Synthesis of scalable and tunable slightly oxidized graphene *via* Chemical Vapor Deposition

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ABSTRACT

Semiconducting, large sheets of carbon as an active material in optoelectronic research are missing and reduced graphene oxide (rGO) can be a good candidate. However, chemical synthesis cannot produce large sheets of rGO (*i.e.* maximum: 20 ~ 30 μm) as well as high quality rGO due to the restraints of fabrication method. Thus, a novel strategy for the synthesis of large sheets of semiconducting rGO is urgently required. Large area slightly oxidized graphene (SOG) is fabricated at the interface of silicon dioxide (SiO_2) and silicon *via* Chemical Vapor Deposition (CVD) method, herein for the first time. Carbon atoms bond with oxygen functionalities (*i.e.* C=O, C-OH) at the time of diffusion in SiO_2 allowing for

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C/O ratios from 7 ~ 10 adjustable by the variation of SiO₂ thickness, indicating the tunable oxidation. Moreover, electronic structure and morphology of SOG are similar to the chemically grown rGO. The fabrication mechanism of SOG is also investigated.

1. Introduction

The carbon family consists of several allotropes from perfectly metal (i.e. graphene[1]) to insulator (i.e. diamond) as well as a handful of semiconducting carbon types such as carbon nanotubes (CNTs),[2, 3] graphene nanoribbons,[4] graphene oxide (GO),[5] reduced graphene oxide (rGO)[6] and amorphous carbon (a-C).[7-9] Among these semiconducting carbon materials, GO is a two-dimensional (2D) semiconducting material, useful for several applications including photovoltaic devices,[10] batteries,[11] Raman enhancement,[12] fuel cells,[13] and supercapacitors.[14] rGO is obtained by chemically reducing GO to some extent by using suitable reducing agent e.g. hydrazine,[15] or vitamin-C[15]. GO and rGO both beneficial in several practical applications; however rGO is favorable in optoelectronic devices due to the elevated electrical and optical properties in comparison to GO.[16]

To date, the basic hurdle for the utilization of rGO in optoelectronic devices is the small sheet size that should be enhanced from micron size to centimeter scale production for many practical applications. Thus, several research groups are trying to produce large area rGO for example, Hasan *et al.*[17] fabricated large area GO via electrophoretic deposition. On similar lines, Zhang *et al.*[18] also synthesized rGO via this method for use as supercapacitor electrode. Guan *et al.*[19] has developed a new method of the reduction of standing GO sheets via laser processing. Feng *et al.*[20] fabricated rGO via electronic solution reduction. Recently, Voiry *et al.*[21] reported high quality rGO via microwave reduction. However, the sheet size remained micron sized (*i.e.* 20 ~ 30 μm), indicating chemically produced rGO cannot be produced in large sheets due to the limitation of wet chemical process.[22, 23]

Moreover, Ellmer[24] reported that carbon based semiconducting material as an active layer in transparent conducting electrode (TCE) is missing. Thus, large area slightly oxidized graphene (SOG) could be an affective material as a TCE in several optoelectronic devices as well as tunable oxygen contents make it favorable for efficient devices, which is not produced previously to the best of our knowledge.

Herein, we used thin layers (*i.e.* 100 ~ 500 nm) of silicon dioxide (SiO₂) on silicon as a catalyst and oxygen donor for the production of SOG for the first time, using Chemical Vapor Deposition (CVD) method, which is close to industrial production methods. Several characterization tools are used to investigate electronic structure, morphology, and chemical states of the surface atoms of SOG. A significant similarity to rGO has been observed in SOG. Moreover, oxygen contents are controllable by the thickness of SiO₂, indicating beneficial as compared to the conventional reducing agents such as hydrazine.

