

# **UNIVERSITI PUTRA MALAYSIA**

# OPTICAL PROPERTIES OF ZINC OXIDE THIN FILMS FABRICATED VIA RADIO FREQUENCY MAGNETRON SPUTTERING FOR OPTICAL HYDROGEN GAS SENSOR APPLICATION

SITI NOR ALIFFAH BINTI MUSTAFFA

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By

SITI NOR ALIFFAH BINTI MUSTAFFA

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Master of Science

October 2017

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

## OPTICAL PROPERTIES OF ZINC OXIDE THIN FILMS FABRICATED VIA RADIO FREQUENCY MAGNETRON SPUTTERING FOR OPTICAL HYDROGEN GAS SENSOR APPLICATION

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#### SITI NOR ALIFFAH BINTI MUSTAFFA

October 2017

Chairman: Suriati binti Paiman, PhD Faculty: Science

This thesis focused on the optimization of zinc oxide (ZnO) thin films for optical hydrogen (H<sub>2</sub>) gas sensor using radio frequency (RF) magnetron sputtering technique. Various strategies were adopted to produce optically controlled thin films with the desired properties. This work focused on the effect of deposition parameters that included deposition time, RF power, argon/oxygen (Ar/O<sub>2</sub>) gas percentage, and annealing condition on thin film thickness, surface roughness, crystal phase, phonon modes, and optical band gap. The thin films' surface morphology and thickness were characterized carefully using atomic force microscopy (AFM) and surface profilometry, respectively, while crystallographic structure was examined using X-ray diffraction (XRD). Ultraviolet visible spectroscopy (UV-VIS) was used to investigate the optical transmittance and band gap of the produced films. Fourier transforms infrared spectroscopy (FTIR) was performed to examine the functional group, while Raman spectroscopy was used to characterize the phonon modes.

Deposition time was found to have a very significant effect on thin film thickness, where the thicker thin film obtained when deposited for 180 min was  $851.35 \pm 4.45$  nm. XRD analysis confirmed that RF power of 150 W with influence of post-deposition annealing was able to promote growth of crystal structure with crystal plane orientation of (002) as hexagonal wurtzite structure. Furthermore, increasing the RF power from 50 to 150 W also reduced the surface roughness from 88.2 to 6.86 nm. In order to improve the optical properties, O<sub>2</sub> gas percentage was reduced from 50% to 4%. However, there was an existence of diffraction peak at (011) plane despite improving the intensity of diffraction peak at plane (002) at 4% of O<sub>2</sub> gas percentage. This was due to O<sub>2</sub> atoms that induced the breaking and reforming of Zn-O bonds, which could modify the ZnO bonding network. Finally, optimized ZnO thin films

were successfully deposited with RF power of 150 W and 4% of O<sub>2</sub> gas percentage for 180 min. It was found that Raman active phonon modes for the optimized ZnO thin films were at E2 (high) and A1 (LO) which were 440 and 565 cm<sup>-1</sup>, respectively. The FTIR analyses showed that ZnO absorption bands in the fingerprint region between 500-450 cm<sup>-1</sup> had arisen from inter-atomic vibrations due to stretching of Zn-O bond. Hence, the optimized ZnO thin films were tested for H<sub>2</sub> optical sensing application. At the operating temperature of 27 °C with concentration of H<sub>2</sub> gas at 2 mol%, it was found that gas sensing characteristic of novel RF-sputtered ZnO thin film was strongly influenced by crystalline at the size of 124.10 nm, thickness of 399.43 ± 1.47 nm and surface roughness of 18.9 nm. The gas sensing mechanism of the novel RF-sputtered ZnO thin film was based on the surface reaction between adsorbed oxygen and the H<sub>2</sub> gas where more oxygen was chemisorbed in the form of O<sub>2</sub><sup>-</sup>, O<sup>-</sup>, and O<sup>2-</sup> by ZnO thin film. The calculated molar absorptivity,  $\varepsilon$  increased with the increase of rms surface roughness whereby relatively high surface roughness is better to optically absorb H<sub>2</sub> gas. Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

