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Improvement of gas sensing behavior in reduced graphene oxides by electron-beam irradiation

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ABSTRACT

We first report the mechanism of gas sensing improvement of reduced graphene oxides (RGOs) by electron-beam irradiation. We have irradiated the RGO samples by the electron beam with doses of 100 and 500 kGy. Raman spectra indicated that electron-beam irradiation generates defects. X-ray diffraction and X-ray photoelectron spectroscopy and initial resistance data consistently suggest that oxygen functional groups were increased by the electron-beam irradiation, with them being decreased by increasing the dose from 100 to 500 kGy. By the sensing test with respect to NO_2 gas, we revealed that the NO_2 response was increased not only by the electron-beam irradiation but also by increasing the electron dose. We revealed that the mechanism of the electron-beam-induced improvement of gas sensing behavior was dependent on the amount of electron dose. While the oxygen functional groups are likely to play a key role in enhancing the adsorption behavior of NO_2 molecules in case of 100-kGy irradiation, further sensing enhancement at 500-kGy irradiation originates from the non-oxygen defects. The results suggest that the electron-beam irradiation can be a useful tool to turn the RGOs into more favorable sensing materials.

1. Introduction

Graphene has been highly expected to be an ideal gas sensor, because of its peculiar characteristics, including nanometric thickness, high electrical conductivity, high aspect ratio, and good mechanical property. Graphene-based gas sensors will be able to detect the adsorption of individual molecules, for the following reasons [1]. First, graphene has low Johnson noise owing to its metallic conductivity. Second, it has a highest surface-to-volume ratio, with the whole volume being exposed to surface adatoms. Third, its crystalline integrity allows few defects and thus a low level of excess noise.

Actually, recent studies on the interaction of graphene with gas molecules have indicated that it can act as a good sensor [1–8]. Schedin and co-workers [1] have shown that the increase in the charge carrier concentration induced by gas molecules adsorbed on the surface of graphene can be used to fabricate sensitive gas sensors.

Additionally, the two-dimensional (2D) feature of graphene on substrates matches with the well-developed silicon integration technologies. Accordingly, graphene has been used for detecting a variety of gases, including NO_2 [9], NH_3 [10], CO_2 [11], O_2 [12], and H_2 [13].

In spite of its ideal sensing capability, it has some drawbacks, which include the inferior adsorption probability of detection gas. This drawback may originate from the perfect crystallinity of the graphene. In order to improve the adsorption property, it is necessary to functionalize or modify the surface.

It has recently been revealed that the electron-beam irradiation changed the characteristics of graphene. For example, it generated nanopore, slit [14], hillock [15], and vacancies [16]. Also, by means of the electron-beam irradiation, Raman spectrum has been slightly changed [17] and the shift of charge neutral point in graphene field effect transistor was reported [18].

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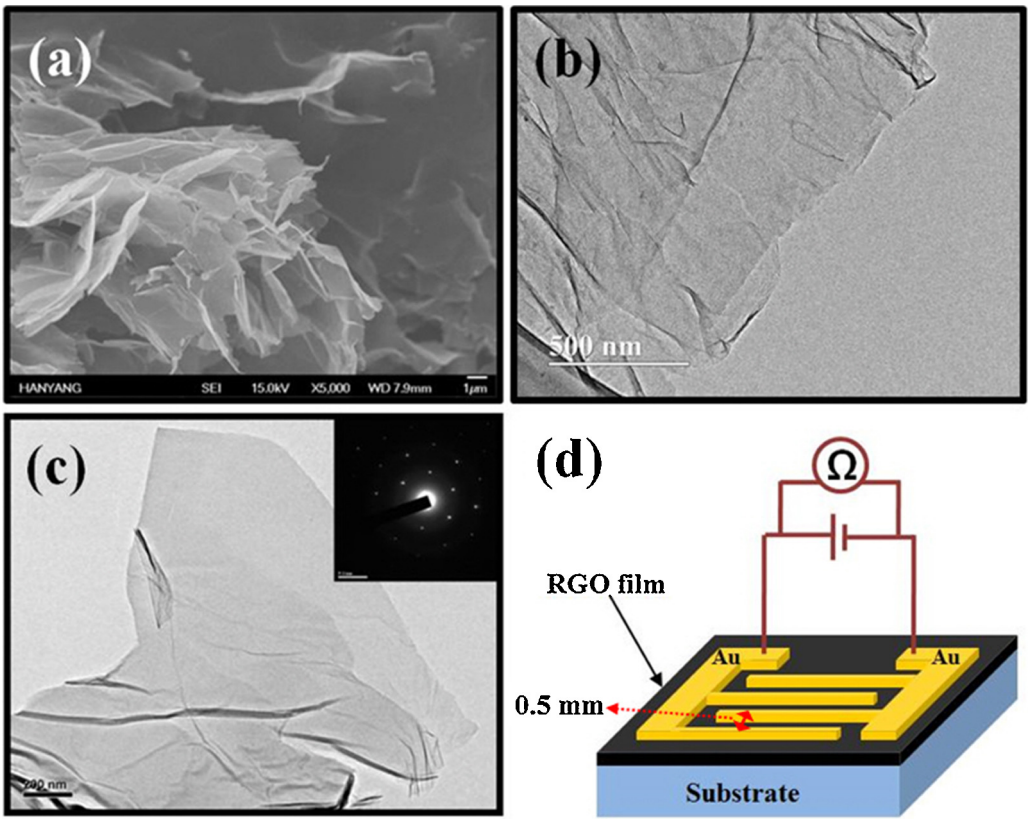

