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Fabrication and Characterization of Graphene-on-Silicon Schottky Diode for Advanced Power Electronic Design

(Fabrikasi dan Pencirian Grafin-atas-Silikon Diod Schottky untuk Rekaan Kuasa Elektronik Terkedepan)

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ABSTRACT

In this study, graphene-on-silicon process technology was developed to fabricate a power rectifier Schottky diode for efficiency improvement in high operating temperature. Trench-MOS-Barrier-Schottky (TMBS) diode structure was used to enhance the device performance. The main objective of this research was to study the effect of reduced graphene oxide (RGO) deposited on silicon surface for Schottky barrier formation and heat transfer in Schottky junction. The study showed RGO deposited on silicon as a heat spreader could help to reduce the effect of heat generated in the Schottky junction that leads to a leakage current reduction and efficiency improvement in the device. With comparison to the conventional metal silicide (titanium silicide and cobalt silicide), the leakage reduced by two-orders of magnitude when tested under high operating temperature (>100°C). TMBS rectifier diode that uses graphene-based heat spreader could produce highly reliable product able to withstand high temperature operating condition.

Keywords: Graphene-on-silicon; heat spreader; power rectifier; Schottky diode

ABSTRAK

Dalam kajian ini, teknologi proses grafin-atas-silikon telah dibangunkan untuk memfabrikasi diod penerus kuasa Schottky bagi meningkatkan kecekapannya pada suhu operasi yang tinggi. Struktur diod Parit-MOS-Halangan-Schottky (TMBS) telah digunakan untuk meningkatkan prestasi peranti. Objektif utama kajian ini adalah untuk mengkaji kesan grafin oksida dikurangkan (RGO) yang dimendapkan pada permukaan silikon untuk pembentukan halangan Schottky dan pemindahan haba dalam persimpangan Schottky. Kajian ini menunjukkan RGO yang dimendapkan di permukaan silikon sebagai penyebar haba boleh membantu untuk mengurangkan kesan haba yang terjana dalam persimpangan Schottky yang membawa kepada pengurangan arus bocor dan peningkatan kecekapan peranti. Secara perbandingan dengan logam silisida konvensional (titanium silisida dan kobalt silisida), kebocoran arus elektrik telah berkurang sebanyak dua magnitud lebih rendah apabila diuji di bawah suhu operasi yang tinggi (>100°C). Diod penerus TMBS yang menggunakan penyebar haba berasaskan grafin berkemungkinan boleh menghasilkan produk yang sangat stabil dalam keadaan operasi suhu yang tinggi.

Kata kunci: Diod Schottky; grafin-atas-silikon; penerus kuasa; penyebar haba

INTRODUCTION

In a rapid evolving technology today, there is a growing demand for portability with smaller and more lightweight devices pushing power electronic designers to develop smaller, lighter and even more efficient external power supply. In advanced designs, smaller casing are normally used to fit this power supply and therefore heat dissipation has become an overwhelming issue. Designers are always looking for new solutions to produce effective designs that can reduce this effect to overcome the trade-off between the size of power supply and the heat dissipation. The smaller the power supply, the higher the operating temperature. Excessive heat generated not only creates safety issue, but also severely affect the reliability of the power supply itself. This reliability issue is mainly contributed by the failures of rectifier devices (Schottky diode). The important factor determining the reliability and efficiency of power supply depends on how well these Schottky rectifier diodes perform under high temperature conditions.

The application of Schottky rectifier diodes in power electronics for rectifying alternating current into direct current is common, particularly in power supply industry on account of its capability to handle higher switching speeds approaching zero-time and very low forward voltage drop (V_F) than regular PN junction diodes. However, the Schottky rectifier diode performances are frequently limited by high-temperature operation that cause high leakage current and consequently leads to premature device failure as a result of early thermal runaway effect. In the operation of the Schottky diode, electrical energy consumed in Schottky junction is converted into thermal energy through heat dissipation process, which then affects energy efficiency of the rectifier device. It is important to reduce the cumulative of heat generated in the Schottky junction to maximize power conversion efficiency. Therefore, excessive heats within the Schottky junction need to be removed as effective and as quick as possible to the ambient in order to prevent thermal runaway and reliability issues. Heat loss in the form of thermal energy to the case and heat-sink is primarily by thermal conduction (Plesca 2011). Hence, the purpose of this paper was to study the effect of using graphene as a heat spreader in Schottky rectifier diodes.

