Dielectrophoretic assembly and atomic force microscopy modification of reduced graphene oxide

Yu Zhang, Lianqing Liu, Ning Xi, Yuechao Wang, Zaili Dong et al.

Citation: J. Appl. Phys. 110, 114515 (2011); doi: 10.1063/1.3665212
View online: http://dx.doi.org/10.1063/1.3665212
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v110/i11
Published by the American Institute of Physics.

Related Articles
Electrical conductivity in Li2O2 and its role in determining capacity limitations in non-aqueous Li-O2 batteries
Refinement of the theory for extracting cell dielectric properties from dielectrophoresis and electrorotation experiments
Biomicrofluidics 5, 044109 (2011)
Current-controlled negative differential resistance due to Joule heating in TiO2
Quantitative characterization of acid concentration and temperature dependent self-ordering conditions of anodic porous alumina
AIP Advances 1, 042113 (2011)
Direct solar energy conversion and storage through coupling between photoelectrochemical and ferroelectric effects
AIP Advances 1, 042104 (2011)

Additional information on J. Appl. Phys.
Journal Homepage: http://jap.aip.org/
Journal Information: http://jap.aip.org/about/about_the_journal
Top downloads: http://jap.aip.org/features/most_downloaded
Information for Authors: http://jap.aip.org/authors

ADVERTISEMENT

Explore AIP’s new open-access journal
- Article-level metrics now available
- Join the conversation! Rate & comment on articles

Submit Now
Dielectrophoretic assembly and atomic force microscopy modification of reduced graphene oxide

Yu Zhang,1,2 Lianqing Liu,1,a) Ning Xi,1,3,a) Yuechao Wang,1 Zaili Dong,1 and Uchechukwu C. Wejinya1,4

1State Key Laboratory of Robotics, Shenyang Institute of Automation Chinese Academy of Sciences, Shenyang 110016, China
2Graduate School of Chinese Academy of Sciences, Beijing 100001, China
3Department of Electrical and Computer Engineering, Michigan State University, East Lansing, Michigan 48824, USA
4Department of Mechanical Engineering, University of Arkansas, Fayetteville, Arkansas 72701, USA

(Received 19 June 2011; accepted 29 October 2011; published online 8 December 2011)

A simple and controllable method is developed to experimentally study the effects of defects on reduced graphene oxide (RGO) sheets for nanoelectronics application. First, a deterministic technique is developed to assemble a single layer graphene oxide sheet onto the gaps of microelectrodes by optimizing the dielectrophoretic parameters (10 Vpp at 1 MHz for 5 s). This is followed by the utilization of atomic force microscopy–based mechanical cutting method to form line defects on RGO sheets. Based on these two procedures, the experimental studies of the effects of line defects on RGO are investigated, which provides an alternative approach to study the influence of defects on graphene. The electric transport measurement results show that the electrical performance of the defected RGO devices generally decrease due to Anderson localization, which supports the theoretical studies of the influence of defects on the electrical properties of RGO.


I. INTRODUCTION

Graphene, a stable two-dimensional structure, has attracted tremendous attention worldwide,1,2 taking advantage of its unique electrical properties and high crystal quality. It is being predicted to have numerous potential applications and may bring revolutionary influence to the next generation of electronic devices. Although graphene-based FETs,3–4 gas sensors,5 solar cells,6 etc. have been successfully demonstrated with excellent properties, the structural defects induced during fabrication in experiment will significantly affect the electronic properties of these devices. Consequently, the study of these defects in graphene becomes extremely important. Previous research on defects in graphene has focused on theoretical studies6–15 of defects, such as Stone-Wales defects, vacancy defects, heptagon defects, and pentagon defects. To date, there are three mechanisms to induce defects on graphene experimentally:16 (1) crystal growth;17,18 (2) irradiation with energetic particles, such as electrons19–23 or ions,24–27 and (3) chemical treatment.28 The main shortcoming of these three methods is that they are not controllable and, hence, are not able to induce defects at a specific location. Therefore, it becomes absolutely necessary to develop a simple and controllable process to experimentally study the effects of defects on graphene for nanoelectronics development and application. Since one route to obtain graphene is chemical reduction of graphene oxide (GO) sheets, an alternative approach to study the effects of defects on graphene can be realized in the following three steps: The first step is that GO sheets can be deposited between microelectrodes with high yield and the process is controllable. Then, GO sheets are reduced to graphene by wet chemical reduction. Finally, defects are induced in reduced graphene oxide (RGO) by an AFM-based mechanical cutting method, which is also highly controllable.

Among the assembling methods in nanotechnology, dielectrophoresis (DEP) has emerged as a powerful technique for the selective deposition or directed movement of microand nanoscale entities in non-uniform electric fields. DEP has been applied to the assembly of nanoparticles,29 carbon nanotubes,30 DNA,31 and cells.32 Recently, graphene and GO sheets have been successfully assembled by DEP.33–36 However, these works focused specifically on the assembly and not on the layer control. In this paper, GO sheets can be assembled onto the gap of the microelectrode, with layer control depending on different dielectrophoretic deposition parameters. A single-layer GO sheet can be assembled by optimizing the parameters (10 Vpp at 1 MHz for 5 s).