# PENCIRIAN OPTIK SAPUT TIPIS ZINK OKSIDA MENGGUNAKAN PERCIKAN MAGNETRON RADIO FREKUENSI UNTUK SENSOR OPTIK GAS HIDROGEN

Oleh

#### SITI NOR ALIFFAH BINTI MUSTAFFA

Oktober 2017

# Pengerusi: Suriati binti Paiman, PhD Fakulti: Sains

Kajian ini menumpukan kepada saput tipis zink oksida (ZnO) untuk tujuan aplikasi sensor optik gas hidrogen (H<sub>2</sub>) yang telah dihasilkan dengan teknik percikan magnetron radio frekuensi (RF). Terdapat pelbagai pendekatan strategi bagi mengawal penghasilan ciri-ciri tertentu saput tipis ZnO. Oleh itu, kajian ini memfokuskan kepada kesan durasi pemendapan, kuasa RF, nisbah gas argon/oksigen (Ar/O<sub>2</sub>) dan proses sepuh lindap ke atas ketebalan saput tipis, kekasaran permukaan, fasa kristal, mod fonon dan jurang jalur optik. Pencirian kekasaran permukaan dan ketebalan saput tipis masing-masing menggunakan mikroskopi daya atom (AFM) dan profilometri permukaan. Di samping itu, spektroskopi ultralembayung (UV-VIS) digunakan untuk mengenalpasti kehantaran optik dan jurang jalur saput tipis. Selain itu, spektroskopi transformasian Fourier inframerah digunakan bagi mengkaji kumpulan berfungsi, manakala spektroskopi Raman untuk mencirikan mod fonon.

Hasil dapatan kajian mendapati bahawa durasi pemendapan memberi kesan yang ketara ke atas ketebalan saput tipis. Hal ini demikian kerana pada durasi pemendapan selama 180 minit, saput tipis setebal  $851.35 \pm 4.45$  nm telah dihasilkan. Tambahan itu, analisa XRD mengesahkan bahawa kuasa RF sebanyak 150 W dan proses sepuh lindap dapat menggalakan pertumbuhan struktur kristal pada satah (002) sebagai struktur wurtzit heksagon. Begitu juga dengan peningkatan kuasa RF daripada 50 kepada 150 W telah mengakibatkan nilai kekasaran permukaan saput tipis menurun daripada 88.2 kepada 6.86 nm. Bagi menambahbaik ciri-ciri optik saput tipis ZnO, nisbah gas O<sub>2</sub> telah direndahkan kepada 4% daripada 50%. Walaubagaimanapun, terdapat kemunculan puncak belauan pada satah (011) selain peningkatan keamatan puncak belauan (002) ketika nisbah gas O<sub>2</sub> pada 4%. Ini berpunca daripada atom O<sub>2</sub> yang mempengaruhi pemutusan dan pembentukan semula ikatan Zn-O, sekaligus mengubahsuai jaringan pengikatan ZnO. Dalam pada itu, mod fonon Raman juga dikesan pada E2 (tinggi) dan A1 (LO) iaitu pada 440 dan 570 cm<sup>-1</sup>,

masing-masing. Kajian transformasian Fourier inframerah pula mendapati bahawa jalur serapan ZnO adalah pada jurang 500 – 450 cm<sup>-1</sup> yang berpunca daripada hasil getaran atom yang disebabkan oleh regangan ikatan zink dan oksigen. Akhir sekali, saput tipis ZnO yang optimum telah digunakan bagi tujuan aplikasi pengesanan gas H<sub>2</sub> secara optik. Pada suhu 27 °C dengan kepekatan gas H<sub>2</sub> sebanyak 2 mol%, pencirian saput tipis ZnO didapati amat dipengaruhi oleh saiz kristal bernilai 124.10 nm dengan ketebalan saput tipis iaitu 399.43 ± 1.47 nm selain kekasaran permukaan sebanyak 18.9 nm. Mekanisme pengesanan gas ialah berasaskan kepada interaksi reaksi permukaan antara oksigen yang dijerap dengan gas H<sub>2</sub> di mana lebih banyak oksigen telah diserap secara kimia dalam bentuk  $O_2^-$ ,  $O^-$  dan  $O^{2^-}$  oleh saput tipis ZnO. Daya penyerapan molar yang telah dikira,  $\varepsilon$  didapati meningkat dengan peningkatan kekasaran permukaan sebagai lebih baik untuk menyerap gas H<sub>2</sub> secara optik berdasarkan dapatan kajian ini.

