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Highly conductive, monolayer and large-area reduced graphene oxide films fabricated by electrical connection at the two-dimensional boundaries between the tiled graphene oxide flakes

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ABSTRACT

The demand to fabricate graphene film in large wafer-scale with minimum cost is crucial for device applications, and one of the promising techniques is the reduction of graphene oxide (GO) films. We have investigated morphological changes of large-area, monolayer GO films during methane (CH_4)-assisted thermal annealing process and the role of CH_4 in the restoration of their electrical conductivity. We have discovered that long reduction process in high CH_4 flow rates can contribute to the partial reparation of lattice defects and formation of new multilayer graphene that are stacked at the boundary areas between the reduced GO (rGO) flakes. These multilayer graphene layers with graphitic domains operate as the electrical connection between the separated rGO flakes and create new conduction pathways across the entire films. This phenomenon is more important than the sole reduction process (elimination of oxygen functional groups) in the restoration of electrical conductivity of the continuous rGO films. We have achieved in the fabrication of highly conductive rGO films with a minimum sheet resistance value of 1.01 kΩ/sq. This study exhibits a promising reduction method for the mass production of large-area, continuous rGO films for thin film device applications.

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1. Introduction

Since graphene, which is a two-dimensional (2D) material made up of only single layer of carbon atoms, was first discovered [1–3], it has attracted worldwide attention due to its remarkable electrical [4,5], mechanical [4,6] and optical properties [4,7] and is expected for various kinds of device applications in the near future. Above all, graphene exhibits potential applications in the area of flexible, transparent electrode and electrically conductive thin-film devices [8–11] owing to its unique one-atom-thick properties. However, the demand to fabricate graphene films in large-size for mass production and to find the most cost-effective fabrication method is still a challenge. Among all graphene fabrication methods [12–17], reduction of graphene oxide (GO) is expected to be a new potential solution for these obstacles.

GO can be described as single layer of graphite decorated with random distribution of oxygen functional groups, mostly of epoxy (C—O—C) and hydroxyl groups (C—OH) at the edges and basal planes, combined with non-oxidized regions where sp^2 hybridization are preserved [18,19]. These functional groups are the result of oxidizing graphite in a strong acid solution [20,21], where monolayer flakes/sheets of GO with less than 1 nm of thickness [22] can be obtained in a form of aqueous solution. Hence, we will be able to produce large-size GO films by simple methods, such as spin-coating [23] and drop-casting [23] on desired substrates. This can be the fundamental step to fabricate GO films for further applications in mass production scale. To obtain substrates suitable for the GO film formation, our group proposed a method of changing a negatively-charged Si oxide substrate surface to a positively-charged surface by depositing (3-aminopropyl)triethoxylsilane (APTES) self-assembled monolayers (SAMs) in an aqueous solution [24]. As a result, the repulsive force between negatively-charged GO flakes and oxide substrates can be overcome, resulting in a strong attractive force to fabricate large-area monolayer GO films that cover the whole substrate surface. However, GO is almost insulating [23,25] due to the fact that a considerable part of sp^2 bonded carbon atoms with non-localized π electrons are lost and sp^3 hybridized states are formed during the oxidizing process of graphite, degrading its electrical properties. Therefore, for further applications involving electrical conductivity, GO films need to be converted into reduced graphene oxide (rGO) films. To date, there are various techniques to reduce GO, such as chemical reduction method [26–28] and thermal reduction (annealing) method [29–34] where its electrical conductivity can be restored. Yet, even after reduction process, it is still a challenge to obtain rGO that has near-pristine graphene quality because disruption of the carbon plane occurs during the reduction process to

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remove the oxygen functional groups [22]. Therefore, it is crucial to optimize the reduction process of GO films where high conductivity of rGO films with improved graphitic structure and quality can be obtained for further applications.

Thermal annealing method is an effective technique to reduce GO films, especially in large wafer-scale for mass production. Several literature reports show promise in the low temperature thermal annealing method [35–37], where GO films were annealed at temperatures lower than 300 °C [35–37]. However, the demands of a very long reduction time [35], small-area [36] and low electrical conductivity of the conventional rGO films [35,38] are some of the drawbacks that need further improvement. Although Zhao et al. demonstrated synthesis of large-area GO sheets with maximum area that can reach up to several mm^2 [39], it is still difficult to control the size and fabricate continuous films due to the randomness of lateral shapes and sizes of each GO flakes [39,40]. Moreover, high densities of voids or vacant areas still exist [24] between the GO flakes that will cause non-uniformity and low electrical conductivity of the films. In our previous work, we have investigated the morphology of GO films annealed in various atmospheres such as methane (CH_4) and hydrogen (H_2) [24]. Under CH_4 atmosphere, electrical conductivity of the rGO films was greatly improved when the voids between GO flakes were filled with carbon-related materials. However, unlike normal chemical vapor deposition (CVD) synthesis of graphene, where transition metals act as the catalyst for the graphene synthesis [12,13,16,17,41], there is still little knowledge on the best condition for the thermal annealing of GO films and the effect of the new graphene synthesis at the edges towards highly conductive and continuous rGO film fabrication.