Taking the advantage of graphene as a high thermal conductivity material, a novel Graphene-on-Silicon Schottky diode with on-chip heat spreader has been designed with the aim to achieve higher device efficiency in high operating temperature. It could produce lower reverse leakage current, I_R as compared to the leakage current of conventional metal-semiconductor junction. Reduced graphene oxide (RGO) layer has been used in this study. The deposition of the RGO flakes on the trench Schottky diode structure through spray coating process has been optimized by using graphene atomizer system. Multiple layers of RGO flakes that are overlapped and interconnected are deposited on silicon surface to form the Schottky contact. Trench MOS Barrier Schottky (TMBS) diode structure was used to enhance the device performance. The purpose of using trench structure in Schottky diode was to reduce the effect of electric field at the interface of graphene-silicon junction. This will help to increase the blocking voltage capability of the device and further reduce the reverse leakage current (Hussin et al. 2015).

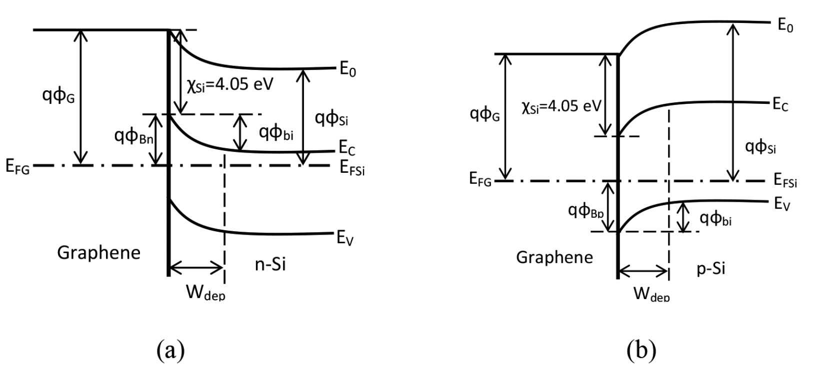
MATERIALS AND METHODS

Graphene can be produced by many ways including mechanical exfoliation, epitaxial growth, chemical vapor deposition and the reduction of graphene oxide (GO). GO has lower quality but it has advantages in terms of cost-effectiveness and mass production. As GO can be reduced to graphene-like sheets by partly removing the oxygen-containing groups, it is usually considered as chemically derived graphene which is known as reduced graphene oxide (RGO) (Eda & Chhowalla 2010). We deposited RGO sheets on lightly doped n-Si epi with trench MOS structure to build TMBS rectifier diode. Graphene as a semi-metal material, when deposited on a lightly doped semiconductor, creates a Schottky junction at the interface. It has become the subject of systematic investigation only in the last five years and still in their early stages (Bartolomeo 2016). Graphene has zero bandgap, which the valence and conduction bands meet at the charge neutrality points (Dirac points) and exhibit a linear dispersion (Novoselov et al. 2005). The Fermi level of graphene, E_{FG} is also precisely positioned at the neutrality points where the conduction and valence bands meet. The minimum energy required to remove an electron from the highest occupied level of electron in the Fermi-Dirac distribution function (E_F) to the vacuum level (E_0) is known as work function. The work function of graphene (Φ_G) is different from semiconductor (silicon) work function (χ_{Si}). As a result, a Schottky barrier (Φ_B) is formed as defined in (1) and produce a relatively large built-in potential (Φ_{bi}) and depletion layer (charge separation) at the G/Si interface:

$$\Phi_B = \Phi_G - \chi_{Si}. \tag{1}$$

χ_{Si} is the silicon electron affinity (The difference between E_0 and E_c). Figure 1 shows the energy levels near the silicon surface, which bend upward (for n-Si) or downward (for p-Si) due to the movement of carriers in silicon substrates to the graphene side. This will then create a depletion layer and built-in potential near the G/Si interface and exhibit rectifying characteristics. One of the advantages of using graphene-on-silicon for Schottky diode is the tunable Schottky barrier height (Bartolomeo 2016), which makes the device more flexible in controlling the forward voltage drop (V_F) hence improving the efficiency in switched-mode power supply applications.

