

Back-to-Back Schottky Diode from Vacuum Filtered and Chemically Reduced Graphene Oxide

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ABSTRACT

This paper presents fabrication of reduced graphene oxide (rGO)/silicon (Si) back-to-back Schottky diode (BBSD) through graphene oxide (GO) thin film formation by vacuum filtration and chemical reduction of the film via ascorbic acid. In order to understand and assess the viability of these two processes, process condition and parameters were varied and analyzed. It was confirmed that the GO film thickness could be controlled by changing GO dispersion volume and concentration. Filtration of 200 ml of 0.4 ppm GO dispersion produced average film thickness of 53 nm. As for the reduction process, long duration was required to produce higher reduction degree. rGO film that underwent two times reduction at before and after transfer process with concentrated ascorbic acid gave the lowest sheet resistance of 3.58 MΩ/sq. In the final part of the paper, result of the BBSD device fabrication and current-voltage characterization were shown. The formed two rGO/Si Schottky junctions in the BBSD gave barrier height of 0.63 and 0.7 eV. The presented results confirmed the viability of fabricating rGO-based device using a simple method and without requirement of sophisticated equipment.

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1. INTRODUCTION

Owing to graphene's fascinating properties and characteristics, it has been regarded as a promising material which could revolutionize semiconductor and electronic technology. Recent years, efforts have been made to incorporate graphene into existing semiconductor devices in order to enhance device performance and its functionality [1-3]. One of the simplest graphene-based devices is Schottky diode made from graphene/semiconductor junction [4, 5]. The device operation has been already demonstrated on various semiconductors such as silicon (Si), gallium arsenide (GaAs), silicon carbide (SiC), and gallium nitride (GaN) [6-8]. Electrical characteristics of the graphene/semiconductor junction is known to be susceptible to certain molecules, thus make it favourable to be exploited in designing and fabricating electronic chemical sensor [9-11].

When two Schottky electrodes are deposited onto a semiconductor substrate, a simple device structure called back-to-back Schottky diode (BBSD) could be formed. The BBSD has simple device structure compared to a common single Schottky diode and it has been investigated for various applications such as photodetector and sensors [12, 13]. In spite of the advantages of the BBSD, reported work on graphene BBSD is relatively limited. This work focuses on fabrication of graphene BBSD structure using simple and low cost fabrication technique. A high-quality graphene grown by chemical vapour deposition (CVD) technique may not be suitable for mass production of a low cost BBSD device. An alternative of the

CVD graphene is reduced graphene oxide (rGO). The rGO is a graphene derivative, which can be chemically functionalized to modify its properties and to enable selective sensing operation [14]. In this work, an rGO film was obtained by means of vacuum filtration of graphene oxide (GO) dispersion and chemical reduction process. Understanding these two processes is significant in order to ensure the feasibility and reliability of the overall fabrication process of the BBSD device.

In vacuum filtration process, volume of GO dispersion was varied to evaluate the possibility of controlling GO thin film thickness. One must be able to control thin film thickness when fabricating semiconductor device. As for chemical reduction process, ascorbic acid (L-AA) was used as a reduction agent. L-AA is a natural and safe reduction agent that is as efficient as widely used reduction agent such as hydrazine [15-17]. Effect of reduction time and L-AA concentration was investigated. Besides, this work also assessed whether the process sequence has significant influence on the electrical characteristics of the rGO film. In the final section of this paper, the electrical characteristic of the fabricated BBSD is presented. From the current-voltage (*I-V*) characteristic, the junction properties, namely barrier height, ideality factor and series resistance were extracted. The extraction of the Schottky junction properties is significant in order to allow analysis of the BBSD operation.

