FABRICATION AND CHARACTERIZATION OF REDUCED GRAPHENE OXIDE/SILICON BACK-TO-BACK SCHOTTKY DIODE

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A thesis submitted in fulfilment of
the requirements for the award of the degree of

Master of Philosophy

Faculty of Electrical Engineering
Universiti Teknologi Malaysia

APRIL 2018

To my wonderful father, mother and brother, family and friends. I am so thankful for the understanding, continuous support, strength and prayer. I would not be the person I am today without prayer and love from you all.

Thanks for loving me.

ACKNOWLEDGEMENT

Alhamdulillah, thanks to Allah S.W.T the most merciful and the most compassionate for the knowledge and guidance in all the effort to finish this piece of work. Peace be upon him. Muhammad the messenger of God. Throughout the time I spend at Faculty of Electrical Engineering, UTM Skudai and Advance Devices and Materials Engineering (ADME) iKohza, there have been many people who helped me in this challenging work. It is a pleasure to thank a few of them here.

Special appreciation goes to my supervisor, Dr Shaharin Fadzli Abd Rahman for his continues guidance and support. He gave me an opportunity to take challenge on this hard task. I have been fortunate work under as I have learned so much from him, not only on how to perform research in the right and most effective way but also on how to be responsible person. This work would not be possibly done without his invaluable advices and guidance. I would like to express my deepest gratitude to Prof. Ir. Dr. Abdul Manaf bin Abdul Hashim for his willingness to co-supervise my research.

Numerous people contributed to the success of this work. It wold not be possible without guidances and advices from my colleagues, Ms. Nur Suhaili Binti Abd. Aziz, Mr. Mohd Faizol, Mr. Muhammad Khairullah Azmi, Ms. Norani binti Ab Manaf and Ms Nurul Fariha binti Ahmad. I also indebted to all of my lab mates at ADME, MJIIT, thank you for the thoughtful advices, guidance and valuable friendship.

I would also like to give my special heartfelt thanks to my parents, Hj Che Azmi bin Abd Rahman and Hjh Azizah binti Mohd Zain and my brother, Mohd Alif. Special thanks to my closest friends, who have been there for me through every single up and down. Thank you for not letting me go through this journey alone.

I also would like to thank to Ministry of Higher Education, Malaysia for financial support of my study through (My MASTER) and Fundamental Research Grant Scheme (4F638). This work has been supported by research university grant (01K24 and 03G22) and Fundamental Research Grant Scheme (4F638) of Ministry of Education, Malaysia

ABSTRACT

Graphene-based back-to-back Schottky diode (BBSD) is a simple device yet possesses promising attributes for applications such as chemical sensor and photodetector. Nevertheless, experimental work on graphene BBSD is relatively limited, where most of the works utilized graphene made from chemical vapor deposition and epitaxial growth. This work investigated the possibility of fabricating the BBSD using low-cost reduced graphene oxide (rGO) and simple fabrication techniques, namely vacuum filtration and chemical reduction via ascorbic acid. Understanding the capability and limitation of these fabrication techniques is important before they can be employed. Formation of graphene oxide (GO) thin film via vacuum filtration with different GO dispersion volume (50, 100, 150 and 200 ml) and concentration (0.4, 0.8, 1.0 ppm) were investigated. Thin films morphology and thickness were characterized using atomic force microscopy. The GO film thickness could be controlled from 30 to 160 nm by varying dispersion volume and concentration. As for reduction process, the correlation between reduction degree with reduction parameters, namely ascorbic acid concentration, duration and process sequence, were analyzed. The reduction degree was assessed by means of Raman spectroscopy and sheet resistance measurement. The lowest sheet resistance at 3.58 MΩ/sq was obtained for rGO film reduced before and after film transfer using 13.6 mg/ml ascorbic acid for 12 hours. Based on the result from vacuum filtration and chemical reduction processes, an rGO/silicon BBSD device was fabricated. The fabricated device was characterized by current-voltage measurement at different temperatures. A nonlinear curve was observed indicating the formation of double Schottky barrier at rGO/silicon junction. Barrier height, ideality factor and series resistance were extracted directly from the measured characteristics. The barrier height inhomogeneity was also assessed. The rGO/Si junction has average barrier height of 1.26 eV with standard deviation of 0.167 eV. In conclusion, the result from this work confirmed the feasibility of fabricating rGO BBSD using a low-cost graphene derivatives and fabrication technique. This is favorable towards mass production of graphene-based chemical sensor and photodetector.