2. Experimental Methods

2.1 Chemical Synthesis of GO

Graphite was oxidized by a modified Hummers' method.[25] In brief, 2 g of graphite flakes was added to a flask containing 50 mL of concentrated sulfuric acid. One gram of NaNO₃ was added to the flask while stirring. Subsequently, 6 g KMnO₄ were poured slowly into the mixture in 20 min. to maintain the temperature under 20 °C. The temperature was then increased to 35 °C and kept at this condition for 1.5 h. Then the mixture was cooled down to room temperature and left over night. Next, 400 mL of DI water was added to the mixture slowly. An amount of 50 mL of H₂O₂ solution was added drop wise to the solution. The reaction mixture was washed with 1.5 L of HCl (5wt% in water), and then with deionized (DI) water (*i.e.* 1 L × 3 times) by using centrifugation at 4000 rpm. The paste obtained after centrifugation was added to 2 L of DI water and tip sonicated for 1 h. After centrifugation

and drying under vacuum, the graphene oxide (GO) was obtained as a brown colored powder.[26]

2.2 Chemical Synthesis of rGO

In a typical experiment, 0.1 g of graphene oxide (synthesized as described above) was dispersed in 50 mL DI water. Then 0.1 mL hydrazine monohydrate was added and maintained at 95 °C for 1 h. Once the reaction is completed, the reduced graphene oxide (rGO) was collected by filtration as a black powder. The obtained material was washed with DI water several times to remove the excess hydrazine, and the final product was dried in a vacuum oven at 80 °C.[27]

2.3 Fabrication of SOG

The rGO has synthesized by using CVD (GSL-1700X, MTI) method at the interface of a SiO₂/Si substrate. A rectangular shaped (*i.e.* 1 × 0.5 cm²) SiO₂/Si was placed in an alumina boat and placed at the center of the CVD furnace tube. Three specimens SiO₂ (~ 100 nm)/Si, SiO₂ (~ 300 nm) and SiO₂ (~ 500 nm)/Si were used for the fabrication under similar growth conditions for comparison purposes.

Fabrication of SOG was done in five steps (Fig. 1 (a)). Firstly, the both ends of the furnace tube was sealed after the insertion of substrates and started a mechanical pump for creating a vacuum of 10⁻¹ torr. Secondly, temperature was increased from room temperature to 100 °C at a rate of 5 °C /min and a mixture of hydrogen/argon gas (*i.e.* ~ 25 % of hydrogen mixed with 75 % of argon) was provided throughout the experiment at the flow rate of 60 cc/min (centimeter cube per minute). Afterwards, the temperature was raised till 1100 °C at a rate of 10 °C /min. Thirdly, specimens were kept at 1100 °C for 10 min. Fourthly, ethylene (C₂H₄) was mixed with already provided mixture of gases at the rate of 100 cc/min for 5 ~ 15 min with maintaining 1100 °C and the C₂H₄ gas stopped mixing after particular growth time. Fifthly, the temperature of CVD furnace decreases in two steps, first step at a rate of

20 °C/min till 500 °C and second step 5 °C/min till room temperature. The specimens were taken off from the furnace when temperature of CVD furnace reached at room temperature.

Fig. 1 (a) Growth conditions of SOG & (b) Schematic of CVD-grown SOG at the interface of SiO₂/Si

The C-H bond of C₂H₄ breaks at 1100 °C during the growth in CVD furnace and the resulting carbon atoms react with SiO₂ to produce SiC and carbon monoxide.

However, all the carbon atoms cannot be utilized forming this reaction. The oxygen vacancies are present in SiO₂ that can make bonding with carbon atoms and travel towards the interface of SiO₂/Si. The thickness of SiO₂ on the top of Si is varied from 100 to 500 nm, act as a catalyst and oxygen donor (Fig. 1(b)). The carbon atoms were precipitated the surface of SiO₂ and absorbed due to the amorphous structure of SiO₂. [28] These carbon atoms diffuse through the SiO₂ layer and reached at the interface of SiO₂/Si and formed a thin layer of SOG.