2. RESEARCH METHOD

A GO thin film was formed by separating GO flake from dispersion solution through vacuum filtration. GO aqueous dispersion with specific volume and concentration was filtered through a mixed cellulose ester membrane (MCE) with average pore size of 20 nm. Prior to the filtration, the GO dispersion was diluted to certain concentrations and was ultrasonicated for 1 hour. This is to allow the GO flakes to be dispersed evenly inside the aqueous solution. GO films were prepared from dispersion with volume of 50, 100, 150 and 200 ml. The concentration of the dispersion was fixed at 0.4 ppm. The selected process parameters were adopted from reported work done by Goki Eda *et al.* [18]. Our preliminary experiment has shown that the GO film thickness could not be precisely determined when the GO is on the rough surface of MCE filter. The filtered film needed to be transferred onto glass substrate before it is ready to be characterized by Atomic Force Microscope (AFM). From the AFM images, film thickness and roughness was analyzed.

Next, for investigation of reduction process via L-AA solution, two L-AA concentrations (i.e. 0.46 mg/ml and 13.6 mg/ml) were considered. The concentration values were selected after reviewing multiple reported works. Reduction process was done by immersing the GO film into L-AA solution heated at 80 °C for various durations ranging from 5 to 720 minutes. The purpose of this observation was to identify the time when the reduction process completed.

It is worth to highlight that most of the reported works on reduction process were using GO dispersion rather than GO film [15, 16]. In case of the GO thin film reduction, only the GO on film surface are exposed to L-AA solution. Subsequently, the GO on the surface will be highly reduced compared to that at the center of the film. In the actual fabrication process flow of our BBSD device, the chemical reduction process can be done before or/and after transfer of GO film onto Si substrate. Table 1 lists up four possible process conditions considered in this work. The difference between these four conditions after reduction and transfer was depicted in the table. For RGO1 and RGO2, only one surface was exposed to L-AA solution. For RGO3 and RGO4, reduction was done twice which are before and after the transfer. In such manner, both thin film surfaces are exposed to the L-AA. The reduced GO was characterized by Raman Spectroscopy with laser wavelength of 514.5 nm to analyze the chemical structural change upon the reduction process. To evaluate the electrical properties of the rGO, the rGO were transferred onto thermally oxidized Si substrate. Sheet resistance of the rGO film was measured using four-point probe measurement with source-measure unit (Keithley model 2400). Based on the obtained Raman spectrum and sheet resistance, the compatibility of process condition in Table 1 is discussed.

Table 1. Four reduction conditions used in this work

Condition label	Description	GO film after reduction and transfer
RGO1	Before transfer (0.46 mg/ml L-AA)	Highly reduced rGO Substrate
RGO2	After transfer (0.46 mg/ml L-AA)	Highly reduced rGO Substrate
RGO3	Before and after transfer (0.46 mg/ml L-AA)	Highly reduced rGO Substrate
RGO4	Before and after transfer (13.6 mg/ml L-AA)	Highly reduced rGO Substrate

Based on the result from the above experiments, the fabrication process flow and process condition were decided. Figure 1 shows the layout and cross-section of the fabricated BBSD and the fabrication process flow. For the actual BBSD device, a GO dispersion with concentration and volume at 0.4 ppm and 200 ml, respectively were used in vacuum filtration process. The formed GO film on filter paper was cut into 0.8 mm × 0.8 mm and then was patterned into a desired shape by delaminating unwanted area using sticky paper. The patterned GO film was transferred onto pre-cleaned n-type Si substrate common method used by other researchers. Reduction process was performed after the transfer using 0.46 mg/ml L-AA solution at 80 °C for 720 minutes. The device fabrication was completed by deposition of gold thin film onto rGO via photolithography and ion coater. The purpose of gold thin film deposition is to minimize contact resistance during probing for electrical measurement. The electrical characterization of the fabricated BBSD was performed using source-measure unit. The voltage was applied at inner rGO electrode, while the outer electrode was set as ground.