Fig. 1. (a) SEM and ((b) and (c)) TEM images of (b) few-layered and (c) single-layered RGO films (Inset: SAED pattern). (d) Schematic of a sensor fabricated with the RGO films.

In the present work, we have irradiated graphene with electron beams with an energy of 2 MeV of different doses. We have studied the relation between the electron-beam irradiation and sensor behavior of the graphene films. In more detail, we have utilized a reduced graphene oxide (RGO), which is a low-cost form of graphene [19]. The RGO could be fabricated by reducing graphene oxide, which can be easily produced on a large scale.

In spite of its advantages, the RGO has suffered from poor sensing performances toward gases, including low sensitivity and irreversibility [20,21]. Accordingly, up to the present, numerous researches were carried out to improve the sensing capabilities of RGOs. The improvement of sensing performances were explored by the use of chemical modification [22], palladium (Pd)-decoration [23], RGO-polyaniline hybrid [24], and inkjet printing of RGO films on polyethylene terephthalate [25]. In addition, the gas sensors based on genuine RGO were prepared by using the RGOs which were reduced by pyrrole [26], *p*-phenylenediamine [27], and by using the spin-coating of hydrazine dispersions on interdigitated planar electrode arrays [10].

Up to the present, the changes of sensor characteristics by the irradiation of Au ion [28], N^+ ion [29], and UV light [30], have been investigated. However, to our best knowledge, this is the first report on the variation of sensing characteristics of graphene sensors by means of the electron-beam irradiation. For evaluating the sensing behaviors, we have adopted the NO_2 gas, which is a typical oxidizing gas. By monitoring the changes in the NO_2 sensing characteristics, we will verify the effects of electron-beam irradiation. We found that the oxygen functional groups created by the electron-beam irradiation play a key role in enhancing the adsorption behavior of NO_2 molecules.

2. Experimental

We have synthesized GOs by using a modified Hummers' method from graphite powders, with the same procedure being described in previous literature [31,32]. By adding hydrazine monohydrate and subsequently heating at $150 \pm 5\,^{\circ}C$ in an oil bath, the exfoliated GO nanosheets were transformed to RGO. The redispersion in DMF and the subsequent mild sonication led to the formation of a homogenous RGO suspension. Following this, the RGO films were prepared by coating the RGO suspension on quartz substrates. They were heated at 250 °C for 180 min to remove the incorporation of moisture. Subsequently, the temperature was raised to 1100 °C in 60 min and the RGO films were annealed for 30 min. The temperature was increased at a rate of 10 °C/min. Finally, the samples were naturally cooled down to room temperature. All heating and cooling processes were carried out with gas flowing of $(Ar + H_2)$ at a rate of 100 sccm. The thickness of the RGO films was observed to be in the range of 100–300 nm.

The as-fabricated RGO films were irradiated with an electron beam. The used equipment was the ELV-8 electron accelerator (EBTech, Daejeon, Korea). Electron beams with an Accelerating voltage, dose, beam current, and pulse duration of electron beam was set to 2 MV, 100–500 kGy, 1 mA, and 400 ps, respectively. The samples were irradiated in air at room temperature in the absence of a vacuum system.

The RGOs were analyzed by a scanning electron microscope (SEM, JEOL, JSM 5900 LV, Japan). X-ray diffraction (XRD) was acquired by using Cu $K\alpha$ (wavelength at 1.54 Å) radiation, 40 kV, 30 mA, Rigaku, Japan. High-resolution transmission electron microscopy (HR-TEM) was carried out with a TECNAI 20 microscope operated at 200 kV. Raman spectroscopy measurements were carried out with an excitation laser wavelength of 532 nm, at