

CHARACTERIZATION OF GRAPHENE FILMS PRODUCED BY LB GO FILM FORMATION, GO REDUCTION AND THERMAL ANNEALING

Yo-Rhin Rhim, Marcia W. Patchan, Lance M. Baird,
Jennifer L. Sample, and Robert Osiander

Applied Physics Laboratory, Johns Hopkins University,
Laurel, MD 20723-6099

Introduction

Graphene, a monolayer of graphite, has become an attractive research topic for many applications. With superior electrical, thermal, and optical properties, graphene is an excellent material candidate for scalable devices. For such purposes, a method for the production of consistently large areas of graphene is needed. Successful reduction of graphite oxide (GO) using hydrazine has been demonstrated [1, 2]. Thus, a technique combining Langmuir-Blodgett (LB) film deposition, chemical reduction of GO, and thermal annealing has been used in this study to yield consistently thin, large areas of graphene for the use in scalable devices.

Experimental

Graphene oxide flakes were purchased from CheapTubes, Inc. (Brattleboro, VT). The as-received graphene oxide (GO) flakes were suspended in a mixture of deionized (DI) water/methanol (ratio 1:5) [3] at a concentration of 2.5mg/mL by sonication for 30 minutes. In this form, GO was transferred onto glass and/or quartz slide substrates via Langmuir-Blodgett (LB) deposition.

A Langmuir-Blodgett trough (Nima Technology, model 611) was thoroughly cleaned with chloroform and filled with DI water prior to each experiment. The GO solution was suspended on the water surface with a glass syringe at the rate of 250uL/min until reaching a surface pressure of 2.5 - 3.0 mN/m (as measured using the Wilhelmy plate method). The film was compressed with a barrier speed of 100 cm²/min to a target surface pressure of ~20 mN/m and the monolayer transferred to the substrate at the rate of 10mm/min. A clean glass or quartz slide was pulled out of the dipping well to yield a deposited film of GO on the substrate, as shown in Fig 1a. The deposited films were air-dried prior to reduction.

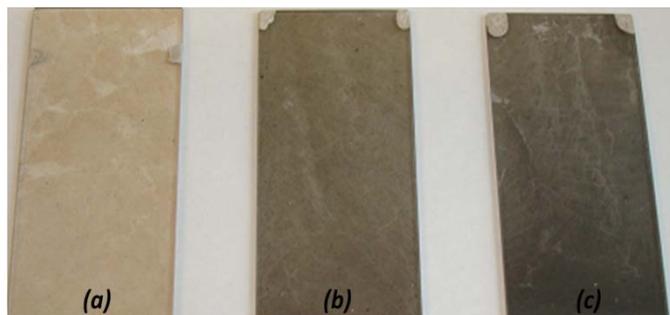


Fig. 1 (a) LB deposited GO film; (b) film after hydrazine reduction; and (c) film after thermal annealing.

Deposited graphene oxide was reduced via a modified version of the method used by Stankovich et al [2]. Substrates with deposited GO films were placed into a drying chamber (Chemglass AF-0556) that had a filter paper placed on the bottom of the vessel. Approximately 0.5 mL of the hydrazine hydrate solution was placed onto the filter paper. The chamber was sealed and reduction was carried out for 18 hours. Reductions were carried out at various temperatures by heating the drying chamber with a temperature controlled silicone oil bath. After the reduction, substrates were dried in a vacuum oven at 110°C. Argon was injected into the vacuum oven, in order to keep the atmosphere inert and decrease the chance of oxidizing the material, resulting in samples as shown in Fig 1b. Samples were then thermally annealed to 400°C at a rate of 20°C/min for 7 hours under a continuous flow of 70 sccm of argon [4] as shown in Fig 1c.

X-ray photoelectron spectroscopy (XPS), a surface sensitive chemical analysis tool, was used to confirm successful chemical reduction and annealing. For XPS analyses, samples were mounted onto a sample stub using double-sided copper tape and placed into an XPS (PHI 5400) analysis chamber (10⁻⁹ Torr). Samples were subjected to Mg K_α irradiation (1253.6 eV) generated from a 04-500 dual-anode X-ray source. All spectra were collected using an electron energy analyzer operating with pass-energy of 44.75 eV and resolution of 0.125 eV/step. Spectra were analyzed and deconvolved using spectral analysis software, CasaXPS. All spectra were aligned by referencing C(1s) peaks to the C-C/C=C component at binding energy of 284.6 eV. All reported areas were calculated by using sensitivity factors of 0.296 for C(1s).

Sheet resistances of sample films were measured using the van der Pauw technique in which voltage drops were measured with a known applied current. Sheet resistivities of two geometries were then calculated using the van der Pauw equation:

$$\exp\left(\frac{-\pi R_{vertical}}{R_S}\right) + \exp\left(\frac{-\pi R_{horizontal}}{R_S}\right) = 1 \quad (1)$$

where $R_{vertical}$ and $R_{horizontal}$ are the measured resistances vertically and horizontally, respectively, given an arbitrary geometry; and R_S is the sheet resistance.

