitivity, large bandwidth, and ease in implementing multiplexed or distributed sensor (Ahuja & Parande, 2012). There are a lot of researches reported using fiber optics as a sensor where it can be applied in physical measurement (i.e. acceleration, temperature, strain, displacement, pressure) as well as chemical measurement (i.e. water pollutants, refractive index, gas sensing) (B. Lee, 2003; Liang, Huang, Xu, Lee, & Yariv, 2005; M. Xu, Li, Ma, & Fan, 2014; Ying Zhang et al., 2001).

There are two categories of optical fiber which are silica optical fiber (SOF) made from glass, and plastic optical fiber (POF) made from polymer. Among the glasses, fused silica which is known as amorphous silicon dioxide (SiO_2) is strongly dominating the materials that has been used in fabricating fiber optics. Fused silica also can be doped or coated with another various material such as semiconductor metal oxide (SMO) material. However, coating process must go through the process of modification to the cladding of the fiber by a technique called tapering or etching. Through this process, evanescent field can be created at the surrounding of modified cladding, thus increase the interaction of light to the surrounding.

SMO gas sensor was invented in the year of 1960's (Seiyama, Kato, Fujiishi, & Nagatani, 1962) and a huge technological effort has been made to improve the performance of semiconductor gas sensors in terms of sensitivity, selectivity, stability and convenience for practical uses. In recent years, the interest of researchers and engineers to SMO has grown substantially due to the progress in nanotechnology and it is practical important role in environmental and safety monitoring, as well as chemical and biological sensing. It is also widely used in the domestic and industrial area for gas detectors, gas-leak alarms, process control and pollution. There are a lot of mechanisms have been established for the detection such as absorption, Raman scattering (Ahuja & Parande, 2012; Yahya et al., 2017; Yunusa, Hamidon, & Rashid, 2013), fluorescence (Chu & Chuang, 2015), surface plasmon resonance (Klantsataya, Jia, Ebendorff-heidepriem, & Monro, 2016; B. Lee, Roh, & Park, 2009), light intensity (Meshginqalam & Alaei, 2017; C. Wang, Yin, Zhang, Xiang, & Gao, 2010), and mechanical-deformation caused by a gas-material interaction.

SMO materials has caught the eye among researchers due to its high sensitivity as a sensing layer and one of the most famous SMO is zinc oxide (ZnO) (Nanto, Minami, & Takata, 1986). The molecular bond of ZnO on the covalence boundary between ionic and covalent semiconductors make it classified as a semiconductor in group II-VI. The properties of ZnO such as wide band gap semiconductor (3.37 eV) and high excitation of binding energy (60 meV) allows an excitonic emission processes above room temperature (Z. L. Wang, 2004). Therefore, ZnO become one of the favourable choices among researchers to venture any opportunity in applying it into electronics, optoelectronics, optical sensor and laser technology.

The purpose of coating is to enhance the sensitivity of the fiber optic sensor. Sensitivity is one of the common criteria to develop a semiconductor sensor including gas sensor. It can be calculated with respect to the mean baseline response of the sensor in exposure to room air, relative to its response to a gas concentration. The measurement for the sensitivity based on the lowest concentration of an analyte gas that can be detected. In addition, response and recovery time of the sensor must be taken into consideration for the semiconductor gas sensor performance. Both are defined as the time taken to achieve 90% of the final change in output following the change of gas concentration.

1.2 PROBLEM STATEMENT

A lot of environmental threats and accidents occurred owing to the exposure to the leaking gas or hazardous have obliged the industries to invest huge amount of money in the gas sensors development both in research and industrial level. Nowadays, the development and optimization of detectors for monitoring airborne pollutants, for protection of workers in the petrochemical oil and industries and for the detection of natural gas leaks from incomplete combustion in boilers in domestic environments have become a high demand. Monitoring of these gases are crucial since most of the gases are hazardous to human beings and environment. Besides, the gases are mostly difficult to detect considering its properties of colourless and odourless. H_2 gas is one of the flammable gas in air possessing a wide range of flammability of 4-75%. The detection at low concentration of H_2 gas is needed to prevent accident at the early stage of leakage. There are numerous gas detections based on electrical measurement, however it is easily affected by EMI and thus compromise the signal response. In addition, electrical system can lead to the malfunction due to high voltage and can produce spark which this effect the system. Hence, there is an urgent solution needed to develop a fast response and high sensitivity sensor which can stand at high temperature. Therefore, in this research, the fiber optic has been used as a platform to overcome the restriction due to EMI and high temperature, with the modification of fiber's cladding through etching technique by coating with ZnO nanorods for better gas molecules-sensing layer interaction and to achieve a high sensitivity gas sensor.

