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Fabrication of reduced graphene oxide micro patterns by vacuum-ultraviolet irradiation: From chemical and structural evolution to improving patterning precision by light collimation

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ABSTRACT

Time evolution of the chemical and structural properties of vacuum-ultraviolet (VUV) reduced graphene oxide (rGO) were studied by X-ray photoelectron spectroscopy and Kelvin-probe force microscopy to reveal the mechanism of VUV photoreduction, which can be ascribed to the local photochemical process on oxygen-containing functional groups. The difference in the efficiency between VUV and ultraviolet was demonstrated and the mechanism was discussed. The lateral electrical conductivity of VUV-produced rGO bilayer was measured by conductive atomic force microscopy, which was found to be higher than rGO monolayer due to the formation of new conductive paths between layers. The precision and resolution of VUV photo-reductive patterning was improved by collimating the VUV light. This new approach succeeded in fabricating highly-resolved 1 μm wide conductive rGO patterns on SiO_2/Si substrate.

1. Introduction

As an oxygen-decorated derivative and a widely-studied precursor of graphene, graphene oxide (GO) has distinctive characteristics compared to graphene. The most important advantage of GO and its corresponding reduced material, reduced graphene oxide (rGO), is that easy mass-production is already available [1], which makes it possible to take advantage of their special mechanical, optical and electrical properties for practical applications [2–4]. Compared with the commonly utilized thermal [5] and chemical [6] reduction of GO, the photoreduction processes demonstrate their special advantages, *e.g.*, higher efficiency, precise control of the oxygen-containing functional groups, feasibility of fabricating rGO micro-patterns along with reduction, less energy consumption and non-release of toxic pollutants [7]. Photoreduction can be categorized into photothermal reduction which utilize laser [8] or camera flash [9] generated heat and photochemical reduction which excite GO by ultraviolet (UV) [10,11], vacuum-ultraviolet (VUV) [12,13] or extreme UV (EUV) [14] light and promote photochemical reactions to remove oxygen from GO.

Practical UV and VUV light sources are expected to be good candidates for fabricating the micro-scaled GO and rGO patterns on solid-state substrates [15,16]. Our group has demonstrated a VUV reductive patterning method which adopted a quartz photomask to define the GO and rGO periodic patterns, as shown in Fig. 1 [12,15]. This method has adaptability to conventional photolithography instruments and quartz photomasks, which demonstrate obvious advantages to realize high throughput, wafer-scale patterning of GO by low cost light source [12]. However, there were still critical questions concerning the photoreduction mechanism, unintended low electrical conductivity and inevitable mismatch of patterns after long-time irradiation. Matsumoto et al. have reported the UV reduction of GO on a substrate in H_2 and N_2 environment, at which a 67 mW cm^{-2} high-pressure Hg lamp was utilized to irradiate GO for 2 h [10]. A self-photocatalytic mechanism was proposed. The electron-hole pairs were generated from the π-π* transition of C=C under UV irradiation and cause the redox reaction in GO [17]. Although the total UV exposure dose of *ca.* 480 J cm^{-2} was much higher than the VUV exposure dose of *ca.* 40 J cm^{-2} that we previously reported, the final oxygen/carbon atomic ratios ($R_{O/C}$)

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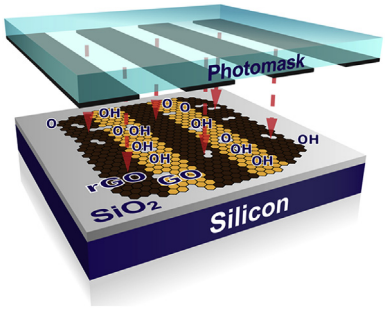

Fig. 1. Illustration of the VUV photo patterning. (A colour version of this figure can be viewed online.)

reached a similar value at 0.25–0.29 [12]. That raised a question on what is the original difference between UV and VUV reduction of GO. Besides, the previously reported VUV photoreductive patterning of GO achieved in fabricating 5 μm wide rGO lines at 10 μm. However, it shows apparent patterning mismatch when increasing the exposure time, which hindered a sufficient reduction of GO and a consequent low electrical conductivity.

Here, we report a study of VUV reduced GO in high vacuum by using X-ray photoelectron spectroscopy (XPS) and Kelvin probe force microscopy (KFM), which provide a deep understanding of the mechanism of VUV photochemical reduction of GO and its difference from UV reduction. Based on the elemental analysis results, the photochemical reactions were clarified. The higher reduction efficiency of VUV reduction than UV reduction was explained. KFM demonstrated the local variation of surface potential during reduction, which revealed that the VUV reduction did not homogeneously progress in GO. By using conductive atomic force microscopy (CAFM), the improvements in conductivity of the rGO bilayer and in-planar structure of rGO were studied. The origin of the VUV photopatterning mismatch was clarified to be the tilted incident light. A hollow column was used to semi-collimate the VUV light, which effectively reduced the mismatch. The reduction level of the rGO patterns achieved a saturated state and 1 μm conductive patterns were successfully fabricated.