Results and Discussion

C(1s) XPS spectra for deposited unreduced GO, hydrazine reduced GO (RGO), and thermally annealed RGO are shown in Fig. 2. Deconvolution of the C(1s) regions showed the existence of C-C/C=C, C-O, and C=O, and COOH bonds, respectively at binding energies of 284.6eV, 286.2eV, 284.8eV, and 288.1eV, for unreduced GO, and such results agree well with previous studies [4, 5]. Deoxygenation is apparent after hydrazine reduction as peaks centered at about 286.2eV shift to binding energy of 285.7eV, denoting the presence of C-N bonding. The appearance of nitrogenated carbon is attributed to the reduction of carbonyl to hydrazone

groups that occurs during the hydrazine reduction process of GO [2, 4]. As suspected, further annealing the hydrazine reduced sample decreases both oxygenated and nitrogenated carbon content, leaving essentially all C-C and C=C bonds as shown in Fig. 2 and reported in Table 1.

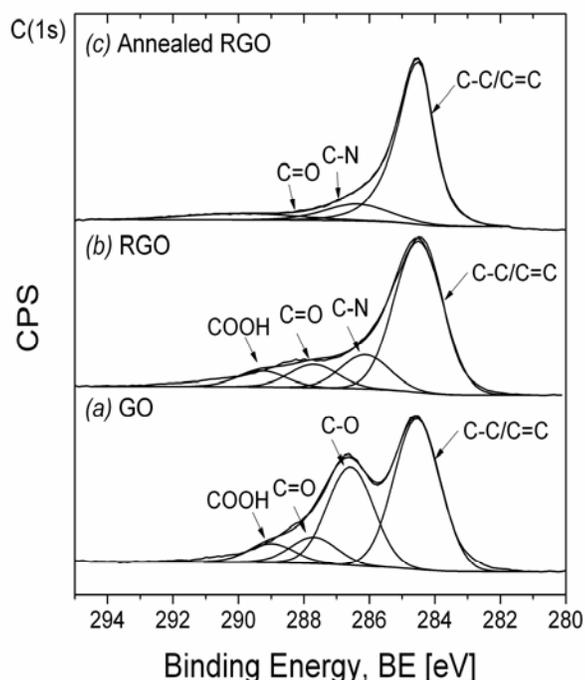


Fig. 2 C(1s) XPS spectra of (a) GO; (b) hydrazine reduced GO; and (c) hydrazine reduced and thermally annealed GO.

Table 1. Calculated Component Percentages via XPS Analysis.

	C-C/C=C	C-O	C-N	C=O	COOH
GO	51.32	33.43		8.87	6.37
RGO	67.34		15.18	10.31	7.16
Annealed RGO	78.25		13.36	8.39	

High percentages in oxygen functional groups make GO an electrically insulating material. The conjugated plane, characteristic of graphene, is highly disrupted by these functional groups, and therefore, the transport of electrons is interrupted. Although electrical property degradation due to defective sites may not be fully recovered, the removal of oxygen functional groups via chemical reduction improves electrical conduction, resulting in sheet resistances in the order of $10^9 \Omega/\text{square}$ [6]. As shown by XPS analysis, reduction causes a decrease in C-O originally observed in unreduced GO. During this deoxygenation process, C-C and C=C increase establishing a less interrupted path of electrons, therefore increasing the electrical conductivity. Although exposure to hydrazine increases the amount of nitrogenated

carbon, the promoted formation of C-C and C=C due to deoxygenation during this process is enough to significantly increase the electrical conductivity.

As suspected, subsequent thermal annealing further increases the electrical conductivity with additional deoxygenation and denitrogenation, leaving essentially only C-C and C=C. Measured sheet resistances of LB deposited graphene films ranged from 2 to 8 k Ω /square after hydrazine reduction and thermal annealing at 400°C.

Conclusions

The deposition of larger area graphene was attempted for its integration to large scale devices. Commercial graphite oxide was suspended in a solution and transferred onto substrates via Langmuir-Blodgett (LB) film deposition. Such films were exposed to hydrazine vapor which caused deoxygenation and formation of nitrogenated carbon. Electrical conductivity was shown to increase as oxygen functional groups disappeared, establishing a less interrupted pathway of electrons. Thermal annealing of reduced GO films in argon worked to further deoxygenate and denitrogenate, leaving essentially only aliphatic and aromatic carbon bonds, resulting in a significant increase in electrical conductivity with measured sheet resistances ranging from 2 to 8 k Ω /square. Results show that a combined technique of film deposition, hydrazine reduction, and thermal annealing is a promising approach in producing large area graphene for scalable devices.

Acknowledgments. Acknowledgments are made to the Milton Eisenhower Research Center of the Johns Hopkins University, Applied Physics Laboratory.

References

- [1] Tung VC, Allen MJ, Yang Y, Kaner RB. High-throughput solution processing of large-scale graphene. *Nature Nanotechnology* 2008; 4: 25-29.
- [2] Stankovich S, Dikin DA, Piner RD, Kohlhaas KA, Kleinhammes A, Jia Y, et al. Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon* 2007; 45(7): 1558-1565.
- [3] Cote LJ, Kim F, Huang J. Langmuir-Blodgett assembly of graphite oxide single layers. *Journal of the American Chemical Society* 2009; 131(3): 1043-1049.
- [4] Becerril HA, Mao J, Liu Z, Stoltenberg RM, Bao Z, Chen Y. Evaluation of solution-processed reduced graphene oxide films as transparent conductors. *ACS Nano* 2008; 2(3): 463-470.
- [5] Li X, Zhang G, Bai X, Sun X, Wang X, Wang E, et al. Highly conducting graphene sheets and Langmuir-Blodgett films. *Nature Nanotechnology* 2008; 3: 538-542.
- [6] Eda G, Fanchini G, Chhowalla M. Large-area ultrathin films of reduced graphene oxide as a transparent and flexible electronic material. *Nature Nanotechnology* 2008; 3: 270-274.