Rapid Reduction of Graphene Oxide Thin Films on Large-Area Silicon Substrate

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Abstract. Graphene oxide thin films were fabricated on 8-inch silicon/silicon dioxide (Si/SiO2) wafers for nanoelectronic applications. The fabrication was performed using an ultrasonic spray coating method and reduced by rapid thermal processing (RTP). The micrometer-sized droplets from an ultrasonic spray of stable dispersion Graphene Oxide (GO) in ethanol form uniforms films on large-area silicon substrates. Optical microscope images clearly showed uniform thin films resulting from the overlapped of GO dispersion droplets. The chemical and structural parameter characterization were performed by field emission scanning electron microscopy and X-ray photoelectron spectroscopy (XPS). The spray coating process using an ultrasonic atomizer system with optimum parameters and the thermal reduction process using RTP at 1100 °C produces low sheet resistance values ranging from 1 to 4 kOhms/sq with non-uniformity less than 20%.

1. Introduction
Graphene is a thin layer of graphite which has great potential in the development of novel electronic nanodevices. Several methods were reported in producing graphene in the previous research works. One of the methods is using graphene oxide (GO) which is reduced thermally or chemically. The results of the reduction produce reduced graphene oxide (rGO) which more closely resembles pristine graphene [1, 2]. The advantages of using GO are due to the hydrophobic properties with bulk processing, hence it delivers high stability in organic solvents and can be deposited on substrates using a spray coating method that have a high potential for upscaling.

One of the most significant current discussions on nanotechnology is the process of fabricating graphene thin films using GO solution based. Various methods of producing graphene thin films on substrates using solution based are found by dip coating [3] and spin coating [4]. Nevertheless, these methods are primarily for a batch process and laboratory scale method [5]. Several studies have revealed that ultrasonic spray coating as an excellent thin film coating for graphene nanomaterials. The advantages of this method are mainly for large area production and producing uniform thickness films. The surface roughness of the thin films was measured by atomic force microscopy (AFM) with a root mean square about 1 nm [6]. In addition, the droplet size can be controlled through the nozzle spray. Thin films with high thickness uniformity can be obtained from the micron size of the droplets and the high nozzle frequency [7, 8]. The ultrasonic spray coating has been applied in the fabrication of nanocomposite thin films such as transparent conducting electrodes for display application [6, 7, 9, 10], and nanodevices such as thin film solar cells, photodetectors [5, 11, 12]. The ultrasonic spray coating process could also enable the seamless integration of nanomaterials with semiconductor processes that...
can benefit the semiconductor industries, especially in nanoelectronic applications. The GO thin films should be further reduced to remove the oxygen-containing functional groups by thermal annealing to make it conductive [13]. Previous works reported thermal reduction ranging from 600 °C - 800 °C for 1 hour with a graphene thin film thickness of around 3.5 to 6 nm produced the sheet resistance ($R_s$) at 14, 5.7 and 7.8 kOhms/sq for 600, 700 and 800 °C respectively [14]. Thermal reduction at a higher temperature above 1100 °C resulted in lower sheet resistance in the range of 1 – 3 kOhms/sq [15, 16].

In this work, graphene oxide thin films have been produced on a large-area silicon substrate. The thin films were prepared by ultrasonic spray coating of GO in an organic solvent on heated 8-inch silicon/silicon dioxide (Si/SiO$_2$) wafers. The surface morphology such as thickness and roughness was characterized using AFM and the thin films formed by the GO droplets were observed using a digital optical microscope. The electrical properties of rGO prepared by different annealing temperatures of the thermal reduction process and the sheet resistance measured by four-point probes were compared. Besides, the rGO thin films were observed using XPS to see the percentage reduction of oxygen-containing functional groups.

2. Method

Graphene Oxide (GO) 5 mg/ml dispersion in ethanol was purchased from GO Advanced Solutions Sdn. Bhd. The dispersion was diluted to 1 mg/ml for ultrasonic spray deposition onto a heated 8-inch Si/SiO$_2$ wafer. The GO thin films were deposited using an atomizer system developed in-house via an ultrasonic nozzle with Nitrogen (N$_2$) as a carrier gas as depicted in Figure 1. The nozzle to sample distance was varied within 10 – 100 mm with a flow rate ranges from 0.2 – 1 ml/min. The ultrasonic spray produces small droplets of a few micron sizes that allow rapid solvent evaporation on the substrate. The thickness of the GO thin films can be controlled by the spray parameters such as nozzle to height sample and N$_2$ pressure. In this work, the ultrasonic spray parameter has been optimized to produce GO thin films with a thickness of less than 40 nm on large substrates. The repetition tests have been performed in 2, 3 and 4 spray-passes for 5 runs spraying experiments.

