

**DESIGN, FABRICATION AND CHARACTERIZATION OF
GALLIUM NITRIDE-BASED CIRCULAR SCHOTTKY DIODE
FOR HYDROGEN SENSING**

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BASED CIRCULAR SCHOTTKY DIODE FOR HYDROGEN SENSING

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*Especially dedicated to my beloved mother, brother and sisters who have encouraged
guide and inspired me throughout my journey in education*

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ABSTRACT

Recent revolutionary progress of the internet and wireless technologies has create a concept of the “ubiquitous network” society for this 21st century. A so called Intelligent Quantum (IQ) chip has been proposed as the promising electronic device for the ubiquitous network society environment. An IQ chip is an III-V semiconductor chip with sizes of millimeter square where not only nanometer scale quantum processors and memories are integrated on this chip but also other devices such as wireless power supply and various sensing devices so that such ideal concept can be realized. This research is carried out to reveal a possibility of utilizing III-V base material as a sensing device, in particular as a hydrogen (H₂) gas sensor. High temperature operation and long term stability are important requirements for a H₂ sensor, thus an undoped-Aluminium Nitride/Gallium Nitride (AlGa_{0.5}N/GaN) high-electron-mobility-transistor (HEMT) structure is chosen as the base material. The sheet concentration and mobility of epitaxial layers determined by Hall measurement were $6.61 \times 10^{12} \text{ cm}^{-2}$ and $1860 \text{ cm}^2/\text{Vsec}$, respectively. The devices fabrication were etched by an inductively-couple-plasma reactive ion etching (ICP-RIE) system for mesa isolation with a Chlorine (Cl)-based gas system consisting of Boron Trichloride (BCl₃) and Chlorine (Cl₂) gases. The ohmic contacts are formed by deposition of Titanium/Aluminium/Titanium/Aurum (Ti/Al/Ti/Au) (20/50/35/50 nm) multilayers followed by rapid thermal annealing at 850 °C for 30 s in nitrogen (N₂) ambient. The Schottky contact was produced by evaporating 5 nm thick catalytic Platinum (Pt) metal. Finally, Titanium/Aurum (Ti/Au) was evaporated as interconnection contact. Typical *I-V* characteristics measured in vacuum and high purity H₂ ambient at room temperature show that both the forward and reverse currents give only a slight change of current upon exposure to H₂ because the diffusion rate for H₂ atom through the catalytic metal is very slow at room temperature. Thus, it can be said that the sensitivity of gas sensor is quite low at room temperature. However, a large current change by the same amount of H₂ concentration is observed as the temperatures increase up to 200 °C because more effective catalytic dissociation of H₂ on the Pt surface can be realized at higher temperature. The time-transient response measured at temperature of 200 °C and forward bias of 1 V shows that there is sufficient cracking of H₂ for the diode to be a sensitive gas sensor. A constant speed is obtained at each cycle where the average of increment and decrement speed of current are estimated to be 27.6 nA/sec and 17.6 nA/sec, respectively. The increment speed is much faster than the decrement speed for each cycle meaning that the absorption of H₂ is faster than desorption. This is because a desorption process requires thermal energy supply, leading to a longer decrement time. These preliminary results indicate that the proposed sensing devices are capable of detecting H₂ gas with acceptable performance.

