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Graphene-based nitrogen dioxide gas sensors

G. Ko, H.-Y. Kim, J. Ahn, Y.-M. Park, K.-Y. Lee, J. Kim *

Department of Chemical and Biological Engineering, Korea University, Seoul 136-701, Republic of Korea

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ABSTRACT

In this study, we demonstrated that graphene could selectively absorb/desorb NO_x molecules at room temperature. Chemical doping with NO_2 molecules changed the conductivity of the graphene layers, which was quantified by monitoring the current–voltage characteristics at various NO_2 gas concentrations. The adsorption rate was found to be more rapid than the desorption rate, which can be attributed to the reaction occurred on the surface of the graphene layer. The sensitivity was 9% when an ambient of 100 ppm NO_2 was used. Graphene-based gas sensors showed fast response, good reversibility, selectivity and high sensitivity. Optimization of the sensor design and integration with UV-LEDs and Silicon microelectronics will open the door for the development of nano-sized gas sensors that are extremely sensitive.

1. Introduction

Graphene has recently emerged as a highly important material for applications in nanoelectronics, flexible electronics, sensors and solar cells due to its unique two-dimensional carbon nanostructure that exists in a honeycomb lattice [1–3]. Wafers covered with a single, bi- or few layers of graphene (FLG) can be processed using conventional photolithography techniques. In sharp contrast, devices based on nanowires, nanorods and carbon nanotubes mostly require expansive electron-beam lithography or focused-ion beam techniques for device fabrications. Several methods have been developed to obtain graphene sheets including the 'scotch tape method', which involves simple mechanical cleaving, the reduction of graphene oxide (GO), high temperature vacuum annealing of Silicon Carbide and the epitaxial growth technique [4–7]. Carbon nanotubes (CNTs), which have a one-dimensional carbon nanostructure, demonstrated very promising results in regards to sensing toxic gases such as NH_3, O_2 and NO_2 [8,9]. Schedin et al. reported that graphene could also absorb NO_2, NH_3, H_2O and CO and could detect individual molecules at very low concentrations [10]. In this study, we employed a simple fabrication process to make two metal contacts to the FLG, which enabled us to monitor the electric currents when various ambients were used. The detection of NO_x gas is especially important because it is one of the most common air pollutants released from industrial complexes and automobiles, and has been known to cause smog and lung diseases such as asthma [11]. Therefore, there is an urgent need for the development of miniaturized, low power consumption, portable NO_x detectors with a very high sensitivity, especially for use in urban areas. In this study, we found that the conductivity of the FLG was changed by the adsorption/desorption process of NO_x molecules in the part-per-million (ppm) range.

2. Experimental details

Graphene was obtained by the mechanical exfoliation of highly ordered pyrolytic graphite (HOPG) [1]. Graphene layers were deposited on a pre-defined SiO_2/Si substrate, where the thickness of thermally-grown SiO_2 was 300 nm. Atomic force microscopy (AFM) was employed to measure the thickness of graphene deposited by the standard 'scotch tape' method [1]. Using this method, the thickness of the graphene layers were found to range from 3.5 nm to 5 nm, which corresponds to 7–10 layers of graphene sheets. The electron-beam lithography technique was used to define and form two metal contacts to the graphene layer, followed by electron-beam evaporation of Pd/Au (20 nm/80 nm) (Insets of Fig. 1). Graphene-based devices were used to obtain the current–voltage characteristics of graphene-based gas detectors at various concentrations of NO_2 gas, which was varied from 100 ppm to 1% at room temperature using an Agilent 4155C parameter analyzer. Gas cylinders with a concentration of 100 ppm, 500 ppm and 1% NO_2 gas was purchased for these experiments.