2.4 Transfer of SOG

The specimens (*i.e.* SiO₂/SOG/Si) were inserted into hydrofluoric (HF) acid for different amounts of time, depending the concentration of HF in the solution (Fig. 2). The SiO₂ layer etched away, while SOG remains on the silicon. Then, acetone was poured into the solution to make it dilute. This step must do carefully, as layers of SOG can be lifted up in the solution easily before the removal of whole HF from the solution. The addition of large quantity of acetone makes the solution increasingly dilutes. However, HF cannot be removed completely with additional amount of acetone. To remove HF to a larger extent, some of the solution was removed and a similar amount of the acetone was added, simultaneously. In this way, the amount of HF in the solution decreases quickly. The removal of HF was observed by monitoring the pH of the solution. The specimens were kept in acetone at pH ~ 7 overnight.

Fig. 2 Transfer of SOG on arbitrary substrate after removing SiO₂ ~ 300 nm layer

2.4 Characterization

The SOG was characterized *via* high-resolution transmission electron microscope (HRTEM, JEOL-2010) and Raman spectroscopy (Renishaw-HR800) for structural analysis. Scanning electron microscopy (SEM-Hitachi, SU-70) and Atomic Force Microscopy (AFM, Shimadzu, SPM-9700) were used for surface & morphology analyses. The chemical state of the surface atoms of SOG was investigated under X-ray photoelectron spectroscopy (XPS- ESCALAB 250 Xi Thermo Scientific, USA). X-ray diffraction (XRD-Rigaku D/max 2500, $\lambda = 1.5406$ Å) was used for the phase of chemical grown rGO (chem-rGO) and SOG.

3. Results and Discussion

The successful fabrication of SOG *via* CVD was proven by several characterization tools after removing SiO₂ ~ 300 nm layer. All specimens in this study were fabricated at the interface of SiO₂ ~ 300 nm and silicon except specimens for the study of growth mechanism. The structure of SOG was investigated under HRTEM and wrinkles on the surface were observed (Fig. 3 (a)) as well as were observed in SEM images. These wrinkles are the feature of graphene and its derivatives. In the AFM images, we also observed similar feature (Fig. S1). Moreover, the *d*-spacing of SOG was similar to chemically produced rGO ~ 0.36 nm, indicating similar atomic and electronic structure to rGO (Fig. 3 (b)). Selected area

diffraction (SAED) pattern of SOG showed rings as well as bright dots, indicating the presence of stacked graphene layers in arbitrary directions (inset of Fig. 3 (b)). The SOG was transferred onto SiO₂ for cross-sectional view (Fig. S2). The thickness of 5 nm shows a *d*-spacing of 0.357 nm, indicating that layers of SOG have similar *d*-spacing to rGO. It is revealed that larger scale thin sheets of SOG can be obtained after the transfer, however small areas of SOG shows wrinkles due to air trapped (Fig. 4 (a) & (b)). These wrinkles are a special feature of graphene derivatives.[29]

Fig. 3 (a) large area SOG & (b) High-resolution image shows a *d*-spacing of 0.36 nm (inset: SAED).

Functional oxygen groups (*e.g.* hydroxy and epoxy etc.) are attached on the graphene surface during the chemical synthesis reaction, however non-oxygenated rings are also present in both GO and rGO (Fig. 5 (a)). XPS is a powerful tool for the observation of the amount of these oxygen functionalities as well as non-oxygenated rings. In XPS analysis of SOG, a peak at 287.9 eV was observed, corresponding to the oxygenated rings and a peak at 284.6 eV corresponding to non-oxygenated rings (Fig. 5 (b)). Full width at half maximum of non-oxygenated rings was wider as compare to graphene, thus another peak of carbon and hydrogen C-H can be fit well under it. This indicated that C-H bonding was also present in

SOG. These peaks in SOG are similar to the data found for chemically produced rGO. The C/O ratio in SOG was around ~ 8 , which is in close to the amount in chemically produced rGO.

Fig. 4 (a) Large area transferred & (b) Wrinkles on the surface of SOG that was fabricated by using a substrate of $\text{SiO}_2 \sim 300 \text{ nm}$.