ABSTRAK

Diod Schottky dengan sambungan saling membelakangi (BBSD) yang berasaskan grafin merupakan peranti yang ringkas dan mempunyai ciri-ciri yang mempunyai harapan untuk aplikasi seperti sensor kimia dan pengesan cahaya. Walau bagaimanapun, eksperimen tentang grafin BBSD agak terhad, di mana kebanyakan hasil kerja menggunakan grafin yang dihasilkan adalah daripada pemendapan wap kimia dan pertumbuhan epitaksi. Projek ini menyelidik kemungkinan bagi fabrikasi grafin BBSD menggunakan grafin oksida terturun (rGO) yang lebih murah dan dengan menggunakan teknik-teknik fabrikasi yang ringkas, iaitu penapisan vakum dan penurunan kimia dengan asid askorbik. Memahami keupayaan dan batasan teknik-teknik tersebut adalah penting sebelum boleh digunakan dalam proses fabrikasi. Pembentukan selaput nipis grafin oksida (GO) melalui penapisan vakum dengan isipadu cecair sebaran (50, 100, 150 dan 200 ml) dan kepekatan (0.4, 0.8 dan 1 ppm) yang berbeza, diselidik. Struktur permukaan dan ketebalan selaput nipis dicirikan dengan menggunakan mikroskop tenaga atom. Ketebalan selaput nipit GO dapat diubah dari 30 nm hingga 160 nm dengan mengawal isipadu dan kepekatan cecair sebaran yang digunakan. Bagi proses penurunan, hubungan antara tahap penurunan dengan parameter proses iaitu kepekatan asid askorbik, masa dan urutan proses dianalisis. Darjah penurunan dinilai melalui kaedah spektroskopi Raman dan ukuran rintangan lembaran. Rintangan lembaran terendah yang diperoleh ialah 3.58 MΩ/sq untuk selaput nipis rGO yang diturunkan sebelum dan selepas proses pemindahan dengan menggunakan 13.6 mg/ml asid askorbik selama 12 jam. Berdasarkan keputusan eksperimen penapisan vakum dan penurunan secara kimia, peranti BBSD simpang rGO/silikon telah difabrikasi. Pencirian peranti dijalankan dengan pengukuran arus-voltan pada suhu yang berbeza. Lengkungan tidak linear yang diperhatikan pada ciri arus-voltan menandakan pembentukan halangan Schottky pada kedua simpang rGO/silikon. Ketinggian halangan, faktor idealis dan rintangan sesiri telah diekstrak terus dari ciri-ciri yang telah diukur. Keseragaman ketinggian halangan juga telah dinilai. Simpang rGO /silikon mempunyai ketinggian halangan purata sebanyak 1.26 eV dengan sisihan piawai sebanyak 0.167 eV. Secara kesimpulan, hasil dari eksperimen ini telah mengesahkan kebolehan bagi fabrikasi BBSD dengan menggunakan jenis grafin dan teknik fabrikasi berkos rendah. Ini sesuai bagi pengeluaran skala besar peranti sensor kimia dan pengesan cahaya berasaskan grafin.

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LIST OF ABBREVIATIONS

AFM	-	Atomic Force Microscopy
Au	-	Aurum /Gold
BBSD	-	Back-to-back Schottky diode
C/O	-	Carbon-to-Oxygen
CVD	-	Chemical vapour deposition
Si	-	Silicon
rGO	-	Reduced graphene oxide
GO	-	Graphene oxide
XPS	-	X-ray photoelectron spectroscopy
L-AA	-	Ascorbic acid
UV-Vis	-	Ultraviolet-Visible spectroscopy
OH	-	Hydroxyl
NO_2	-	Nitrogen dioxide
NO	-	Nitrogen oxide
NH_3	-	Ammonia
SO_2	-	Sulphur dioxide
MCE	-	Mixed Cellulose Ester
H_2O_2	-	Hydrogen Peroxide
XRD	-	X-ray Diffraction
FTIR	-	Fourier-transform infrared spectroscopy