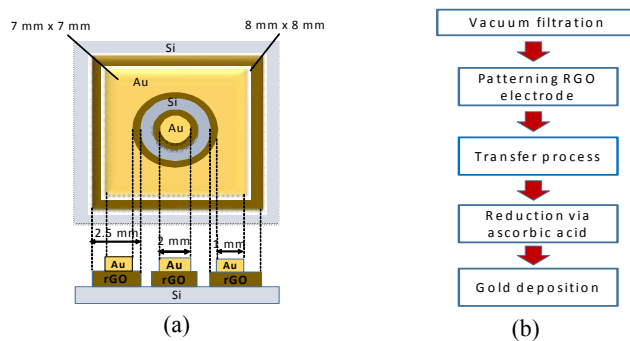


Figure 1. (a) Structure of the BBSD and (b) Device fabrication process flow

3. RESULTS AND ANALYSIS

3.1. Vacuum filtered GO film

Figure 2 and 3 shows AFM images and height profiles for GO film on glass substrates, respectively. From the line profile, the thickness and root-mean-square (RMS) roughness for each sample were determined and plotted in Figure 5. The GO film made from 50 ml GO solution seems to have grainy and rough surface and poor uniformity. Its surface roughness was clearly higher than other samples. We speculate that in case of 50 ml, the number of GO flakes was not enough to cover all the filter membrane surface. Above the volume of 100 ml, the GO average thickness increased in proportional to GO solution volume. The minimum film thickness which could be obtained using our setup is around 20 nm. On the other hand, no significant correlation between dispersion volume and surface roughness. The roughness of the formed film is around 3 to 7 nm. Note that the effect of transfer process to the quality of the GO film needs to be considered when analyzing the AFM images. The observed cracks, ripples and folds in the AFM images might be caused by the transfer process.

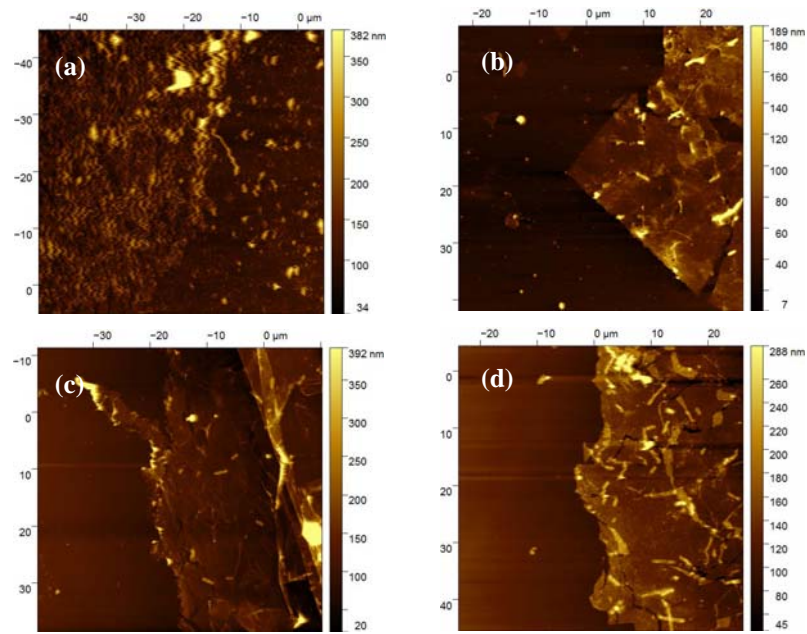


Figure 2. AFM images for GO film from different solution volume ((a) 50, (b) 100, (c) 150 and (d) 200 ml)

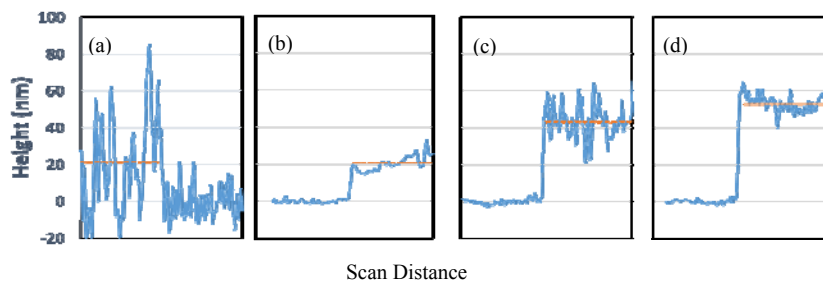


Figure 3. Height profiles along the red line in the AFM images ((e) 50, (f) 100, (g) 150 and (h) 200 ml)