Graphene was also reported to have ultrahigh thermal conductivity as high as 5300 $W/m^{-1}K^{-1}$ due to its strong sp^2 bonds (Balandin 2011; Balandin et al. 2008) as compared to copper and aluminium, their thermal conductivities are only about 200 to 400 $W/m^{-1}K^{-1}$. Therefore, graphene deposited on silicon not only can be used for tunable Schottky barrier height but also for heat spreader to manage



(a) (b)

FIGURE 1. Energy band diagram of graphene-on-silicon Schottky junction for (a) n-type silicon (b) p-type silicon substrate (Bartolomeo 2016; Mohammed et al. 2012)

heat at hotspot areas in Schottky junction. For illustration, the layout design of graphene heat spreader and cross sectional view of TMBS rectifier diode with heat sink are shown in Figure 2.

FABRICATION PROCESS FOR TMBS DIODE STRUCTURE

The TMBS rectifier diode structure was fabricated in MIMOS Wafer FAB. N-type silicon epi wafer with resistivity 0.60 Ω.cm, phosphorus doping ~8.5×10^{15} cm^{-3} and thickness of 6 um was used to fabricate the diode. The epi layer was grown on highly doped n-type substrate with resistivity < 0.003 Ω.cm and 700 um thickness which later was thinned down to 200 um to reduce the series resistance in TMBS diode. The process started with formation of 2.5 um trench MOS structure in epi layer. The overall process flow for this experiment is shown in Figure 3. An oxide (SiO_2) hard mask (4000A) layer was used to pattern the trench and silicon was etched through reactive ion etching (RIE) process in SF6 plasma at Applied Materials AMAT Centura DPS etching system. Gate oxidation was then performed in high temperature oxidation furnace Hitachi Kokusai Vertron-III to grow gate oxide inside the trench. This step used wet oxidation process run at 950°C for 50 min to grow 1600A thickness of oxide layer (T_{ox}). It was then followed by gate electrode (undoped polysilicon with ion implantation) formation and Contact Etch Stopper Layer (CESL) deposition. CESL is normally used as a protective film from plasma etching during contact etch process which helps to improve the over etching effect on silicon substrate (Hussin et al. 2015). In this case, however, the CESL layer is not only used as a protective layer but it is also used as a hardmask for self-aligned pattern of graphene heat spreader. Pre-metal Dielectric (PMD) layer which consists of tetraethoxysilane (TEOS) oxide and Borophosphosilicate glass (BPSG) was deposited prior to contact formation. Contact etch is the next critical process step for the formation of Schottky junction. The contact must be very clean with low structural damage on trench top corner especially at the edge of the die before graphene deposition to ensure good interface formation between graphene and silicon. The RGO was immediately deposited on silicon TMBS diode structure after contact cleaning process and followed by thermal annealing at 180°C in vacuum for about 1 h to improve the formation of graphene-silicon interface. The RGO layer was then patterned using self-aligned lift-off process as a heat spreader. Finally, 4 um Aluminium Copper (AlCu) was deposited on the top for metal pad.

GRAPHENE SYNTHESIS AND DEPOSITION

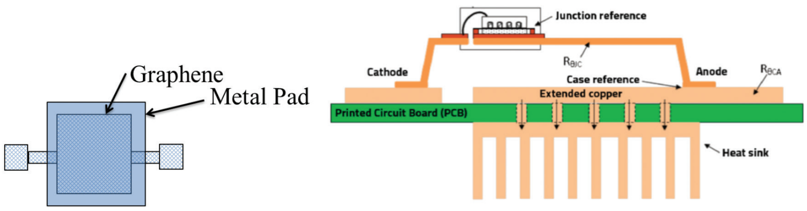
Chemically derived graphene or more specifically reduced graphene oxide (RGO) was used in this study. The graphene material was synthesized using chemical exfoliation via graphene oxide, which is known as modified Hummers's Method (Coa & Zhang 2014; Shahriary & Athawale 2014). Liquid-phase exfoliation of graphite is based on exposing the materials to a solvent with a surface tension that helps an increase in the total area of graphite crystallites (Blake et al. 2008; Hernandez et al. 2008). There are three process modules involved in this work. The details descriptions of each process module are as follows.