1.3 RESEARCH MOTIVATION

The U.K. Marine Accident Investigation Branch's (MAIB) reported on two explosions happened due to the ignition of hydrogen (H_2) gas released from the cargo there (Marex, 2017). While another news reported there was one hydrogen tanks exploded in Rochester, New York due to leakage H_2 of gas (Thomas, 2010). These are the numerous news that have been reported on the incident happened due to the leakage of H_2 gas, and it is important to develop a sensor that can sense a leakage of H_2 gas at early stage.

1.4 RESEARCH OBJECTIVES

This research aims to develop a high sensitivity optical gas sensor by fabricating ZnO nanorod coated on the etched single mode fiber (SMF) via low temperature process. To achieve this, few objectives have been proposed to guide the research direction, i.e.:

i. To synthesis ZnO nanorods by using hydrothermal method.
ii. To characterize optical and physical properties of etched optical fiber-based ZnO nanorods.
iii. To analyse the performance of etched optical fiber coated with ZnO nanorod-based hydrogen gas sensor.

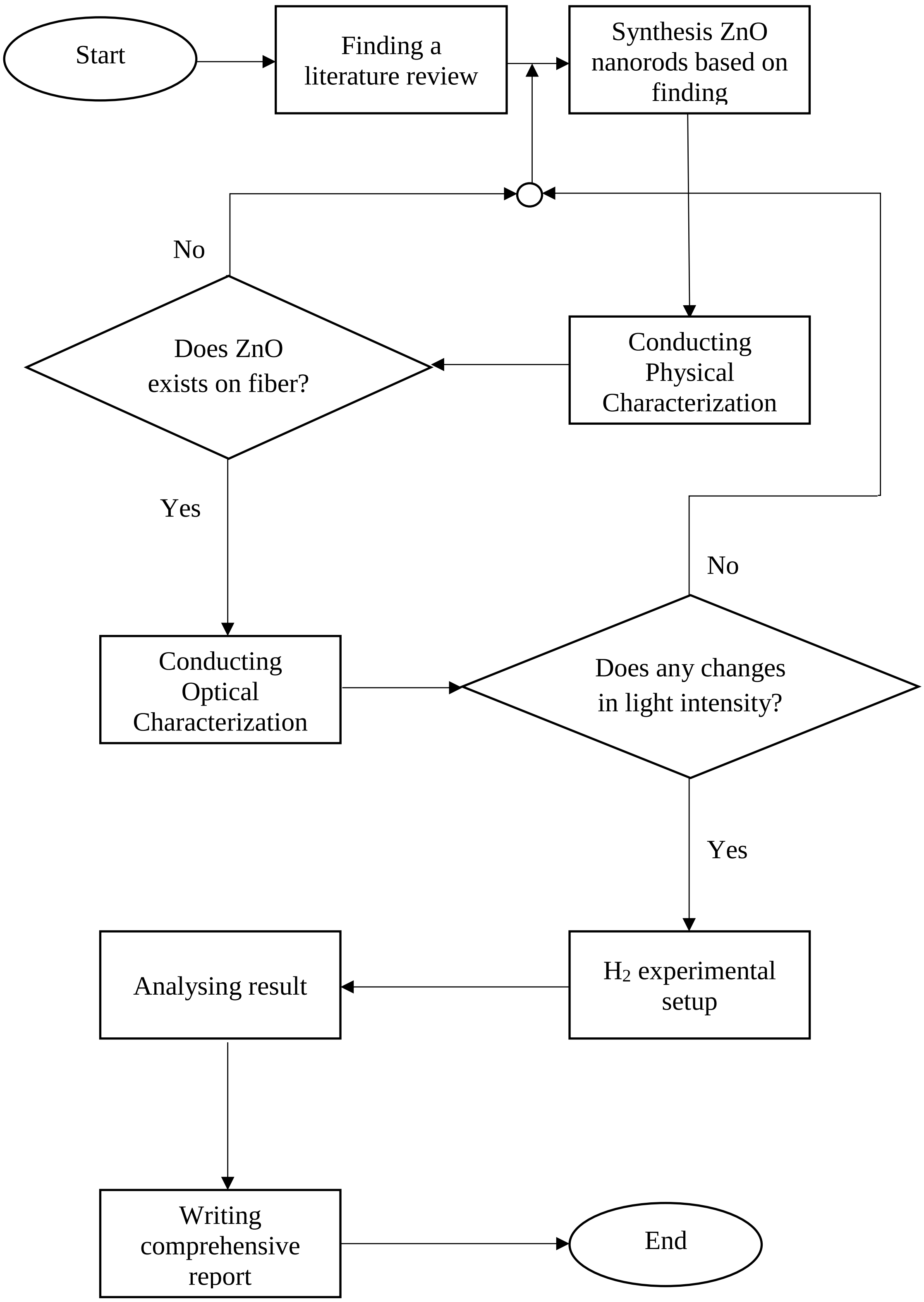
1.5 RESEARCH SCOPE

The main objective of the research is to enhance the sensitivity of optical gas sensor by some modification of cladding with semiconductor metal oxide as a sensing element. The research scopes are as follows:

i. Hydrothermal process is used as a synthesis method to fabricate ZnO nanorods.
ii. Physical characterization of ZnO nanorods is done through Fields Emission Scanning Electron Microscope (FESEM), Energy Dispersive Spectroscopy (EDS) and X-Ray Power Diffraction (XRD).
iii. Cladding of single mode fiber is modified through etching process.
iv. Optical characterization is done through experimental set up using Amplified Spontaneous Emission (ASE) and Optical Spectrum Analyzer (OSA) as a source and to measure the light intensity, respectively.
v. ZnO nanorods was coated on the etched-optical fiber to replace the passive cladding for developing hydrogen gas sensor to enhance sensitivity.

1.6 RESEARCH METHODOLOGY

To achieve research objectives as mentioned above, the research work will be conducted as follow.


Start
Finding a literature review
Synthesis ZnO nanorods based on finding
No
Does ZnO exists on fiber?
Conducting Physical Characterization
Yes
No
Conducting Optical Characterization
Does any changes in light intensity?
Yes
Analysing result
H2 experimental setup
Writing comprehensive report
End

1.7 OUTLINE OF THE THESIS

This thesis presents research works on the fabrication of a ZnO nanorods coated on the etched SMF as a sensing layer for hydrogen gas sensing.