ABSTRAK

Kemajuan internet dan teknologi tanpa wayar telah mencipta satu konsep “*ubiquitous network society*” untuk abad ke-21. Cip Kuantum Pintar (IQ) dicadangkan sebagai peranti elektronik yang berpotensi untuk persekitaran “*ubiquitous network society*”. Cip IQ adalah cip semikonduktor III-V yang berukuran milimeter persegi atau kurang dimana bukan sahaja mempunyai pemproses skala kuantum nanometer dan ingatan yang dimuatkan dalam satu cip tetapi peranti lain seperti bekalan kuasa tanpa wayar dan pelbagai peranti penderiaan maka konsep ideal itu boleh direalisasikan. Penyelidikan ini telah dijalankan untuk mendedahkan kemungkinan penggunaan bahan asas III-V sebagai peranti penderiaan khususnya sebagai penderia gas hidrogen (H_2). Kebolehpayaan beroperasi pada suhu tinggi dan kestabilan jangka panjang merupakan syarat-syarat penting bagi sesuatu penderia gas H_2 , oleh yang demikian struktur transistor-mobiliti-elektron-tinggi (HEMT) Aluminium Nitrida/Galium Nitrida (AlGaN/GaN) yang tidak didopkan telah dipilih sebagai bahan asas. Kepekatan lapisan dan kebolehergerakan lapisan epitaksial yang diukur menggunakan pengukuran Hall masing-masing adalah $6.61 \times 10^{12} \text{ cm}^{-2}$ dan $1860 \text{ cm}^2/\text{Vsec}$. Peranti yang difabrikasi dipunarkan oleh sistem pemasangan beraruhan plasma punaran ion reaktif (ICP-RIE) untuk pembentukan mesa dengan asas klorin yang mengandungi gas-gas Boron Triklorida (BCl_3) dan klorin (Cl_2). Sesentuh ohmik dibentuk oleh pemendapan pelbagai lapisan Titanium/Aluminium/Titanium/Aurum (Ti / Al / Ti / Au) (20/50/35/50 nm) diikuti dengan pelindapan haba pantas pada suhu $850 \text{ }^\circ\text{C}$ selama 30 s dalam ambient nitrogen (N_2). Sesentuh Schottky telah dihasilkan dengan penyejatan 5 nm logam pemangkin platinum (Pt). Akhirnya, Titanium/Aluminium (Ti / Au) disejatkan sebagai sesentuh saling sambung. Pencirian I-V bagi penderia telah diukur dalam ambien vakum dan ambien yang mengandungi H_2 ketulenan tinggi pada suhu bilik menunjukkan perubahan arus ke depan dan arus balikan yang kecil disebabkan kadar resapan atom H_2 pada logam pemangkin adalah rendah pada suhu bilik. Maka, sensitiviti penderia adalah rendah pada suhu bilik. Namun, perubahan arus yang besar diperolehi apabila suhu dinaikkan sehingga $200 \text{ }^\circ\text{C}$ disebabkan kadar resapan atom H_2 lebih efektif pada pemangkin apabila suhu meningkat. Kadar respon penderian telah diukur pada suhu $200 \text{ }^\circ\text{C}$ dan pincang hadapan 1 V menunjukkan terdapat penceraian H_2 untuk diod bertindak sebagai penderia yang sensitif. Ini menunjukkan purata kelajuan peningkatan arus dan kelajuan pengurangan arus yang malar dianggarkan masing-masing 27.6 nA/sec dan 17.6 nA/sec . Kelajuan peningkatan arus adalah lebih cepat daripada kelajuan pengurangan arus pada setiap kitar yang bermaksud penyerapan H_2 lebih cepat daripada penyaherapan. Ini disebabkan proses penyaherapan memerlukan bekalan tenaga haba. Analisis awal membuktikan bahawa peranti penderiaan yang dicadangkan berkebolehan mengesan gas H_2 dengan prestasi yang berguna.

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LIST OF ABBREVIATIONS

2DEG	-	Two Dimensional Electron Gas
AlGaN	-	Aluminium Gallium Nitride
Au	-	Aurum
BCl ₃	-	Boron trichloride
BHF	-	Buffered Hydrofluoric Acid
Cl ₂	-	Chloride
FET	-	Field Effect Transistor
GaAs	-	Gallium Arsenide
GaN	-	Gallium Nitride
H ₂	-	Hydrogen
HCl	-	Hydrochloride Acid
HEMT	-	High Electron Mobility Transistor
HF	-	Hydrofluoric Acid
HNO ₃	-	Nitric Acid
ICP	-	Inductively Coupled Plasma
InP	-	Indium Phosphide
MEK	-	Methyl Ethyl Ketone
MOS	-	Metal Oxide Semiconductor
N ₂	-	Nitrogen
NH ₄ F	-	Ammonium Fluoride
Pd	-	Paladium
PECVD	-	Plasma Enhanced Chemical Vapor Deposition
Pt	-	Platinum

RIE	-	Reactive Ion Etching
RTA	-	Rapid Thermal Annealing
Si	-	Silicon
SiC	-	Silicon Carbide
SiO ₂	-	Silicon Dioxide
SnO ₂	-	tin oxide
Ti	-	Titanium
UV	-	Ultra Violet
ZnO ₂	-	zinc oxide

LIST OF SYMBOLS

A	-	area of the metal-semiconductor contact
A^*	-	Effective Richardson constant
I_H	-	current levels in hydrogen containing ambient
I_O	-	current levels in vacuum ambient
I_s	-	reverse saturation current
R_H	-	sheet resistance in hydrogen containing ambient
R_O	-	sheet resistance in vacuum ambient
T	-	absolute temperature
V_t	-	thermal voltage
V_{th}	-	threshold voltage
ϕ_B	-	Schottky Barrier Height (SBH)