LIST OF SYMBOLS

A*	-	Richardson constant
R_s	-	Series resistance
R_{sheet}	-	sheet resistance
Ω/sq	-	Ohm per square
mg	-	milligram
ml	-	millilitre
$Ø_b$	-	Barrier Height
I_s	-	Reverse saturation current
σ_s	-	Standard deviation
°C	-	Celcius
eV	-	electron volt
k	-	Boltzmann constant
v	-	Voltage
I	-	Current
t	-	Temperature
I_o	-	saturation current
S/cm	-	Siemens per centimetre

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CHAPTER 1

INTRODUCTION

1.1 Research background

Graphene is a two-dimensional carbon material that draws attention due to its amazing properties such as ultrahigh charge carrier mobility high optical transparency, large surface-to-volume ratio [1] and high sensitivity towards adsorbates [2]. Owing to these fascinating properties and characteristics, it has been regarded as a promising material which could revolutionize semiconductor and electronics industry. Up to date, tremendous efforts have been made to incorporate graphene into existing semiconductor devices in order to enhance the device performance and its functionality. One of the investigated electronic devices is Schottky diode.

Schottky diode is a simple device that operates based on the carrier transport across metal/semiconductor junction. In the graphene-based Schottky diode structure, graphene is replacing metal as Schottky electrode [3-6]. Graphene/semiconductor junction resembles metal/semiconductor junction where a potential energy barrier is formed at the interface. The potential barrier leads to rectifying current-voltage (*I*-*V*) characteristics of the Schottky diode. In contrast to the typical metal/semiconductor junction, the potential barrier height of the graphene/semiconductor junction can be tuned according to modification of graphene work function [7-8]. The modification can be done through chemical doping and functionalization. Such feature allows the graphene-based Schottky diode to be used in application such as chemical sensor [9], photodetector [10] and solar cell [11]. In the operation of a graphene-based Schottky diode sensor, when graphene Schottky electrode is exposed to certain chemical molecules, graphene work function changes and subsequently leads to the change in potential barrier height and *I-V* characteristics. In case of photodetector and solar cell applications, tuning of electrode work function is important to improve the device efficiency.

This research project focuses on one of the variations of Schottky diode called back-to-back Schottky Diode (BBSD) as a potential device structure for simple and low cost chemical sensor. **Figure 1.1** shows the difference in basic device structure between the common Schottky diode and the BBSD devices. A Schottky diode is generally a two-electrode device with a Schottky and an ohmic electrodes. The ohmic contact is required for biasing and enabling current to flow to semiconductor substrate. The ohmic contact should have minimum contact resistance to ensure that the contact has minimum influence to the *I-V* characteristics. On the other hand, the two electrode of the BBSD structure is made from similar Schottky electrode. As the BBSD has simpler structure, it can be fabricated with lesser fabrication step. In certain diode structure using compound semiconductor such as gallium arsenide and gallium nitride, obtaining good ohmic contact is quite challenging [11]. The issue regarding poor ohmic contact resistance could be ignored for BBSD as no ohmic contact is needed.

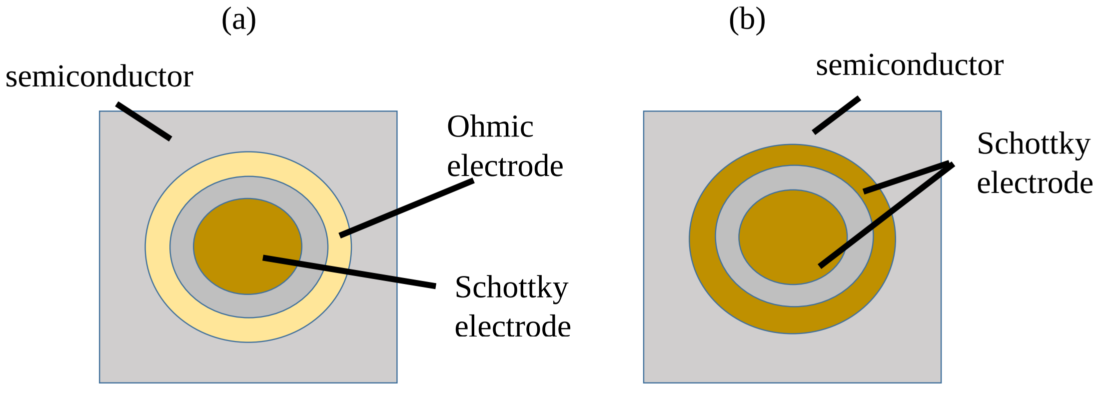

Figure 1.1 The device structure of (a) single Schottky diode and (b) BBSD

In term of device operation, due to the back-to-back connection of two Schottky electrodes, the BBSD will always be in reverse-bias operation. The absence of forward-bias operation in the device is not a significant concern for the sensing operation. Singh *et al.* demonstrated that the operation of graphene Schottky diode sensor at reverse bias gives higher sensitivity rather than at forward bias operation [12].