For the introduction of line defects, several methods have been proposed, such as catalytic cutting technique,37–39 scanning probe microscope (SPM)-based electric field tailoring technique,40,41 and energy beam cutting method.42,43 The drawback to these methods is that they all require complicated experimental conditions. In this paper, an AFM-based mechanical cutting method is developed to introduce line defects in RGO. This method is highly controllable and simple to be performed.
II. EXPERIMENTS

A. Dielectrophoretic assembly and reduction of graphene oxide

Stable aqueous dispersions of GO were obtained from the Institute of Metal Research (IMR), Chinese Academy of Sciences. It was synthesized by a modified Hummers method. The original aqueous GO solution was diluted by 1:1 and then sonicated for 4 min at 59 Hz in the Ultrasonic Oscillator (Shanghai KeDao Limited Company of Ultrasonic Instrument, SK5210LHC). A droplet (2 μl) of the diluted solution was dispensed on the freshly cleaved mica. The prepared sample was dried at room temperature and then imaged using an AFM (Veeco, Dimension 3100). Figure 1(a) shows a tapping-mode AFM image of the GO sheets along with their height analysis. More than 90% of the sheets were monolayer GO, the height of which is ~1 nm, as shown in Fig. 1(b). This height is similar to monolayer GO sheets’ heights reported in previous studies.45,46

Figure 2 depicts a schematic of the DEP setup. The electrodes of the present study were fabricated by standard photolithography and lift-off techniques. The gold electrodes have a thickness of 40 nm and a gap of 1-2.5 μm between them, as depicted in Fig. 3.

\[\text{FIG. 1. (Color online) Height images of GO on mica in an AFM tapping mode. (a) GO sheets imaging sonicated for 4 min. Scan size: } 70 \mu \text{m} \times 70 \mu \text{m. Data scale: } 10 \text{ nm. (b) Height analysis trace, showing the thickness of the GO (white line indicating) in (a) is } 1.15 \pm 0.1 \text{ nm.}\]

\[\text{FIG. 2. (Color online) Schematic of the DEP setup.}\]

\[\text{FIG. 3. (Color online) Electrode chip schematic.}\]

\[\text{FIG. 4. (Color online) Schematic of graphene cutting by an AFM scratching technique.}\]
A small droplet (0.5 $\mu l$) of the aqueous GO solution was placed onto a chip, and a sinusoidal potential difference (5-10 Vpp at 1 MHz) was applied to the bias electrode by a function generator (Escort, EGC-3230). After 10-40 s, the generator was switched off and the droplet dried at room temperature. Then, the chips were characterized using an AFM. Lastly, the GO sheets were reduced by chemical reduction. The chips with GO sheets’ bridged gaps were dipped in 55% hydroiodic (HI) acid for 3-5 min at 100 $^\circ$C, which is performed by the Institute of Metal Research, Chinese Academy of Sciences.

B. Formation of line defects by AFM

The line defects were induced by AFM scratching techniques. The tip is scanned under strong loading forces to
FIG. 7. (Color online) Current-voltage measurement of the junction before and after reduction. (a) An AFM image of GO junction before reduction, including height trace, displaying the sheet thickness in the channel is around 25 nm. The scan size is $17.4 \mu m \times 17.4 \mu m$ and the data scale is 150 nm. (b) An AFM image of RGO junction with the height trace. The thickness is down to 5.0 nm. The scan size is $17.4 \mu m \times 17.4 \mu m$ and the data scale is 150 nm. (c) Current-voltage characteristics of the GO sheet before and after reduction, exhibiting an electrical resistance from $R = 161 \ M\Omega$ (shown by the dash-dot line) down to $R = k\Omega$ (indicated by the solid line).

FIG. 8. (Color online) Electrical transport measurement on the RGO sheet before and after cutting. (a) An AFM image of RGO sheet after cutting. The white circle displays the position of the cutting. The scan size is $10.0 \mu m \times 10.0 \mu m$ and the data scale is 150 nm. (b) Current-voltage characteristics of the RGO sheet before and after cutting. The resistance before cutting is $397.4 \ k\Omega$, which is denoted by the dash-dot line. After cutting, the resistance is up to $1.9730 \ M\Omega$, which is denoted by the solid line. (c) and (d) Additional result. The scan size is $16.0 \mu m \times 16.0 \mu m$ and the data scale is 150 nm. The resistance is $61.2 \ k\Omega$ before cutting, which is denoted by the dash-dot line. The resistance decreases to $194.5 \ k\Omega$ after cutting, which is denoted by the solid line.
remove the substrate or resist. Normal antimony-doped tips (type: MPP-11100-10 with a radius of 8-12 nm) with a normal spring constant 40 N/m (Veeco Company) is used to perform the experiment. The normal length, width, and thickness of the cantilever are 125 μm, 35 μm, and 3.75 μm, respectively. GO sheets were cut automatically using Nano-Man software of the AFM (in contact mode under feedback on) by setting different deflection setpoints, which adjusts the cutting force, as shown in Fig. 4. Figure 5 shows formation of line defects in GO sheets by an AFM nanocutting technique.