PRE-TREATED OXIDATION PROCESS (BEFORE HUMMER'S METHOD)

In the pre-oxidation process, the graphite powder (2.0 g) was added into a solution of concentrated hydrogen sulphide (H_2SO_4) (20 mL), potassium persulfate ($K_2S_2O_8$) (1.0 g) and phosphorus pentoxide (P_2O_5) (1.0 g) mixture that were completely dissolved at 80°C. Then the mixture was kept at 80°C for 4.5 h using an oil bath. After that, the mixture was cooled to room-temperature and diluted with 1L de–ionised (DI) water and left overnight. Subsequently, the resulting product was filtered (0.2 μm Millipore membrane) and washed with DI water until the pH of filtrate water become neutral in order to remove any residual acid. Then the oxidation process of Hummers method was performed.

OXIDATION PROCESS (MODIFIED HUMMER'S METHOD)

Graphite powder (1 g) was put into cold (0°C) concentrated H_2SO_4 (40 mL). Then, $KMnO_4$ (5 g) was added gradually under stirring and the temperature of the mixture was kept to be below 20°C by cooling (ice bath). Successfully, the mixture was stirred at 35°C for 2 h and diluted with DI water (83 mL). The addition of water in concentrated



(a) (b)

FIGURE 2. (a) Layout structure of graphene heat spreader with extended pad to reduce thermal resistance and (b) illustration of heatsink cooling system for the chip