1.2. Problem statement

Before the performance of the BBSD-based chemical sensor can be further analyzed, knowledge on the device fabrication and characterization is crucial. The first aim of this work is to fabricate a graphene-based BBSD with simple and low-cost fabrication technique so that it is favorable for mass production. Several papers had demonstrated the fabrication of BBSD structure that utilized graphene and its derivatives as the Schottky electrode where most of the work focusing on photodetector application. An *et al*. have used graphene made using chemical vapor deposition (CVD) as the Schottky electrode onto p-type silicon (Si) [13]. Another work done by Hicks *et al*. presented the fabrication of a BBSD structure from graphene grown on silicon carbide substrate via process called sublimation [14]. These type of graphene is relatively expensive as the growth process required sophisticated equipment.

Much cheaper alternative of the CVD and epitaxial graphene is reduced graphene oxide (rGO). The rGO is obtained from graphene oxide (GO) which can be mass-produced from graphite though low-cost wet chemical process [15]. Although the rGO has lower electrical conductivity compared to the CVD and epitaxial graphene film, the presence of many defect sites allow the film to be chemically functionalized. Some of the purpose of chemical functionalization are to enhance the sensitivity and selectivity which important in sensing application [16]. One reported work had demonstrated the operation of BBSD device having rGO Schottky electrode [17]. A simple drop casting technique was employed to form rGO thin film electrode.

Nevertheless, experimental work on the fabrication of the rGO-based BBSD is quite limited. In fact, there are various possible technique to apply rGO in device fabrication process [18-20]. Drop casting technique used in reference [17] is a simple process but has poor film uniformity compared to spin coating, spray coating and vacuum filtration. This work investigates the viability of vacuum filtration technique for formation of thin film rGO. Apparatus used in the vacuum filtration is less sophisticated. The research question that will be addressed is how GO film properties such as film thickness and roughness are influenced by the process parameters.

Another important process that need to be considered when depositing rGO film is the reduction process. The GO need to be reduced to obtain conductive rGO. In this research, the reduction is performed after the formation of GO film via vacuum filtration. Based on our preliminary experiment, reduction before vacuum filtration was found that the agglomeration of rGO when dispersed in any solution, thus leads to non-uniformity of deposited film. **Figure 1.2** shows the proposed process flow of the rGO thin electrode formation on the Si substrate. Note that the vacuum filtered GO film need to be transferred onto the substrate before reduction process. As for reduction process, chemical reduction using ascorbic acid (L-AA) is adopted. L-AA is known as efficient natural and safe reducing agent [21] which is as efficient as other reduction agents such as hydrazine. The research question that will be addressed is what is the optimal reduction condition to obtain highly reduced GO film. In most of fundamental studies on GO reduction via L-AA, the reduction process was done on GO dispersion, rather than GO film [22-23]. Difference in reduction process rate can be anticipated. Another research question that need to be address is whether the sequence of reduction has significant influence to the properties of the formed rGO film. For example, in contrast with process flow in **Figure 1.2**, the reduction also can be performed before vacuum filtered GO film transferred onto the Si substrate. Detailed explanation can be found in chapter 3.