III. EXPERIMENTAL RESULTS

Figure 6 depicts the tapping-mode AFM images of GO sheets deposited by DEP along with their height analysis. Firstly, an AC voltage of approximately 5 Vpp at 1 MHz was applied to the electrode pair for 20 s. The result shows that the thickness varies from 12 to 25 nm in the channel (Fig. 6(a)). This is followed by an AC voltage of 10 Vpp at 1 MHz applied for 10 s. The result shown in Fig. 6(b) indicates that the thickness is down to 5 nm by AFM analysis. When the time decreased to 5 s, the thickness of the sheet is 1.3 ± 0.3 nm, indicating a single layer GO sheet assembled in the channel, as shown in Fig. 6(c). It can be seen that it is possible to deposit a single-layer GO sheet by optimizing the DEP deposition parameters (10 Vpp at 1 MHz for 5 s). Figure 6(d) is the phase image of Fig. 6(c), from which a nanochannel can be clearly seen. This nanochannel would be used to study quantum computing.

After assembly, GO sheets’ bridged gaps were reduced by chemical reduction. The current-voltage (I-V) measurements at room temperature and ambient condition are presented in Fig. 7. The height of the GO sheet decreases from 25 nm to 16 nm after chemical reduction, as shown in Fig. 7(a) and Fig. 7(b). Because the chip is dipped in HI acids for 3-5 min, some GO sheets beside electrodes have been soaked away. The GO sheets are electrically insulating. After reduction, GO sheets change from insulating to conducting. The total electrical resistance, consisting of the sheet and contact resistance, decrease from $R = 161 \text{ MΩ}$ to $R = 32 \text{ kΩ}$ (Fig. 7(c)). Good ohmic contacts are verified by the linear relationship.

The effects of line defects on the electrical properties of the RGO junction have been investigated. After reduction, line defects were induced by AFM-based mechanical cutting. Then, current-voltage measurements were performed. It is found that all RGO devices show electrical performance degradation after defects induced (see Fig. 8), which is consistent with theoretical studies.48–50 In Figs. 8(a) and 8(b), when a horizontal line defect was formed in the RGO sheet, the resistance increased from 397.4 kΩ to 1.9730 MΩ. When a vertical line defect was introduced, the resistance increases from 61.2 kΩ to 194.5 kΩ, as shown in Fig. 8(c) and Fig. 8(d), respectively. By using the optimizing DEP parameters, the influence of line defect on single layer RGO has been investigated too. Figure 9(a) displays the height image of the defected single layer RGO with its height analysis. From the height analysis, it can be seen that the thickness of the RGO is around 0.879 nm, indicating that a single layer GO sheet has been assembled in the channel. The phase image (Fig. 9(b)) shows more clear details. After inducing a line defect, the electrical transport measurement is performed immediately. The resistance of the defected single layer RGO also increases (from 137.7 kΩ to 291.5 kΩ), as shown in Fig. 9(c).
IV. CONCLUSIONS

In conclusion, a DEP-based deterministic approach to assembling GO sheets onto the gaps of microelectrodes with controllable layers is presented. Single layer GO sheet assembly is demonstrated with optimized dielectrophoretic deposition parameters of 10 V_{pp} at 1 MHz for 5 s. This results in high quality and controllable assembling of GO-based nanodevices that have the potential for real advances in GO-related developments. In addition, an AFM-based mechanical cutting method is developed to form defects in RGO sheets. The amazing advantage of this method is that it can realize massive fabrication through the parallel multi-tip technology, which makes it possible to fabricate defects in RGO at low cost and high efficiency. This process will ultimately provide opportunities and means for large scale nanomanufacturing of RGO-based nanodevices. Furthermore, the effect of line defects on a RGO sheet has been experimentally investigated based on these two methods, which shows that all of the resistance increases with the introduction of defects. This is the first experimental result and procedure to show the influence of introduced defect on the electronic properties of RGO and provide solid proof to the theoretical studies.

ACKNOWLEDGMENTS

The authors acknowledge the support of the National High Technology Research and Development Program of China (Grant No. 2009AA03Z316), National Natural Science Foundation of China (Project Nos. 60904095, 51050110445, and 61175103), and the CAS FEA International Partnership Program for Creative Research Teams. Additionally the authors would like to thank Jinping Zhao and Zhongshuai Wu for helpful discussions and support.