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# LIST OF ABBREVIATIONS

| Ar             | Argon                             |
|----------------|-----------------------------------|
| DC             | Direct Current                    |
| FT-IR          | Fourier Transform Infrared        |
| H <sub>2</sub> | Hydrogen                          |
| IR             | Infrared                          |
| LO             | Longitudinal Optical              |
| MOS            | Metal Oxide Semiconductor         |
| O <sub>2</sub> | Oxygen                            |
| PVD            | Physical Vapour Deposition        |
| RF             | Radio Frequency                   |
| ТО             | Transverse Optical                |
| UV-VIS-NIR     | Ultraviolet-Visible-Near Infrared |
| XRD            | X-ray Diffraction                 |
| ZnO            | Zinc Oxide                        |

 $\bigcirc$ 

# CHAPTER 1

#### INTRODUCTION

This chapter highlights the project background, motivation, problem statement and research objectives of metal oxide semiconductor thin film for optical gas sensor technology.

## 1.1 Background and Motivation

Before man's civilization era in industrialization began, air pollution was mainly contributed by open fire burning that resulted in carbon dioxide  $(CO_2)$  and carbon monoxide (CO). With the beginning of man-made industries, the emission of numerous air pollutants rose with time. Diseases such as asthma, lung cancer, heart disease, chronic obstructive pulmonary disease (COPD), and other examples of dangerous health consequences are connected to harmful gases according to the American Heart Association (Lang et al., 2009; Matamis et al., 2012). Hence, gas sensor technology is a worldwide hit agenda and vigorously adopted by many industries to monitor the chemical species and their concentrations.

Hydrogen (H<sub>2</sub>) gas, while not considered a pollutant gas itself, is proclaimed to be the fuel of the future (Pimentel et al., 2008). Hydrogen is the most abundant element in the universe, and is nominated as the most potential sustainable energy supply system (Dincer, 2008). In medical purposes, hydrogen gas mixture can be an exclusive antioxidant (Ishibashi, 2013). In solid state science, despite its potential as an electron donor in many oxide materials, hydrogen gas can also help to stabilise material properties by saturating broken ("dangling") bonds of amorphous silicon and amorphous carbon (Wang et al., 2016).

Hydrogen is nature's lightest and smallest atom with atomic number 1, nontoxic, odorless, and tasteless. With less than 12% of oxygen concentration in a closed system, a small leak of  $H_2$  gas will cause immediate unconsciousness and severe asphyxiation, a deficient supply of oxygen to the body that arises from abnormal breathing (Pan et al., 2016). At a standard atmospheric temperature, 4-75% concentration of hydrogen is flammable, and at 15-59% concentration, it could possibly cause an explosion (Al-Salman et al., 2013).

Additionally, the  $H_2$  gas leak is extremely hazardous because common electrostatic discharge (ESD) or lightning is enough to be the source of ignition.

Other than that, metal hydrides technology is mainly used for hydrogen storage, but brittle metal hydride is due to mechanical instability in the corroded metals caused by the H<sub>2</sub> gas itself (Lototskyy et al., 2015). Without exception, highly sensitive H<sub>2</sub> gas sensors with low operating temperatures are also demanded in many critical applications such as hydrogen generation plants (Henriksen et al., 2016), fuel cell electric vehicle (Abdollahi et al., 2012), and volatile nuclear reactors (Moore, 2017). Therefore, studying the sensing material and sensing mechanism of H<sub>2</sub> gas is extremely crucial as conducted throughout this project.