Two peaks were observed in the XRD signatures of chemically produced rGO at 21.6° and 41.4° , indicating polycrystalline nature of chemically produced rGO (Fig. 5 (c)). On similar lines, XRD signature of SOG showed two peaks at different position 23.4° and 40° , indicating slight oxidization. It is the fact that graphene peak was observed at 24° , which moved backward to 10° in the case of GO and depending upon the oxidation it varied from 10 to 24.57° . [6] Moreover, two peaks at 23.4° and 28° can be fit under the wide XRD signature of SOG (Inset of Fig. 5 (c)). We believe that the peak fit at 28° is due to the background effect of SOG/substrate, which did not appear in rGO XRD signature as it was in powder shape, while SOG was transferred on a substrate.

Four bands D, G, 2D and D+D' were observed in the Raman signature of chemically produced rGO as well as SOG (Fig. 5 (d)). The D band initiated due to the presence of defects and in perfectly crystalline graphene is almost absent. However, in the case of rGO and SOG, G band was intense, indicating these materials had higher structural defects in

comparison to graphene. The 2D band is the overtone of these defects, which is very intense in graphene. It was intense in SOG case, while not intense for chemically produced rGO. The G band corresponded to the non-oxygenated rings, which was intense in SOG case due to thickness. The S3 band was also observed in both rGO and SOG.

Fig. 5 (a) C/O ratio and graphene derivatives (i.e. GO & rGO), (b) XPS spectra of SOG, (c) XRD signatures & (d) Raman of chemically produced rGO and SOG (SOG specimen was fabricated by using SiO₂ ~ 300 nm substrate)

The comparison of chemically produced rGO and SOG is summarized in Table. 1. Firstly, the fabrication method of SOG is CVD rather than Hummer's method or any other chemical method. Novoselov[30] described in his novel road map for the graphene that CVD is the best industrial fabrication method for the fabrication of cost affective and high quality graphene. Secondly, chemically produced rGO cannot have sheet size bigger than 20 ~ 30 μm ,

owing to the restriction of production method. Thirdly, C/O ratio of SOG can be tuned from 7 ~ 10, depending upon the thickness of SiO₂ layer and it shows similar oxygen functional group in SOG as rGO other than C-O bond. Fourthly, XRD signatures of both SOG and chemical produced rGO show similar peak position. Fifthly, Raman spectrum shows four bands in both SOG and chemically produced rGO. Finally, the structure of chemically produced rGO and SOG is similar under HRTEM.

Table. 1 Comparison of chem-rGO & SOG

Chem-rGO ^{Ref.}		SOG (Present Study)
Fabrication	Hummer's Method[25]	Chemical Vapor Deposition (CVD)
Method	Improved Chemical Method[5]	
	Other Methods[6, 19, 29, 31, 32]	
Sheet size	20 ~ 30 μm [22, 23]	> 200 μm
XPS	C-C ~ 284.5 eV[15, 33]	C-C ~ 284.6 eV
	C=O ~ 287.8 eV[15, 33]	C=O ~ 287.9 eV
	C-O ~ 286.5 eV[15, 33]	---
	C/O ratio ~ 7-9[15, 33]	C/O ratio ~ 7-10
XRD	2 θ ~ 10.27 to 24.57°[6]	2 θ ~ 23.4° (SOG)
Raman	D band[6] ~ 1334 cm ⁻¹	D band ~ 1341 cm ⁻¹
	G band[6] ~ 1581 cm ⁻¹	G band ~ 1581 cm ⁻¹
	2D band[6] ~ 2700 cm ⁻¹	2D band ~ 2700 cm ⁻¹
	S3 band[6] ~ 2910 cm ⁻¹	S3 band ~ 2910 cm ⁻¹
HRTEM	d-spacing[6] ~ 0.36 nm	d-spacing ~ 0.36 nm