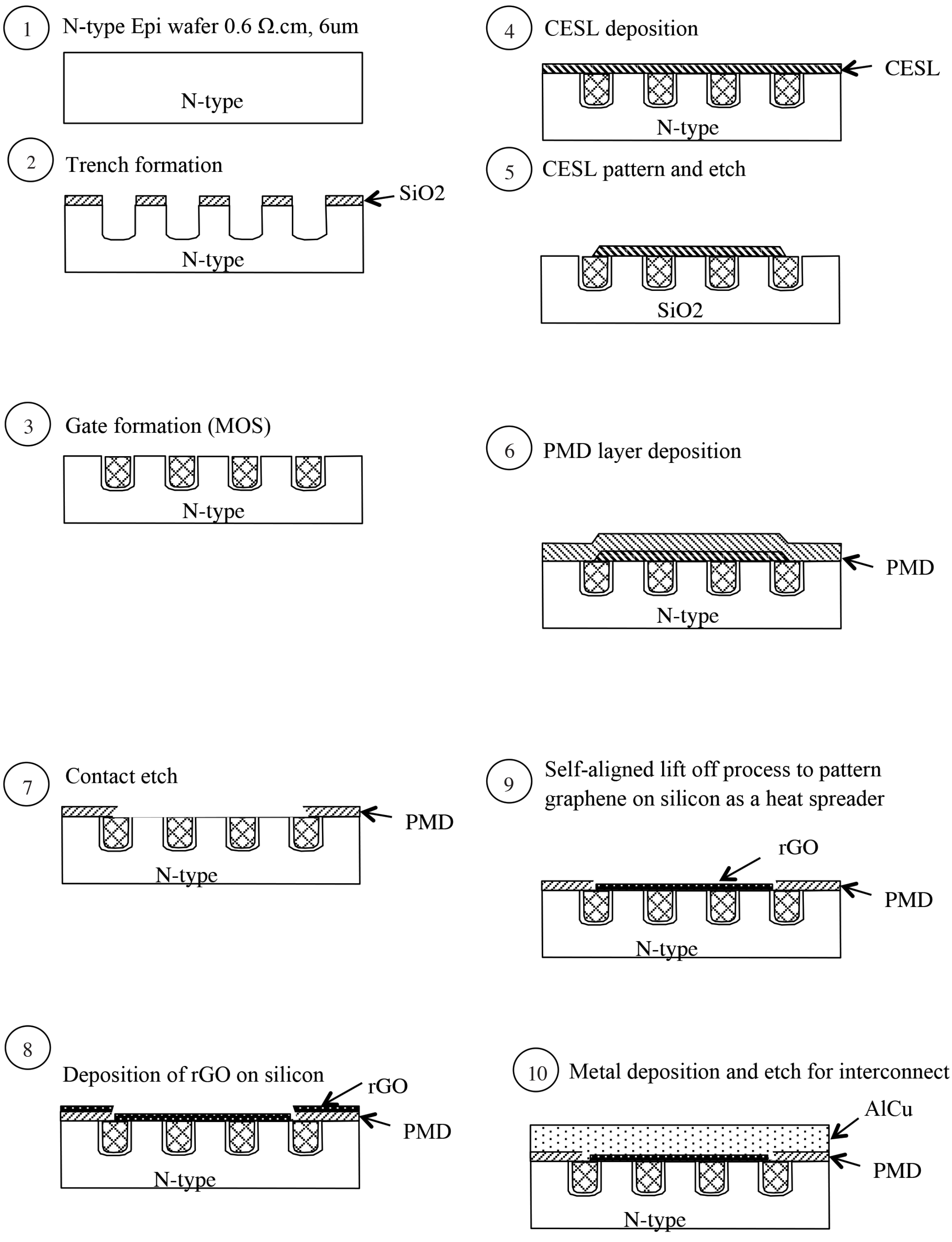


FIGURE 3. Fabrication process flow for graphene-on-silicon Trench MOS Barrier Schottky rectifier diod

H_2SO_4 medium released a large amount of heat, the addition of water carried out in an ice bath to keep the temperature below 50°C. After adding all 83 mL DI water, the mixture was stirred for 2 h and then, addition of 233 mL of DI water was added. Shortly, after the dilution with 233 mL of water, 6.7 mL of 30% H_2O_2 (hydrogen peroxide) was added to the mixture. The colour of the mixture changed into yellow along with bubbling. The mixture was filtered and washed with 1:10 HCl solution (1L) to remove metal ions followed by 1L of DI water to remove the acid. The resulting solid was dried in air and diluted to make a GO dispersion (0.5% w/w). The exfoliation was carried out by sonicating 0.1

mg/mL GO dispersion under ambient condition for 20 min. Forces between layers were destroyed and finally the GO could be fully exfoliated to single layers.

REDUCTION OF GO USING $NABH_4$ (SODIUM BOROHYDRIDE)

A reducing agent, sodium borohydride ($NaBH_4$) powder (37.83 g/mol) was used to produce 12 mL of RGO solution. The 45.4 mg $NaBH_4$ was slowly mixed in 12 mL DI water with magnetic stirring 200-300 rpm for about 2 h under temperature 0°C. The mixed solution was then filtered and washed with DI water (12 mL) before it was sonicated for 5 min.

The RGO solution was deposited on silicon substrate through ultrasonic atomization spray coating method. This ultrasonic atomization has two advantages over conventional spray coating process. It can generate very small droplets with extremely narrow range diameter size, and it can reduce 'bounce back' effect from target surface. These features enable high-quality deposition of RGO coating on silicon substrate.

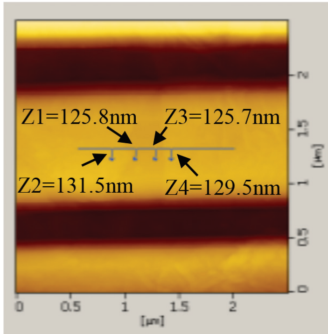
RESULTS AND DISCUSSION

ANALYSIS OF GRAPHENE MATERIAL USING ATOMIC FORCE MICROSCOPY (AFM)

AFM analysis was performed on the fabricated sample to measure the thickness of graphene sheets deposited on silicon TMBS diode structure. AFM image of the deposited RGO on silicon TMBS diode structure is shown in Figure 4. From the measurement, it shows that the thickness is in the range of 3.8 to 5.7 nm indicating few layer RGO sheets were deposited. If we consider a single layer RGO is about 1.2 nm (Shi et al. 2015), then the RGO sheets deposited on TMBS diode structure are in the range of 3 to 5 layers.