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CHAPTER 1

INTRODUCTION

1.0 Research Background

Explosive growth of internets and wireless technologies starting in the late 20th century has opened up prospects towards an advanced ubiquitous network society [1]. The vision of ubiquitous network society suggests a world in which any information can be accessed from anywhere at any time and by anyone [2]. New and existing technologies making this vision a reality. A so called Intelligent Quantum (IQ) chip has been proposed as the promising electronic device for the ubiquitous network society environment [3]. An IQ chip is an III-V semiconductor chip with sizes of millimeter square where not only nanometer scale quantum processors and memories are integrated on this chip but also other devices such as wireless power supply and various sensing devices so that such ideal concept of IQ chip can be realized [3]. This research is carried out to reveal a possibility of utilizing III-V base material as a sensing device, in particular as a hydrogen gas sensor.

Hydrogen gas sensors become increasingly important in the leak detection systems for the industrial fabrication process, medical treatment and hydrogen-fueled vehicles due to the vast expenditure of hydrogen in modern technologies. Until now, metal-oxide compound semiconductors such as SnO₂ and ZnO₂ have been reported

as chemical sensors [4, 5]. Conversely, the sensing mechanism of these compound semiconductors is related to various defects such as oxygen vacancy, metal vacancy or other defects cooperating with the sensing species [6].

The polycrystalline SnO₂ has been known to have good sensitivity to many gases compared to the single crystalline SnO₂ film, but it suffers from poor selectivity and long term drift of sensor signal [7]. Furthermore, when SnO₂ is applied to the micro-sized device for the integration on chip, it is known that there are critical problems, such as the steep deterioration of sensitivity by reducing size of sensing film and difficulty in compatibility with other processes.

MOS capacitors or FETs using Si-based material can be made as a gas sensor by using catalytically active materials as Schottky gate contacts [8]. However, in view of practical applications, there is a severe limitation of Si-based devices such as their inability of working continuously at temperature higher than 250 °C [8]. Therefore, this research is going to focus on a new material with good sensitivity, stability and selectivity.

Gallium nitride (GaN)-based sensor devices have a strong interest for applications such as fuel leak detection in automobiles and aircraft, fire detectors, exhaust diagnosis and emissions from industrial processes. Furthermore, those wide bandgap materials are capable of operating at temperatures higher than 600 °C [9, 10]. In addition, the gas sensors using these materials could be integrated with other high temperature electronic devices on the same chip using straight-forward planar technologies. The latest, only few works have been reported on these wide bandgap chemical sensors especially gas sensors with an unclear mechanism [11, 12].

1.1 Research motivation

Smart sensors based on semiconductor micro-fabrication have attracted much attention for industrial applications [13]. Semiconductor micro-fabrication can allow the miniaturization of sensors down to micro-scale as well as nano-scale. Furthermore, it can be also integrated with signal processing circuit on a single chip with minimal space and energy consumption. Smart sensor is formed by integrating the sensing devices with various sensing functions in micro-computer chip to enhance the reliability and functionality [13]. The aim of the development of sensor systems is to make them more easily adaptable to communication networks and control systems.

The toxic and combustible gas sensor market is one of the major sectors in chemical sensors [14]. Solid-state electronic gas sensors have got a strong interest due to their outstanding advantages compare to the other types of chemical sensor technology [14]. A great strength of solid-state electronic gas sensors is long life expectancy in clean applications [14]. The intention of gas sensors is at catalytic bead sensors, which suffered from their short life time because their sensitivity lose with time due to poisoning and burning when exposed to high gas concentrations. In contrast, at solid-state gas sensor, gas absorbs on the sensor surface and changes their electric properties and the sensor returns to their original condition when gas disappears [15]. Hence, the solid-state gas sensors offer a long life expectancy because no sensor material is consumed in the exposing process. Additionally, their unique features are versatility of detecting more than 150 different gases and wide ranges in low and high combustible levels [15].

Up to date, high temperature operation and long term stability are important requirements for gas sensors. In addition, semiconductors with wider bandgaps are capable to operate as gas sensors at higher temperatures. Thus, wide bandgap compound semiconductors like GaN-based material have attracted great attention for alternative candidates because of their better thermal stability. Therefore, this

research is going to study the feasibility of undoped AlGa_N/Ga_N heterostructure as a gas sensor.