The growth mechanism of SOG was also investigated with the help of XPS. The C/O ratio can be tuned with the help of thickness of SiO₂. As SiO₂ ~ 300 nm/Si is amorphous in nature and at high temperature dangling bonds start OH bonding at the surface of SiO₂ due to the ability of hydrogen gas. Hao *et. al.*[34] reported that OH bond is more favorable for the fabrication of large area graphene with the help of density functional theory (DFT). They described that hydrogen terminated edges of the graphene limits the expansion of the monolayer graphene sheet. In the viewpoint of this study, OH bond is useful for the fabrication of large area graphene and presence of this bond in SOG may help for the fabrication of large area. Moreover, Chen *et. al.*[28] successfully fabricated graphene on the top of SiO₂ substrate with the help of oxygen as well as described that carbon atoms can diffuse into SiO₂. However, they obtained graphene rather than oxidized graphene and, thus, their results cannot be compared with SOG. However, we can expect that oxygen plays an important role for the production of large area graphene and carbon atoms can diffuse into SiO₂.

Fig. 6 (a) XPS survey of SOG fabricated by using different thick SiO₂ layer (100 ~ 500 nm). (b) Schematic of SOG fabrication

Therefore, CVD is used for the fabrication of SOG without adding oxygen while using SiO₂ as a catalyst and oxygen donor. Therefore, three specimens of SiO₂, 100, 300 and 500 nm are used as catalyst and oxygen donor. The XPS analysis of the product from these three specimens shows significant difference in C/O ratio, indicating tunable oxygen impurities

1 depending upon the thickness of SiO₂ (Fig. 6 (a)). The carbon atoms travel from top to
2 bottom of SiO₂ and reach at the interface of SiO₂/silicon (Fig. 6 (b)). The carbon atoms
3 cannot diffuse more due to the perfectly crystalline silicon surface. However, these carbon
4 atoms bring oxygen impurities from SiO₂ during their flow from top to bottom. Thus, these
5 carbon atoms are collected at the interface and reduction of temperature forces them to lose
6 the energy. These molecules start forming bonds with each other and subsequently an
7 ultrathin layer of SOG is formed.
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19 **4. Conclusions**

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21 Herein, we reported successful fabrication of centimeter scale SOG via CVD for the first time
22 according to the best of our knowledge. Several chemical based fabrication methods for the
23 preparation of rGO are favorable among the research groups to produce large area oxidized
24 graphene. However, these methods could not produce larger than micron size as these
25 methods are using wet chemical strategy, which is not useful for producing centimeter scale
26 oxidized graphene. Therefore, we used SiO₂ layers (100 ~ 500 nm) as a catalyst and oxygen
27 donor for the production of SOG by using an industrial production method CVD. Moreover,
28 we produced chemically GO and reduced it via hydrazine for comparison purposes. The SOG
29 is analyzed with different characterization tools and found similar morphology. HRTEM
30 results clearly demonstrate that SOG is similar to chemically produced rGO. Raman and
31 XRD signatures also were compared with chemically produced rGO and similarities were
32 found. The electronic structure of SOG is similar to rGO and we believe that it can be very
33 useful material in optoelectronic materials. In addition, the production of centimeter size
34 SOG will be beneficial as an active material in transparent conducting electrode (TCE).
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Author's Contribution

R. U. R. Sagar has fabricated, observed, and explained the SOG. F. J. Stadler helped in composing and analyzing the data. Moreover, he is head of the group and as such responsible for research funding and lab facilities for all experiments. The remaining co-authors helped in data interpretation.

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Figure Captions

Fig. 1 (a) Growth conditions of SOG & (b) Schematic of CVD-grown SOG at the interface of SiO_2/Si

Fig. 2 Transfer of SOG on arbitrary substrate after removing $\text{SiO}_2 \sim 300$ nm layer

Fig. 3 (a) large area SOG & (b) High-resolution image shows a d-spacing of 0.36 nm (inset: SAED).

Fig. 4 (a) Large area transferred & (b) Wrinkles on the surface of SOG that was fabricated by using a substrate of $\text{SiO}_2 \sim 300$ nm.

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Fig. 6 (a) XPS survey of SOG fabricated by using different thick SiO_2 layer (100 ~ 500 nm).
(b) Schematic of SOG fabrication