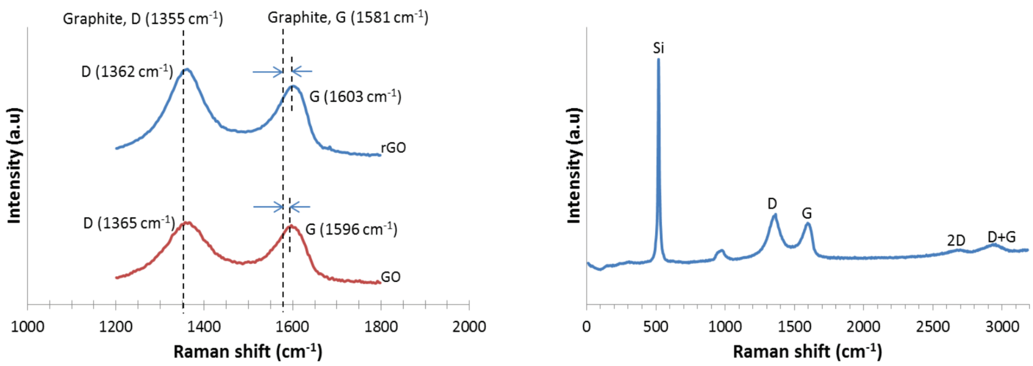
ANALYSIS OF GRAPHENE MATERIAL USING RAMAN SPECTROSCOPY

Raman spectroscopy is the most direct and non-destructive method to characterize the structure and quality of carbon materials (Some et al. 2013). Raman spectra of GO and RGO sample are shown in Figure 5. The results showed both GO and RGO samples have typical Raman spectra of graphene oxide that consist of D band and G band, which are originated from the prominent features of graphite. As a reference point, the G peak of graphite spectrum is around 1581 cm^{-1} corresponding to the inplane vibration of the graphite lattice and the D peak is around 1355 cm^{-1} that originates from a breathing mode forbidden in perfect graphite and activated by defects (Ferrari 2007). In GO, the G peak blue-shifted to form a broad band at 1596 cm^{-1}, which has been explained by the amorphous model of GO by Kudin et al. (2008). For the RGO sample, the same shift is expected, as the structure has not been changed by the chemical reduction (Eda & Chhowalla 2010). The G peak for RGO in this study is around 1603 cm^{-1}. The ratio of intensity of D band and G band (I_D/I_G) could represent the inplane correlation length (the average sp^2 region dimension), $L_a = 44Å/(I_D/I_G)$ (Ferrari & Robertson 2000). Table 1 shows the GO and RGO samples in-plane correlation lengths derived from Raman spectra. The result showed that RGO has slightly lower in-plane correlation length compared to GO but further statistical analysis required to confirm the difference. The results are consistent with previous reports, which showed the sp^2 region dimension in GO and RGO is between 3 and 5 nm (Eda et al. 2010; Shi



Thickness-1, $\Delta Z_{2-1} = 5.7$ nm
Thickness-2, $\Delta Z_{4-3} = 3.8$ nm

FIGURE 4. AFM measurement on the fabricated sample of TMBS diode to measure the thickness of graphene sheet



(a) (b)

FIGURE 5. Raman spectroscopy analysis for (a) GO and RGO samples (b) RGO deposited on silicon TMBS diode

et al. 2014). Analysis of Raman spectra was also done on RGO deposited on silicon TMBS diode structure. From the analysis, there are first-order and second order scattering of Raman spectra at ~520 and ~950 cm^{-1} representing the existence of single-crystal silicon (Parker 1967). A weak and broad 2D peak at 2680 cm^{-1} is also observed in the analysis, which another indication of disorder. The D+G peak at ~2950 cm^{-1} is another defect-activated peak. The 2D peak and D+G peak, however, are not obvious.

ANALYSIS OF GRAPHENE MATERIAL USING XPS

Figure 6 shows the XPS analysis of the RGO and GO sample. The C-C binding energy was assigned at around 284.8 eV with chemical shifts +1.2 eV, +2.2 eV and +3.2 eV for C-O, C=O and O-C=O, respectively. The CC/CO intensity ratio of GO and RGO samples are shown in Table 1. The GO sample (1.05) showed much lower CC/CO intensity ratio as compared to RGO sample (5.73), which 'CC' refers to the sum of C-C and C=C bonds and 'CO' applies to all combinations of carbon and oxygen atoms bonds. The results showed that a significant reduction of oxygen functional groups (hydroxyl, epoxy, carbonyl groups) in RGO sample. This indicates the reduction process of GO using a reducing agent; sodium borohydride ($NaBH_4$) was successful and effective.