Chapter 1 of this thesis explains a brief background of the research idea, followed by problem statement, research objectives, research methodology, scope of research and ended with thesis organization.

Chapter 2 reports on a brief overview on successful ZnO integration in optical sensors and hydrothermal synthesis method followed by literature reviews of past researches employing ZnO nanorods for gas monitoring.

Chapter 3 focuses on experimental methodology process of the synthesis of ZnO nanorods on using hydrothermal method. This chapter also explains briefly on the physical characterization of the fabricated ZnO nanorods and the outcome from the characterization.

Chapter 4 presents experimental details of the proposed gas sensor and the optical characterization of ZnO nanorods before and after modification of cladding. The comparison on the light intensity of different growth duration of ZnO nanorods is also discussed in this chapter. Finally, analysis and discussion of the experimental results on the ZnO nanorods coated on a surface of an etched optical fiber for hydrogen (H_2) gas sensor is included.

The main conclusion of overall work is concluded in Chapter 5 with recommendations on possible areas for future research. This chapter also states the limitation faced during research.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

In this chapter, the first section introduces the principle theory of fiber sensors which evanescent wave and refractive index mechanisms are used for developing optical sensor. The following section describes the characteristics of zinc oxide (ZnO) material to be used as a sensing element which briefly discussed on the different methods reported for synthesizing ZnO nanorods specifically giving the attention to hydrothermal method. In the sub-section, the factors that influence the nanorods in terms of morphology and size of nanorods is also discussed. Lastly, a discussion on the effect of SMO towards H_2 gas sensor applications is also provided.

2.2 FIBER SENSOR

Optical fiber has gained tremendous interest in various applications such as in fiber laser, sensors, and communication. There are two categories of fiber which are silica optical fiber (SOF) made from glass, and plastic optical fiber (POF) made from polymer. In SOF, the fiber is divided to two subcategories which is single-mode fiber (SMF) and multi-mode fiber (MMF). The major difference of these two are the diameter of the core. SMF has small core usually less than 10 µm in diameter and transmit infrared laser light at wavelength 1300 to 1550 nm while MMF has larger cores about 62.5 µm in diameter and transmit infrared light at 850 to 1330 nm (Peters, 2011). Both SMF and MMF have same cladding size which is 125 µm.