Study of Reduced Graphene Oxide for Trench Schottky Diode

Nur Samiah Khairir\textsuperscript{1,2}, Mohd Rofei Mat Hussin\textsuperscript{2,3}, Iskhandar Md Nasir\textsuperscript{2}, A.S.M. Mukhter Uz-Zaman\textsuperscript{3}, Wan Fazlida Hanim Abdullah\textsuperscript{1}, Ahmad Sabirin Zoolfakar\textsuperscript{1}

\textsuperscript{1} Faculty of Electrical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Malaysia
\textsuperscript{2} MIMOS Berhad, Technology Park Malaysia, 57000 Kuala Lumpur, Malaysia
\textsuperscript{3} Faculty of Engineering, Multimedia University, 63100 Cyberjaya, Malaysia

Emails: ahmad074@salam.uitm.edu.my

Abstract. This paper presents the study of reduced Graphene Oxide (RGO) for trench Schottky diode by replacing conventional metal layer that forms schottky contact with a nanostructured carbon thin film via Reduced Graphene Oxide (RGO) technique. The RGO was synthesized by chemical exfoliation in which modified Hummer’s method was approached. It was then deposited on the trench schottky pattern substrate by pressurized spray coating. The sample was then characterized by FESEM, Raman Spectroscopy and I-V test. The results of FESEM and Raman showed good characteristics and well deposited nanostructures of RGO flakes. The two-point I-V test showed that the samples have a low turn-on voltage and a higher break-down voltage, which is better than the conventional schottky diode used in the market.

1. Introduction

A Schottky diode is a semiconductor diode which has a low forward voltage drop and a very fast switching action [1]. In a Schottky diode, a semiconductor–metal junction is formed between a semiconductor and a metal, thus creating a Schottky barrier. Throughout the history, it has many kinds of schottky structure and one of it is the trench approach which had been proven to have a lot of advantages [2].

However, the device is experiencing limitation in conductivity tolerance at higher temperature due to the limitation characteristics of metal layer in the schottky point interface [3]. By using metal, it is hard to achieve tolerance in heat variation since metal is also having high thermal conductivity [4].

Figure 1. Atomic Structure of Carbon Nanotube (CNT) and Graphene

Thus, nanostructured carbon which is known with superior electronics and thermal properties as well as high carrier mobility is potential to replace conventional metal layer of the schottky diodes [5]. Most of nanoscale carbon materials consist from graphite, the standard form of carbon. In definition,
graphite means “an allotropic form of the element carbon consisting of layers of hexagonally arranged carbon atoms in a planar condensed ring system” [6].

A hypothetical material called graphene, which known to be a 'single, one-atom thick, sheets of graphite' was gaining more attention [7]. Many breakthroughs of graphene have been exposed from researches as well as in the mass production system. The atomic structure of the 1D representation of carbon can be seen in Figure 1.

Graphene is the first two-dimensional atomic crystal discovered and has outstanding properties such as extreme mechanical strength and high electronic conductivity of as well as thermal [7]. Graphene and its compounds are increasingly used to make transistors that show extremely good performance which exhibits a definite progress for the raw material [8].

A lot of research on graphene focused on the reduction of Graphene Oxide (RGO) thin films by both chemical and electrochemical methods [9-12] due to the limitation of extracting graphene via mechanical exfoliation. Chemistry of graphene and its related compounds often deals with the exfoliation techniques that could be scaled up for industrial needs. This usually means that exfoliated product should exist in a form of dispersion. Reduction of graphene oxide, as seen in Figure 2, produces graphene-like structures and graphene oxide could be an environmentally friendly way to large-scale production of one to few layer graphitic thin films [13].

![Figure 2. Reduction Process of Graphene Oxide](image)

This paper is to discuss the effect of replacing the conventional metal layer that had been used for creating schottky contact with the nanostructured carbon, which in this case is RGO. It’s been proven that a nanostructured carbon has a proper quality of conduction like a metal, which what the current industry is seeking of; a potential material to be incorporated with current transistors and diodes; that can enhance their performances as well as beneficial towards environment.

2. Methodology

Figure 3 shows the process of overall workflow of this research. It started off with benchmarking and literature review of the other researches, to obtain general idea of the current drive and gap for the RGO technology. Then, the experiment started with the fabrication of RGO *via* modified hummus method [14], which is one of the branches of chemical exfoliation.
Figure 3. Process Flow of RGO Fabrication and Characterization
2.1. Preparation of Reduced Graphene Oxide (RGO)

2.1.1 Chemical Exfoliation and Reduction Process

The first step in RGO synthetization was the production of graphene oxide (GO) solution via modified Hummer’s method by using graphite powder. The powder was mixed with Sodium Nitrate (NaNO$_3$) and concentrated sulphuric acid (H$_2$SO$_4$). The solution was stirred at a constant speed. Then, after sometime, while being stirred, potassium permanganate (KMnO$_4$) was gradually added before the solution was being diluted with a portion of distilled water [11].

This caused the formation of active species; diamanganese heptoxide (Mn$_2$O$_7$). It has the ability to selectively oxidize unsaturated double bonds that causes great significant in graphitic structure [15] and reaction pathways during oxidation [16]. The following equation shows the reaction that occurs between the two solutions [17]:

\[
\text{KMnO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{K}^+ + \text{H}_3\text{O}^+ + 3\text{HSO}_4^- \\
\text{MnO}_3^+ + \text{MnO}_4^- \rightarrow \text{Mn}_2\text{O}_7
\]

To reduce the graphene oxide solution, aqueous ammonia (NH$_3$H$_2$O) and hydrazine hydrate was added to form agglomeration of graphene-based nanosheets [17].