ELECTRICAL CHARACTERIZATION

Electrical measurements were performed on the fabricated device to characterize the current-voltage (IV) characteristics at various temperatures starting from 25°C to 125°C as shown in Figure 7. Strong rectification behaviour was observed from the IV curve with the forward-bias characteristic well described by thermionic emission theory. The forward voltage drop, V_F is relatively high, which could be due to series resistance effect. The measurement was done at wafer level, which the high series resistance should be expected. Based on the layout structure design (6.25 mm^2), the device should be capable to handle 10A current rating at forward bias. The device can be operated up to 20V blocking voltage before it reaches the pre-set maximum leakage current of 100uA at 125°C. Comparison of reversed leakage current, I_R of the device with conventional metal silicide shows significant amount of stability over different temperatures applied which also consistent with previous studies (Khairir et al. 2016, 2015). The I_R improvement is by two-orders of magnitude when operated above 100°C.

CONCLUSION

In this paper, the fabrication and characterization of a graphene-on-silicon Trench MOS Barrier Schottky (TMBS) rectifier diode with heat spreader working at different temperature, is reported. We proved that RGO deposited on silicon as a heat spreader could help to reduce the effect of heat generated in the Schottky diode. This leads to a leakage current reduction by two orders of magnitude when operated above 100°C and hence improve the thermal runaway effect.

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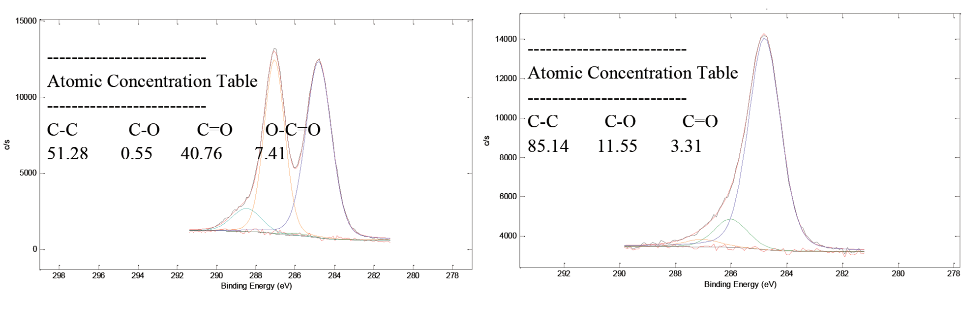
TABLE 1. Basic information of GO and RGO samples

Parameter	Graphene oxide, GO	Reduced graphene oxide, RGO
I_D/I_G	1.0008	1.0117
L_a (Å)	43.96	43.49
CC:CO ratio	1.05	5.73



(a) (b)

FIGURE 6. X-ray photoelectron spectroscopy (XPS) analysis for (a) GO and (b) RGO samples

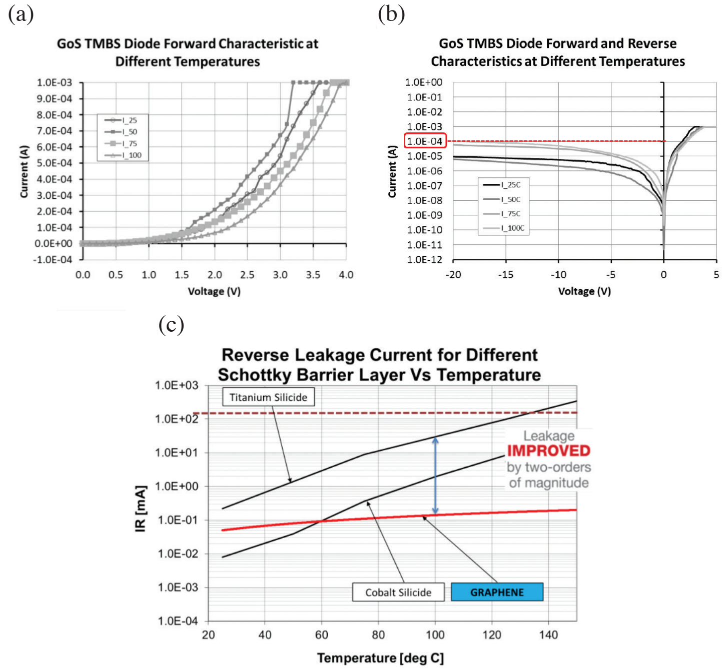


FIGURE 7. (a) Forward characteristic, (b) forward-reversed characteristics of graphene-on-silicon TMBS rectifier diode across different temperatures and (c) comparison of reversed leakage current, I_R measured at different temperatures for various metal-silicon Schottky junctions

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