2. Experimental

2.1. Preparation of GO

GO sheets were prepared through a modified Hummers' method as described in Ref. [1]. After preparation, GO sheets were dispersed in water (ultra-pure water with a resistivity of 18.2 MΩ cm, produced by RFD250NB, Advantec) at the concentration of *ca.* 0.5 g L^{-1}.

2.2. Photochemical reduction and patterning process

A highly doped p-type silicon (001) substrate with 90 nm thermal oxides (Electronics and Materials Co., Ltd.) was utilized as the substrate and was carefully cleaned to remove impurities and hydrophilically modified by a VUV treatment under ambient air. (See details in Section 1 in Supplementary data). After that, GO was spin-coated onto the substrates at 2000 rpm by using a spincoater (SC2005, Aiden Co. Ltd.). The sample was then set into a high vacuum (<10^{-3} Pa) chamber (manufactured by Sensors and Works) and irradiated by VUV light (172 nm, UER 20-172, Ushio Inc.) at 1 cm distance from the lamp window with power density of 13.8 mW cm^{-2} (See Fig. S1, Supplementary data). The power density of the VUV lamp was measured in N_2 environment by an accumulated UV meter (UIT-150, Ushio Inc.). For comparison, GO was also reduced by irradiating UV light (high pressure Hg lamp, REX-250, λ = 240 nm–440 nm Asahi spectra Co., Ltd.) on GO coated SiO_2/Si substrate at 100 mW cm^{-2} in a high vacuum (<10^{-3} Pa) chamber. The power density of the UV lamp was measured by a laser power meter (PM-335, Neoark Co.).

The patterning experiments were conducted as follows: a GO spin-coated substrate was set into the high vacuum chamber (<10^{-3} Pa) and then irradiated by VUV (172 nm, 2.7 mW cm^{-2}, See Fig. S4a, Supplementary data) at 5 cm via a photomask (100 nm thick Cr patterns on a 2 mm thick quartz plate – *ca.* 90% transparency at 172 nm). A hollow column was utilized to collimate VUV light to reduce the mismatch of pattern (See details in Section 4, Supplementary data).

2.3. Elemental and structural characterization

The elemental analysis of the samples was conducted using X-ray photoelectron spectroscopy (XPS, ESCA-3400 electron spectrometer, Shimadzu). An Mg target was applied with accelerating voltage and current of 10 kV and 10 mA, respectively. The chamber pressure during the measurement kept at *ca.* 5×10^{-7} Pa. The pass energy for the measurement was 75 eV. XPS analyses were conducted to reveal the time evolution of each of the functional groups and $R_{O/C}$ (See details in Section 3, Supplementary data). The micro Raman spectroscopy (μRS) measurements were conducted with a Horiba XploRA Raman microscope that uses a 532 nm laser as the excitation source. The KFM observations were made using an Asylum MFP-3D atomic force microscope (AFM, Oxford Instruments) with Rh-coated-probe cantilever (SI-DF3-R, 1.6 N m^{-1}, 23 kHz, Hitachi Hi-tech Co. Ltd.). KFM surface potential images were acquired in lift-mode under an ambient environment (15–25 °C with a relative humidity of 30–40%). The as-coated GO was also subjected to evacuation before measurement, which helped to create a similar condition to the irradiated samples. CAFM was also performed on the same AFM to measure the electrical conductivity of rGO. Before the electrical measurement, a Ti/Au electrode (10 nm for each, Ti layer acting as an adhesion layer) was deposited onto reduced or patterned samples through a shadow mask to form an electrical contact. A home-built transimpedance *I–V* amplifier with a 1 GΩ feedback resistor was used to amplify the current signal and a Rh-coated-probe cantilever [SI-DF3-R (100 nm Rh coated), 1.6 N m^{-1}, 23 kHz, Hitachi Hi-tech Co. Ltd.] was used for mapping the local current from the samples. A built-in optical microscope assisted the observation of the target rGO sheet. The tip bias was set to be −1 V to ensure that no redox reaction happened on the GO or rGO [18]. The applied tip load was 17.4 nN to keep a good electrical contact. The optical microscopic images were acquired by an optical microscope (Eclipse, ME600, Nikon Co.).

3. Results and discussion

3.1. Stepwise study of VUV photoreduced GO

The VUV light irradiated GO on the SiO_2/Si substrate in the high vacuum; this is called the HV-VUV process hereafter. The elemental composition and chemical bonding evolution of GO and rGO were analyzed by XPS elemental analysis. The C1s core-level XPS spectra of GO and the rGO after 32 min (namely rGO_{32}) irradiation are shown in Fig. 2a and b. All the scales of the spectra were calibrated to the Si2p (SiO_2) main peak at *ca.* 103.5 eV and normalized to the intensity of the C1s main peak. The typical C1s spectrum of GO contained two main peaks at around 284.8 eV and 286.8 eV, which originated from the carbon-bonded carbon and the oxygen-bonded carbon, respectively. To better understand the evolution of the