2.1.2 Deposition of RGO Thin Film

The RGO thin film was deposited on a substrate (see Figure 4) by pressurized spray coating method. The dispersion was produced by chemical reduction of GO, and the amount of spray volume controls the film thickness [18].

Figure 4 shows the schematic representation of trench-pattern schottky device which was used as a platform to characterize the electrical parameters of schottky behavior with the incorporation of RGO to replace conventional metal films. The RGO thin film sits on the surface of the trench pattern to form the schottky contact between the polysilicon and the RGO sheets itself.

![Figure 4. Cross-sectional schematic diagram of trench schottky structure before RGO deposition](image)

2.2. Sample Characterization

2.2.1 Field Effect Scanning Electron Microscopy (FESEM)

By using FESEM, ones can observed the RGO films on the trench patterns, and show contrast between the thickness layers [19]. This is the same type of processes as optical microscope, obtaining views from various sides to be observed. However, it has a resolution ranging from a few nanometers to hundred micrometers, and this suggest that it fills an important gap between the Centre for Microscopy’s atomic force microscope and digital 3D optical microscope. The FESEM is used primarily for ultra-high resolution electron imaging of surfaces and interfaces.
The morphology of the sample was observed by looking at the deposited graphene flakes formed at the surface of the trench schottky diode. By this method, we observed the distribution of the RGO coating and also looking to the deposited flakes size range.

2.2.2 Raman Spectroscopy

Carbon properties on the substrate were analyzed by using Raman. The sample was illuminated with a laser beam in the ultraviolet (UV) range. Scattered light was collected with a lens and was sent through interference filter or spectrophotometer to obtain raman spectrum of the sample. A great deal of detail on the fine structure of graphene can be extracted from the raman spectra [20].

2.2.3 I-V Characteristic

I-V characteristic is used to characterize the electrical properties of the device. It can be done either by using two-probe method or four-probe method. The ideal conductivity and resistivity pattern graph should result in a smooth slightly curved diagonal line of proportional I-V. This project used the two-point probe of Keithley 2400 to measure the schottky curve which focused on the turn-on and breakdown voltage.

3. Result and discussion

Figure 5 illustrates the SEM top view image of RGO flakes of different sizes and conditions. From the SEM images, ones can noticed that the RGO flakes synthesized are either multi layered or single layered as shown in figure 5(a) and 5(b) respectively.

3.1 FESEM Images

It is been observed the flakes are scattered almost thoroughly and obtained high coverage on the substrate surface. The average size of the flakes is found to be around 1um to 13um in diameter, though there are some nano-sized flakes spotted on some area. There are also more folded multi-layered of graphene sheets can be found compared to single layer sheets. A single layer flake or sheet is one-atom thick, and considered to have the highest quality of graphitic properties.

![Figure 5. FESEM surface images of RGO deposition on top of silicon trench patterned](image_url)

a) A few multi-layered RGO flakes on silicon
b) One layer of RGO flake on silicon
Then, the devices undergone Raman Spectroscopy to obtain the quality of carbon flakes and show the characteristics of graphene that had been deposited (Figure 6). The Raman peaks shows good production of RGO which the D peak shows Raman shift at around 1360 cm$^{-1}$ while G peak shows Raman shift at around 1600 cm$^{-1}$.

This is at consistency, not considering minor differences, with other researchers [21,22], with slight shift of 10 cm$^{-1}$ in G band when being compared to GO G band (1590 cm$^{-1}$). This is mostly due to the effect of electron-phonon coupling that caused an upshift to the band. G band represents the relative degree of graphitization, which assigns the $E_{2g}$ phonon of $sp^2$ Carbon atoms while D band can define the defects in structures and disorders induced breathing mode of $A_{1g}$ symmetry [22].

![Figure 6. Raman Spectroscopy tested on Schottky surface with RGO deposition](image)

The sample was then tested electrically using a two-point probe to test the schottky contact I-V curve. The position of the probe can be seen at the inset of Figure 7, where the first probe was located on the RGO thin film flake and the other was grounded.

Based on the curve shown, it exhibits a schottky curve flow with low turn-on and high breakdown voltage which are 1V and -10V respectively. The turn-on voltage is reasonable for schottky devices and their breakdown voltage is superior [23] as the schottky devices are required to have larger breakdown voltage. This is due to the known high conductivity of graphene sheet; producing great performance in rectifying the voltage to form schottky curve. The test was conducted on different dies multiple times and based on the observations; the curve produced was similar to the same pattern.
4. Conclusion

The trench schottky diode is widely used by the industry in various applications as it is one of the most basic electronic devices in the market. RGO has the potential of replacing the conventional metal layer of schottky pattern as it has characteristics of better conductivity as well as a one-atom layer in thickness. The fabrication of RGO is achieved by modified Hummers method and deposited by pressurized spray coating onto the trench schottky substrate. When the sample had being tested for characterization, results show that by incorporating and replacing the metal layer with RGO on the schottky diode, the device exhibits better performance and have great potential and beneficial in the industry of nano-scaled transistors and diodes.

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