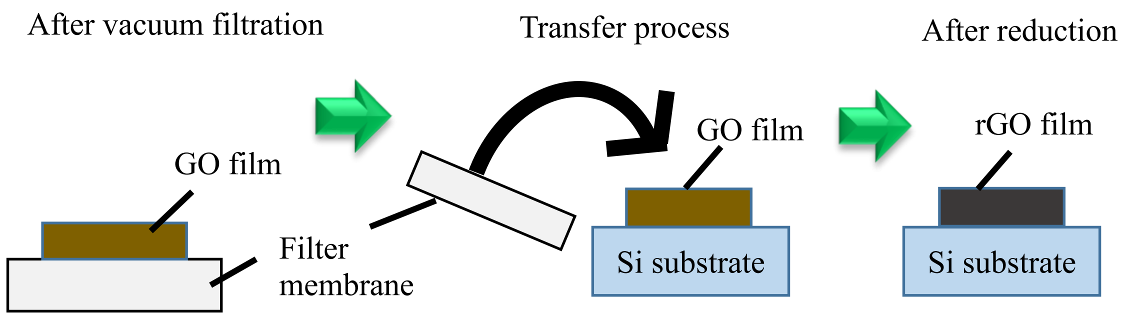

Figure 1.2 Proposed process flow of rGO deposition onto Si substrate

The second aim of this work is to analyze Schottky parameters of the junctions in the rGO-based BBSD. In applications as photodetector and chemical sensor, the operation of Schottky diode based sensor is largely attributed to the change of the barrier potential height. For fundamental study of the BBSD sensor, extracting Schottky parameters such as barrier height is significant. It is worth noting that there is not much work demonstrating Schottky parameters extraction directly from *I-V* characteristics of the graphene-based BBSD. In reported work done by An *et al.* a single Schottky diode structure was fabricated to analyze the Schottky parameters. Some of the works did not present detailed analysis on the Schottky parameters [17].

1.3 Research objectives

Research objectives of this study are as follows:

i. To assess the thickness and roughness of the GO thin film formed via vacuum filtration.

ii. To investigate the influence of reduction process conditions, namely reduction time, L-$_{AA}$ concentration and process sequence, to the reduction degree of the rGO thin film.

iii. To fabricate and analyze electrical characteristics of rGO/Si based BBSD device. The Schottky junction properties, namely barrier height, ideality factor as well as series resistance is directly extracted from the measured electrical characteristics.

1.4 Research Scopes

The research scopes are as follows;

i. The vacuum filtration process was performed using GO aqueous dispersion prepared by research students of Advanced Devices and Material Engineering Research group, Malaysia-Japan International Institute of Technology, Universiti Teknologi Malaysia. The volume of the filtered dispersion was in the range of 50 and 200 ml. The dispersion concentration used in this work were 0.4, 0.8 and 1 ppm. Characterization of the formed thin film focused on analysis of film thickness and roughness using Atomic Force Microscope (AFM).

ii. For reduction process, reduction time from 5 to 720 min was consider. The L-$_{AA}$ concentration used in this work were 0.46 and 13.6 mg/ml. The reduction degree was assessed by means of Raman spectroscopy and sheet resistance measurement.

iii. The rGO-based BBSD device was fabricated on n-type Si substrate with resistivity of 1-10 Ω.cm. The measurement of the fabricated rGO/Si BBSD rGO/Si was done at different temperature from 27 to 60 °C (300K-333K).

iv. The Schottky parameter extraction was performed under consideration that current transport is purely by thermionic emission theory. Extraction method proposed by Averine *et al.* was adopted [24].

1.5 Overview of thesis structure

This thesis is organized into 6 chapters. This first chapter gives an overview of the research background and problem statement. The objectives and scopes of research are also presented.

Chapter 2 provides an overview of rGO synthesis methods and material characterization techniques. The overview focuses on the reduction method of GO. As for the characterization techniques, optical observation, AFM, Raman spectroscopy, XPS and electrical characterization are described. Next, the characteristics of graphene/semiconductor Schottky diode is discussed. Then, the overview on graphene/semiconductor BBSD are described.

In chapter 3, the flows of research activities are briefly described. The experimental procedures are presented starting with vacuum filtration of GO, reduction via L-AA and transfer process of rGO film onto Si substrate. The characterization techniques of rGO film and fabricated device are explained.

Chapter 4 presents the findings and discussion from the experimental procedures in fabrication of rGO/Si BBSD. The thickness and morphology of rGO film is describewere characterized using AFM. Then, the efficiency of reduction process using ascorbic acid on rGO film were tested by Raman Spectroscopy and electrically characterized using sheet resistance measurement.

Then, in chapter 5, the electrical characteristics of fabricated rGO BBSD are briefly explained. The rGO/Si junction properties were observed and analyzed by extracting the Schottky junction parameters. The temperature dependent measurements were used to validate the device performance in different temperature.

Finally, chapter 6 concludes the main findings of present work and the directions of future work.

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APPENDIX A

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