# 1.2 Metal Oxide Semiconductor Thin Film for Optical Gas Sensing Technology

In this 21<sup>st</sup> century, the ultimate capability of a gas sensor has progressed rapidly. The biggest challenge is to identify and gain comprehensive information about the variety of gases present in an air ambient environment. Different applicability and inherent limitations of gas sensor technology influenced the characteristic of measured gas. Despite the rising number of gas sensors being introduced, metal oxide semiconductor (MOS) gas sensor still remains far from being satisfactorily understood.

MOS such as  $SnO_2$ ,  $Fe_2O_3$ ,  $TiO_2$ , ZnO,  $In_2O_3$ , and  $WO_3$  are being widely investigated for gas detection application because of their intriguing working mechanism. It was found that the surface morphology of MOS thin film plays an important role in gas sensing performance (Sun et al., 2012). On top of that, ZnO thin film demonstrates good sensitivity with the chemical environment and reliable material towards high temperature application.

Various chemical and physical deposition techniques have been employed to produce ZnO thin film, for example, chemical vapor deposition (Ye et al., 2003), physical vapor deposition (Pattini et al., 2015) and pulsed laser deposition (Zhao et al., 2007) methods. In this work, such properties of ZnO thin films deposited using radio frequency magnetron sputtering will be used towards gas sensor application. Furthermore, structural, optical, and surface morphology features of ZnO thin film will be studied to investigate their effects on  $H_2$  gas sensing mechanism.

The general detection mechanism responsible for ZnO gas sensor is the change of electrical resistance due to the electron conduction across grain boundaries (Gruber et al., 2003). These oxygen rich grain boundaries lead to potential barriers that deplete the carriers surrounding them and impede the current flow.

Apparently, the integration of ZnO thin film with the optical gas sensor is believed to yield better performance by incorporating it with optical fibre (Dikovska et al., 2007). The optical techniques employed to measure the

response in gas sensing are mounted on absorbance, reflectance, refractive index or luminescence change induced by the interaction between ZnO thin film and test gas. In this work,  $H_2$  gas sensing mechanism and properties of pure ZnO thin film deposited on glass substrates are therefore studied using the optical gas sensor at room temperature.

#### 1.3 **Problem Statements**

At present, several major research challenges in the field of gas sensing specialization have been gaining attention. A sensing element is expected to have high selectivity, stability, and sensitivity towards the targeted gas with the ability to operate at room temperature with low electrical power consumption. Other than that, there is no environmental degradation during its usage and without using expensive noble transition metals or dopant materials during the fabrication process.

Multifunctional semiconducting metal oxide, particularly ZnO, is being investigated for  $H_2$  gas detection application. Recently, numerous studies have focused on how to optimize the structural and optical properties of ZnO thin films during its preparation. Several techniques have been employed for the preparation of ZnO thin film. Nonetheless, a few methods often suffer from the disadvantages of using noble metal catalyst and requiring high temperature, which causes a more complex preparation procedure and leaving catalyst impurities that degrade the properties of ZnO thin films. Therefore, an alternative technique such as radio frequency (RF) magnetron sputtering is the most suitable method that satisfies these limitations.

Besides that, post-deposition annealing will be implemented to improve the structural properties of ZnO, because of its capability to promote crystallinity of ZnO thin films and control the thin film's thickness. This work will also focus on the contribution of both surface roughness and grain size on optical gas sensing mechanism.

Essentially, thickness plays a vital role in optical gas sensor application and clearly needs to be optimized during the deposition process. Therefore, it is believed that by increasing the deposition time, it will also enhance the ZnO thin film's thickness. Apart from that, the phase structure of ZnO thin film is also a concern towards efficiency in sensing mechanism. For that, the optimization of other parameters such as RF power and  $O_2$  gas percentage will significantly improve the crystallinity of ZnO thin films. Yet, the sensing mechanism is one of the crucial properties of optical-based ZnO gas sensor. However, the changes of optical properties in terms of absorptivity of pure ZnO thin films when exposed to H<sub>2</sub> gas are yet to be fully explored.