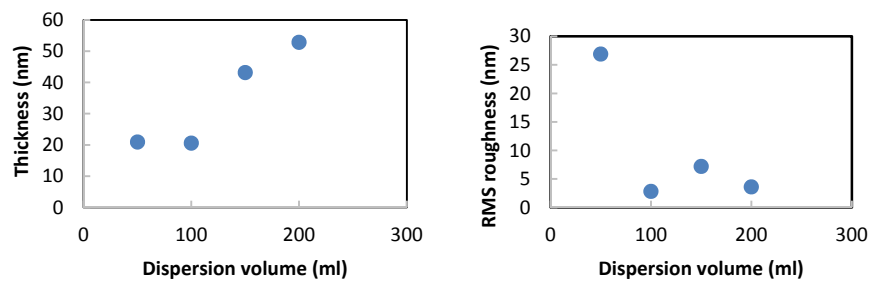


Figure 4. (a) Average thickness and (b) roughness as a function of dispersion volume

3.2. Reduced GO film

In order to determine the electronic and structural properties changes in GO and rGO film, Raman spectroscopy was carried out to interpret the change in the obtained spectra. Figure 5 shows Raman spectra of GO and rGO. Two prominent peaks appear at around 1347 and 1597 cm^{-1} , which are labelled as D and G peaks, respectively [19]. A so called 2D band appeared at 2688 cm^{-1} . D over G intensity ratio (I_D/I_G) can be

used to assess the reduction degree of GO. The higher intensity ratio indicate higher reduction degree which is generally attributed to a decrease of the average size of the sp² domains after the reduction [17]. Based on Figure 5, I_D/I_G increased from 0.99 to 1.15 after the reduction.

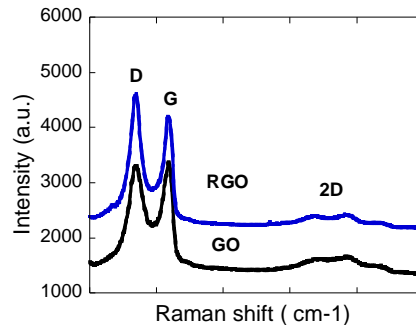


Figure 5. Raman spectra of GO and rGO

Figure 6 summarizes the change of I_D/I_G over reduction time for different reduction condition. There was no significant difference between all the reduction conditions. In general, higher reduction degree was achieved at longer reduction time. No clear sign of completion of the reduction process even after 720 minutes. This result indicates that compared to GO dispersion reduction, GO thin film reduction is a process with much slower rate. After 720 minutes reduction, RGO2 gave the highest I_D/I_G value. As depicted in Table 1, the characterized surface for sample RGO2 (i.e. top surface) is the surface which was directly exposed to L-AA. This explains the difference between RGO1 and RGO2. RGO3 gave the lowest I_D/I_G value. In case of double-sided reduction, the reduction time is calculated as the total of reduction time at both sides. For 720 minutes reduction, reduction time for one side was 360 minute. We speculate that the reduction time was not long enough to produced high reduction degree. This resulted in the low I_D/I_G value. RGO4 gave the second highest reduction degree. Based on the obtained result, reduction after transfer process may produce better reduction degree.