1.2 Research Objectives

The objectives of this research are:

- i. To fabricate undoped-AlGa_N/Ga_N HEMT Schottky diode for hydrogen gas sensor and at the same time, to construct the measurement setup that can provide measurement in vacuum and also in highly pure gas environment.
- ii. To investigate the response characteristics of fabricated Schottky diode upon exposure to hydrogen gas at various temperatures and pressures.

1.3 Research Activities

Basically, the research activities of this study are divided into two main parts as shown in Figure 1.1. The first part is going to deal with the device fabrication while another part is going to deal with the construction of sensing measurement system.

In the initial stage of the fabrication part, the required physical properties and structure of the Ga_N based wafer is designed and determined. A Schottky diode-type of sensors is fabricated. Basically, our sensing devices is fabricated in a clean room using the equipments such as electron beam lithography, mask aligner for photolithography, electron beam evaporator, rapid thermal annealer, plasma-enhanced chemical vapor deposition, reactive ion etching etc.

For measurement setup part, the measurement system is designed and constructed. After completion of the measurement system, leakage testing is performed. The construction of measurement setup is carried out in parallel with the device fabrication. The sensing responses of fabricated sensor are evaluated using the constructed measurement system. Current-voltage (I - V) characteristics of the Schottky diodes are measured at various temperatures.

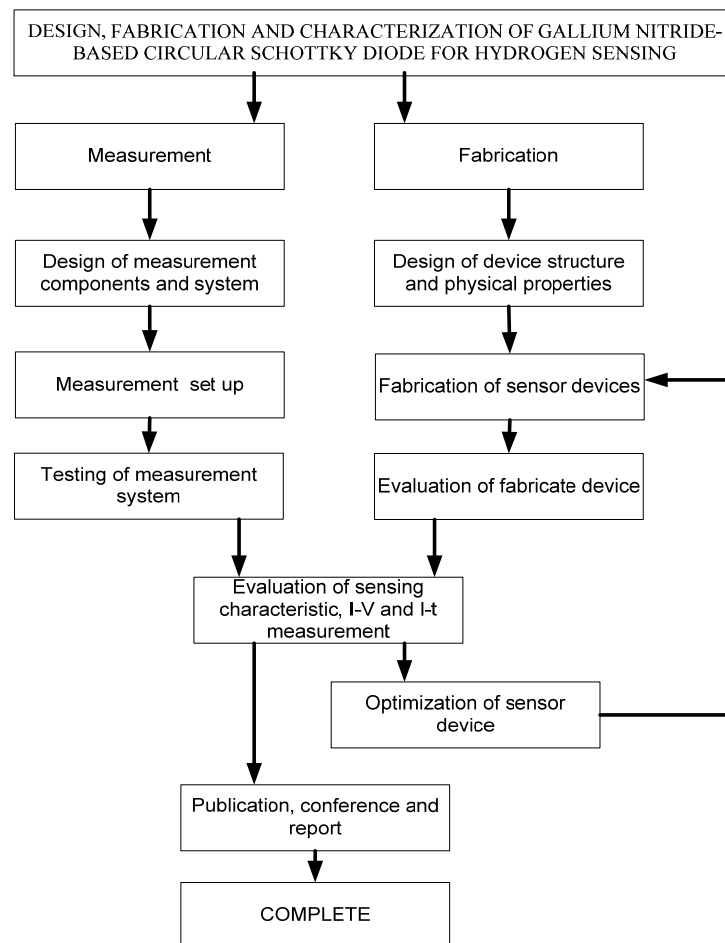


Figure 1.1: Flowchart of research activities

1.4 Dissertation outline

This dissertation consists of five chapters. Chapter 2 discusses the material properties of AlGaIn/GaN heterostructures and their promising potential for various sensor applications in harsh environments. The previously reported work of chemical gas sensors based on solid state devices is also briefly reviewed.

Chapter 3 describes the details of design and device fabrication of AlGaIn/GaN Schottky diode for gas sensor application. The newly developed gas sensor measurement setup and the sensing characterization technique are described.

Chapter 4 demonstrates the experimental results of circular Schottky diode mainly, the measured current-voltage characteristics of Schottky diode at various temperatures.

Finally, chapter 5 presents a summary of this master dissertation and some suggestions for future work.