![Figure 1. Atomizer system with an ultrasonic nozzle spray and GO solution in ethanol.](image-url)
GO thin films are electrically insulating due to the heavy oxygenation of graphene sheets [17]. Therefore, to establish it as a conductive nanomaterial, the GO thin films were thermally annealed to produce reduced graphene oxide, rGO. High temperature removes the oxygen from the thin film through the conversion of sp3 to sp2 carbon in the graphitic lattice. In this work, the GO was thermally annealed using two different methods and the sheet resistance was measured and compared. The first reduction method was performed using Rapid Thermal Processing (RTP) equipment (Centura RTP). The 8-inch Si/SiO2 wafer with deposits GO was heated at a constant temperature at 1100 °C for 300 sec under the protection of the N2 flow of the RTP process. On the other hand, the second reduction was performed by plasma-enhanced chemical vapor deposition (PECVD) in an Oxford instrument Nanofab-700 System. The sample was cut into an inch size with the process was fixed at a temperature of 700 °C for 240 and 1800 sec.

Characterization of GO and rGO thin films was performed using several analytical tools to study the fundamental physical and chemical properties. Field emission scanning electron microscopy, FESEM (JEOL JSM 7500F) and atomic force microscopy (AFM) by tapping mode were used to investigate GO thin film surface morphology. Each sample was evaluated in 3 different regions. An optical microscope (DSX 500 Olympus) was used to observe the GO droplets that form into thin films and also after it was reduced. The element present in the thin film was identified by ULVAC PHI Quantera II x-ray photoelectron spectroscopy (XPS). Electrical conductivities were analyzed by the four-point technique with Prometrix RS75 tools at 49 different coordinate points distributed radially from the center of the whole 8-inch SiO2 wafer right after the reduction process using RTP. The sheet resistance measurements of the PECVD thermal reduction samples were measured using Jandel RM3-AR four-point probe.

3. Result and discussion

The morphology of GO thin films for 3x spray passes produced by ultrasonic spray coating on a large Si substrate was observed under Field Emission Scanning Electron Microscope (FESEM) as depicted in Figure. 2a). From the top-view of the FESEM image, it was observed the GO droplets were overlapped with one another to form thin films on the 8-inch Si/SiO2 wafer. Therefore, the thin films are considered adequately uniform due to the spray coating method with controlled parameters. The annealing process by RTP at 1100 °C does not significantly alter the morphology and structure of the rGO thin films as shown in Figure. 2b). The optical images for GO and the corresponding rGO thin films for 2x, 3x and 4x spray passes were provided by optical microscope on a 1307 x 1307 μm² field of view as shown in Figure 2c), d) and e). The diameter of the droplet patterns on the wafer is about 100 micron on average as measured by the optical microscope (Figure. 2a) top image). As the spray passes increases to 3x and 4x, the GO droplet was also becoming thick as can be seen from Figure. 2d) and e) top images. The top yellow layer was removed after RTP and most of the Si/SiO2 wafer surface was covered by rGO coating as shown at the bottom images of Figure. 2c),d) and e). The AFM images and 2-D thickness profiles are depicted in Figure. 3 a), b) and c) for 2x, 3x and 4x spray passes. The average thickness is 12.67, 19.50 and 37.02 nm and the corresponding surface roughness root mean square average is 5.09, 5.59 and 9.18 nm for the number of spray passes of 2x, 3x and 4x respectively. As a result of the ultrasonic spray process, multiple layers of graphene were prepared as the film thickness exceeds the thickness of a single layer of graphene which is at approximately 1 nm. The correlation between the number of spray passes and the thickness is shown in Figure. 3d).

The composition and construction of the GO and rGO thin films were characterized by using X-Ray Photoelectron Spectroscopy (XPS). The results are shown in Figure. 4. The survey spectrums of the CO include the peak of C1s and O1s for both GO and rGO thermally annealed by PECVD and RTP respectively (Figure. 4a)). The relative contents of C1s and O1s are shown in Table 1. From the survey spectra, there is only a slight decreased in oxygen content which is at 22.82 % from 35.83 % of GO after it was reduced using PECVD. However, a significant reduced of oxygen content can be observed after annealing by RTP which is reduced to 5.45 %. The content ratio of oxygen to carbon, O1s/C1s were calculated to be 57.23 %, 43.34 % and 6.02 % corresponding to GO, rGO_PECVD and rGO_RTP. These results reveal that most of the oxidized group was eliminated during the annealing by RTP at high
temperature, 1100 °C. Figure 4b) shows XPS spectra of highly oxidized GO with the C1s spectrum consists of a peak at 284.61, 285.08, 286.94 and 288.53 eV assigned to C-C, C-O, C=O and C(O)O. The C1s spectrum of GO shows two large peaks corresponding to the carbon components of C=O and C-C binding. In contrast to rGO C1s spectra, it can be seen the oxygen double bonded to carbon C=O peak was weakened peak and the C–C bond remained dominant as a single peak at higher energy as compared in GO after the reduction by PECVD (Figure.4c)). On the other hand, annealed rGO by RTP shows extremely decreasing for the double-bonded oxygen species C=O and highest C-C peak observed in Figure. 4d). This C=O lower intensity reflects the total amount of oxygen was strongly reduced during the annealing process at 1100 °C.