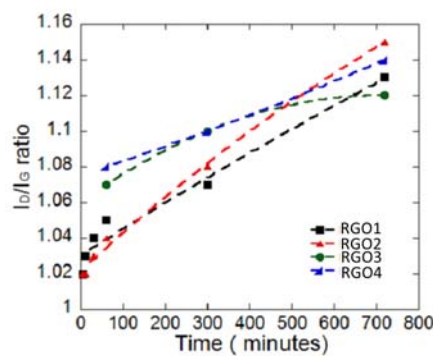


Figure 6. I_D/I_G as function of reduction time for different conditions

The reduction degree was also evaluated from the measurement of thin film sheet resistance. Film with high reduction degree should have low sheet resistance. Table 2 shows the obtained sheet resistance for samples after different reduction conditions. The reduction time was fixed at 720 minutes. The obtained result showed almost good agreement with the Raman spectroscopy result. RGO4 has the lowest sheet resistance of 3.58 MΩ/sq. This value is in the comparable order with finding reported by G. Eda *et al.* [18]. RGO2 condition gave second lowest sheet resistance. The value was 2.3 times higher than that for RGO4. Although the RGO4 gave the lowest sheet resistance, we have chosen the RGO2 process condition for the actual fabrication of the BBSD. It was found that, chemical reduction before transfer was prone to GO film delamination from the filter. This may produce void and crack at the resulted rGO film.

Table 2. Sheet resistance of rGO film obtained from different reduction condition

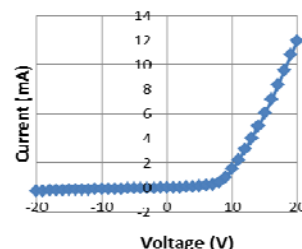
Sample	Sheet resistance (M Ω /sq)
RGO1	15.59
RGO2	8.23
RGO3	13.23
RGO4	3.58

3.2. Fabricated BBSD device

Figure 7(a) shows the image of transferred rGO on Si substrate. Almost all the patterned rGO film was transferred onto the substrate. Figure 7(b) shows the completed BBSD device after gold film deposition. The measured I - V characteristics is shown in Figure 8. The obtained curve shows similarity with the characteristics of a single Schottky diode. At 10 V, the rectification ratio (i.e. current ratio at forward over at reverse bias) was 12.16. The relatively high rectification ratio could be explained by the non-identical area of the two Schottky junctions in the BBSD. Note that in case of our device and measurement configuration, at positive bias, the BBSD current is determined by the reversed biased outer Schottky electrode. On the other hand, when negative bias is applied, the inner circle Schottky electrode will limit the current value. Since the outer electrode has larger area than inner circle electrode, the current at positive bias became higher than that in negative bias.



Figure 7. Camera images of the (a) rGO film on Si and (b) completed BBSD device

Figure 8. I - V characteristics of the fabricated BBSD

Schottky parameters such as barrier height, ideality factor of the two junctions in the BBSD were extracted by adopting procedure proposed by S. Averine *et al.* Prior to the extraction, effect of series resistance was excluded from measurement result. Series resistance is a total resistance originated from gold/rGO contact resistance, rGO resistance and Si substrate resistance. The series resistance was calculated from the slope of I - V linear region at high positive bias [20]. The series resistance was 843 Ω . Table 3 summarizes the Schottky parameters of the Schottky junction in the device. The estimated barrier heights are higher than reported value by M. Zhu *et al.* [21]. It is difficult to make fair comparison with the reported work as the rGO work function is likely differs with our device.

Table 3. The extracted Schottky parameters

Schottky parameters	Inner electrode junction	Outer electrode junction
Barrier height (eV)	0.63	0.7
Ideality factor	1.004	1.02

4. CONCLUSION

Two main fabrication processes, namely vacuum filtration and L-AA chemical reduction was investigated. Go film thickness can be tuned to some extent by varying GO dispersion volume and concentration. Varying volume of 0.4 ppm dispersion from 50 ml to 200 ml resulted in film thickness from 20 to 53 nm. Next, L-AA reduction process with different reduction conditions was evaluated. The reduction of GO thin film is found to be relatively slow process. Long reduction time was required to highly reduce the GO film. It can be concluded that reduction after the transfer process may produce highly reduced GO film with low sheet resistance. Finally, the BBSD was fabricated and its electrical characteristics was measured. From the obtained curve, the rGO/Schottky junctions possess barrier height of 0.63 and 0.7 eV.

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