To conclude these research questions, the author focused the investigation on pure ZnO thin films deposited by RF magnetron sputtering. It is expected that a sensitive and responsive sensor will be realized by RF-sputtered ZnO thin film with slightly high root mean square surface roughness after post-deposition annealing. It is also proposed that the crystallized ZnO thin films possess the ability to exhibit optical sensing interaction with H<sub>2</sub> gas at room temperature. The ZnO thin films' characterization combined with the gas sensing performance contribute to the fundamental understanding of the gas interaction mechanisms in optical gas sensors.

# 1.4 Research Objectives

This research aims to deposit ZnO thin films using RF magnetron sputtering technique for optical  $H_2$  gas sensor application. These outlined objectives are to attain the emphasized aim:

- i. To deposit ZnO thin films via RF magnetron sputtering technique with various deposition conditions (time, RF power, O<sub>2</sub> gas percentage ,and post-deposition annealing);
- ii. To characterize the structural properties (thickness, crystal structure, surface roughness, and grain size) of ZnO thin films through Surface Profilometry, XRD, and AFM;
- iii. To investigate the optical properties (transmittance, band gap energy, functional group, and phonon modes) of ZnO thin films through Raman, FT-IR, and UV-VIS; and
- iv. To study the optimized ZnO thin films on  $H_2$  gas molecules-sensing layer absorptivity interaction at room temperature through UV-VIS-NIR.

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Siti Nor Aliffah binti Mustaffa received her Master of Science (Nanoscience) and Bachelor of Science (Honour) Physics from the Universiti Putra Malaysia in 2017 and 2013, respectively. Her main research interests are in the field of thin film, material science and nanotechnology. She can be reached by email noralifah@gmail.com.



# LIST OF PUBLICATIONS

#### Peer Reviewed Journal

**Siti Nor Aliffah Mustaffa**, Nurul Assikin Ariffin, Suriati Paiman, Nizam Tamchek, and Abdul Halim Shaari. Post-Annealing Effects on the Structural Properties of RF-sputtered ZnO Thin Films. Journal of Solid State Science and Technology, Vol. 25, No. 2 (2017), page 145-151. ISSN 0128-7389 | http://journal.masshp.net

**Siti Nor Aliffah Mustaffa**, Ahmed Lateef Khalaf, Mohd. Hanif Yaacob Nizam Tamchek, and Suriati Paiman. Room Temperature H<sub>2</sub> Optical Sensing of RF-Sputtered ZnO Thin Films (*in progress*)

Nurul Assikin Ariffin, **Siti Nor Aliffah Mustaffa**, Suriati Paiman, Nizam Tamchek, and Abdul Halim Shaari. Effect of Post-Annealing Treatment on the Structural Properties of RF-Sputtered Germanium Thin Layers. Solid State Science & Technology Letters, 17(2), page 191-194.

Ahmed Lateef Khalaf, **Siti Nor Aliffah Mustaffa**, Hayder Abdulbari, Suriati Paiman, Mohd Adzir Mahdi, and Mohd. Hanif Yaacob. Ammonia Gas Sensing using Sputtered Au/WO3 Integrated Side-Polished Optical Fiber (*in progress*)

#### **Oral Presentations**

Suriati Paiman, **Siti Nor Aliffah Mustaffa**, Nizam Tamchek, Ahmad Lateef Khalaf and Mohd. Hanif Yaacob. Zinc Oxide Thin Films for Optical Gas Sensor Applications. Symposium on Advanced Materials and Nanotechnology (18 & 19 July 2017) at Bangi Hotel, Putrajaya.

**Siti Nor Aliffah Mustaffa**, Suriati Paiman, Nizam Tamchek, Ahmad Lateef Khalaf and Mohd. Hanif Yaacob. Structural and Optical Properties of RF-sputtered ZnO Thin Films for Optical Gas Sensor Application. Fundamental Science Congress (9 & 10 August 2016) at Faculty of Science, UPM.

**Siti Nor Aliffah Mustaffa**, Suriati Paiman, and Nizam Tamchek. Effect of Film Thickness on Surface Roughness of RF-sputtered ZnO Thin Films. Fundamental Science Congress (12 & 13 November 2015) at Faculty of Science, UPM.