**Figure 2.** Image observation of GO films using FESEM and optical microscope. a) Surface morphology by SEM of GO films. b) Surface morphology by SEM of rGO films. c) Optical image of GO films for 2x spray passes and the size of droplet patterns and its equivalent rGO films. d) Optical image of GO films for 3x spray passes and its equivalent rGO films. e) Optical image of GO films for 4x spray passes and its equivalent rGO films.
Figure 3. AFM images for GO films on SiO₂ substrate and its thickness profiles. a) 2x spray passes, b) 3x spray passes, c) 4x spray passes d) Thickness of GO films with the corresponding number of spray passes.

Table 1. Element analysis of samples GO and rGO.

| Samples                  | C1s  | O1s  | O1s/C1s |
|--------------------------|------|------|---------|
| GO (wt%)                 | 62.61| 35.83| 57.23   |
| rGO_PECVD (wt%)          | 52.65| 22.82| 43.34   |
| rGO_RTP (wt%)            | 90.52| 5.45 | 6.02    |

The sheet resistance (Rs) of rGO films reduced by PECVD using two parameters are listed in Table 2. The sample of rGO thin films with 2x and 3x spray passes after it was thermally annealed at 700 °C for 240 sec were not conductive as no response during Rs measurement performed by the four-point probe. On the other hand, the Rs value observed with a similar parameter was too high, > 10 kOhms/sq. Low Rs value approximately at 5 kOhms/sq can be obtained with a thick layer of rGO using the parameter in Table 2.

Figure 5 shows the sheet resistance values of rGO thermally annealed by RTP and its non-uniformity corresponds to the number of spray passes. The measurements were performed right after the wafer was thermally annealed at high temperature using RTP. The sheet resistance value for each number of sprays was studied from the average of sheet resistance values from 49 points measured by the 4-point probe (Prometrix Rs75) on the 8-inch Si/SiO₂ wafer. The sheet resistance value for 3x spray passes is within the range of 2 – 3.6 kOhms/sq while for 4-spray passes is 1 – 3 kOhms/sq within a wafer. However, the four-point probe was able to measure only two wafers for 2x spray passes. This is due to very thin films produced by 2x spray passes thus, some of the GO droplets were not overlapped with one another and as a result, the wafer is not fully conductive. The sheet resistance values are quite higher than the other two spray passes. The wafer sample of 3x and 4x has less than 20% of sheet resistance non-uniformity with only one sample for each spray pass has non-uniformity > 20%. The 49 sampling point sheet resistance wafer contour mapping results were selected randomly from 2x, 3x and 4x spray passes of the wafer are shown in Figure 6. The contour mapping results typically show good conductivity based on the sheet resistance values. From the observation, the distribution of sheet resistance values is approximately 10 kOhms/sq, 3 kOhms/sq and 2 kOhms/sq for 2x, 3x and 4x spray passes respectively.
Figure 4. Analysis by XPS and comparison of C1s peaks of GO and rGO a) Survey spectra for GO and rGO by PECVD and RTP b) C1s of GO. C) C1s of rGO reduced by PECVD. d) C1s of rGO reduced by RTP.

Table 2. Sheet resistances of rGO by PECVD.

| No. of spray passes | Parameter                     | Rs Ohms/sq |
|---------------------|-------------------------------|------------|
| 4x                  | T = 700 °C; 240 sec           | > 100000   |
| 6x                  |                               | ~ 21000    |
| 12x                 | T = 700 °C; 1800 sec          | ~ 9000     |
| 18x                 |                               | ~ 5000     |
Figure 5. Sheet resistance and its non-uniformity of rGO after thermally annealed by RTP a) Rs vs no. of spray passes. b) Non-uniformity vs no. of spray passes.

Figure 6. a) Rs contour plot for 2x spray passes. b) Rs contour plot for 3x spray passes. c) Rs contour plot for 4x spray passes.

4. Conclusion

The graphene thin films on a large area silicon substrate were prepared by ultrasonic spray coating and followed by thermally annealed by PECVD and RTP. An adequately uniform GO thin films due to the overlapping of micron droplets were formed by spray coating with controlled parameters. The method of spray coating produced GO thin films with the average thickness in the range of 12.67 to 37.02 nm with an RMS range of 5.09 to 9.18 nm respectively. Reduction of GO by RTP where the 8-inch wafer was thermally annealed at 1100 °C was found to be improved as confirmed by XPS. The ratio O1s to C1s was extremely reduced from 57.23 % before to 6.02 % after RTP. The sheet resistance values were found in the range of 1 – 4 kOhms/sq corresponding to the number of spray passes with non-uniformity is less than 20 %.

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