In this study, by focusing on the amount of CH_4 flow rate and reduction time, we have investigated the morphological changes of large-area monolayer GO films during CH_4-assisted thermal annealing process and the role of CH_4 in the restoration of electrical conductivity by comparing it with different reduction processes using another atmosphere. For a highly conductive film, we propose the importance of fabrication of continuous rGO film with improved graphitic crystalline structure by connecting the randomly separated rGO flakes. As a result, we have restored the entire film conductivity and fabricated very conductive rGO films to only about one order of magnitude higher than that of pristine graphene (400 Ω) [1].

2. Experimental procedures

GO water dispersion that has a concentration of about 2.78 wt% was prepared from commercially available high-purity natural graphite powder (99.97%, SEC Carbon, SNO-3000) of 3 mm size based on the modified Hummers' method [20,42]. Si substrates with average size of 5 mm × 5 mm and 300 nm of SiO_2 layer were cleaned in a mixed solution of H_2SO_4 and H_2O_2 (volume ratio, 3:1) for 10 min at 90 °C, and then ultra-sonicated in deionized (DI) water for 5 min. The SiO_2/Si surfaces were modified into positively-charged surface by liquid phase deposition of a mixture of dehydrated toluene (99.5%) and APTES (98%, SIGMA-ALDRICH) solution [24]. GO films were fabricated by drop-casting 20 μl of GO water dispersion onto the APTES/SiO_2/Si substrates. Then, the samples were dried in vacuum for 30 min. In order to remove extra multilayer GO flakes, the samples were ultra-sonicated in DI water for 60 s. Finally, only monolayer GO films were prepared [24].

GO films were annealed by using atmospheric pressure CVD (AP-CVD, First Nano) equipment. First, the samples were heated in the quartz-tube furnace for 15 min until the temperature reached 1000 °C in Ar flow. Next, GO films were annealed at 1000 °C in CH_4 atmosphere. During the reduction process, H_2 was used as the catalyst for the dissociation of CH_4 gas [43] and for the elimination of oxygen-functional groups [25] while Ar was used as carrier gas. In 'Experiment1', GO films were annealed for 30 min in different CH_4 flow rate. In 'Experiment2', GO films were annealed in different reduction time while keeping the CH_4 flow rate constant at 1000 sccm. In 'Experiment3', GO films were annealed in only Ar atmosphere, which was similar to as-reported thermal reduction of GO films [44]. H_2 was not used in 'Experiment3' in order to avoid the etching of rGO flakes from the edges [24,45,46]. However, we used H_2 [24,25] in 'Experiment4' to investigate the relationship between the film quality and its entire conductivity by effectively eliminating the oxygen functional groups. The details about all reduction processes are summarized in Table 1. After the annealing processes were completed, samples were cooled to room temperature in Ar flow.

The morphological changes of the samples were analyzed by using contact mode of atomic force microscopy (AFM) manufactured by Hitachi High-Tech Science (SPI4000/E-sweep). For AFM observation, besides the usual topographic images, frictional images were taken in order to differentiate between the SiO_2 surfaces and the rGO flakes after reduction owing to the difference in their hydrophilic or hydrophobic properties. In addition, Nano/Pico Current AFM mode was also used to analyze the local conductivity of the rGO films. Raman spectroscopy of the GO and rGO films were obtained by using a JASCO Laser Raman Spectrophotometer (NRS-300), which is equipped with a 532 nm wavelength laser light, 1800 mm^{-1} gratings and a 100× objective. We investigated the electrical properties of the GO and rGO films using four-point probe transport measurement at room temperature. A total of 10 different measurements were taken for each samples and the average sheet resistance values were calculated. X-ray photoelectron spectroscopy (XPS, Quantera SXM) was used to determine the oxygen compositions of the samples before and after the reduction processes. Finally, the surface of rGO films was observed by using scanning electron microscopy (S-4700, Hitachi High-Tech Science) at room temperature.

3. Results and discussions

Large-area GO films that cover the whole substrate surface were prepared on the APTES/SiO_2/Si substrates [24], as shown in Fig. 1. For each of the GO films, only monolayer GO flakes were observed in AFM images, corresponding to 0.7–1.0 nm of thickness [22,24]. Owing to the oxygen functional groups that were still bonded to both sides of the graphene plane, the apparent thickness before reduction was larger than that of graphene derived from graphite.

Fig. 2 shows AFM images of rGO films annealed for 30 min in 4 sccm (a–b), 30 sccm, (c–d) 200 sccm (e–f), 500 sccm (g–h) and 1000 sccm (i–j) of CH_4 flow rate at 1000 °C. The top row of Fig. 2 (a, c, e, g, i) represents typical AFM topographic images while the bottom row (b, d, f, h, j) represents the frictional images. For the frictional images, brighter regions correspond to the oxide substrates where large frictional force was observed due to the hydrophilic nature of SiO_2 surface. First, after reduction in 4 sccm of CH_4 flow rate (Fig. 2a–b), we

Table 1
Details of the annealing parameters for each experiment.

Experiment	Annealing temperature [°C]	CH_4 [sccm]	H_2 [sccm]	Ar [sccm]	Time [min]
1	1000	4,30,100,200,500,1000	15	500	30
2	1000	1000	15	500	5,10,30,45,60,90
3	1000	0	0	500	5,10,30,45,60,90
4	1000	0	500	500	60

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