3. Results and discussion

Fig. 1 shows the schematic diagram of the gas sensing experiments used in this study. NO_2 gas molecules were absorbed/desorbed on the surface of graphene, depending on the ambient conditions [10,14]. Zhang et al. reported that there are three possible adsorption configurations: the nitro, nitrite and cycloaddition configurations [14]. An increase in conductivity can be attributed

* Corresponding author. Tel.: +82 2 3290 3291; fax: +82 2 926 6102.
E-mail address: hyunhyun7@korea.ac.kr (J. Kim).

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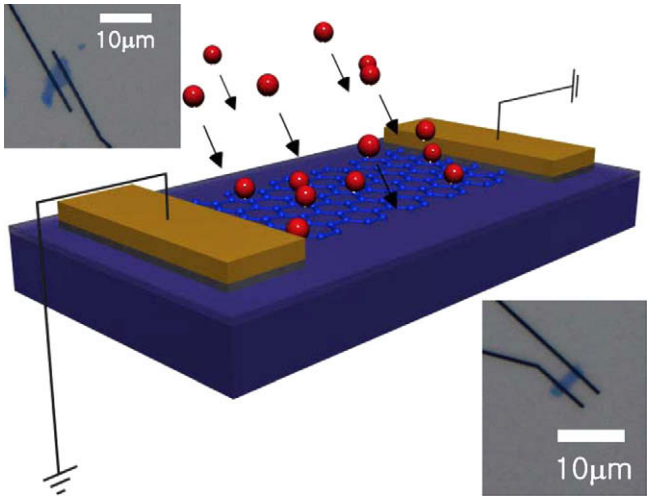

Fig. 1. Schematic diagram of the graphene-based gas sensors (Insets (top and bottom) are the microscope pictures).

to the charge transfer between NO_2 molecules and graphene, where the NO_2 molecules act as an acceptor (Fig. 2) [10,12,14]. This mechanism is also referred to as chemical doping by gas molecules. The sensing mechanism of CNTs has been well established, [13] and the adsorption/desorption properties of SWCNT to graphene is believed to be similar [12]. In addition, the resistance increased when NO_2 gas molecules were not supplied to the system.

Fig. 3 shows the change in conductivity after exposure to a pulse of NO_2 gas. In these experiments, once the graphene was exposed to NO_2 gas, the response in the current–voltage was immediate; however, the recovery (desorption) occurred very slowly. This pattern can be attributed to the chemical reaction on the graphene surface. It has been reported that NO and NO_3 molecules can be generated [13]. In contrast, the desorption time of NO_3 molecules has been experimentally determined to be approximately 12 h at room temperature [13]. A UV lamp was used to expedite the desorption of these molecules.

One of the most important requirements of a gas detector is reproducibility. Therefore, the graphene-based gas detector developed in this study was exposed to a repeated cycling of the ambient gases from air to NO_2 (Fig. 4). In these experiments, there was no sign of deterioration in the sensitivity. In addition, the graphene-based gas sensor was tested using another graphene sheet at

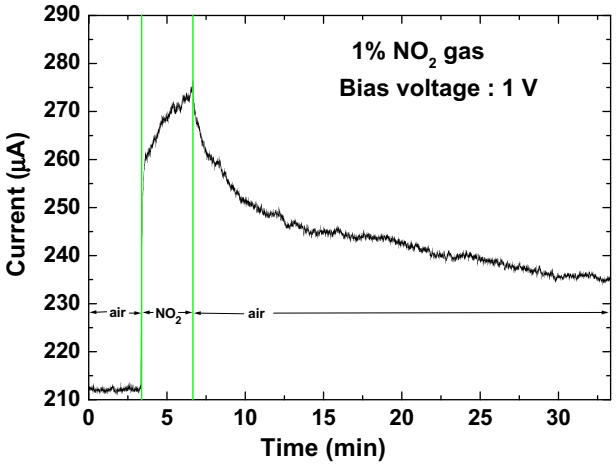

Fig. 3. The time response and decay of graphene-based gas sensors when a NO_2 ambient (1% concentration) was used.

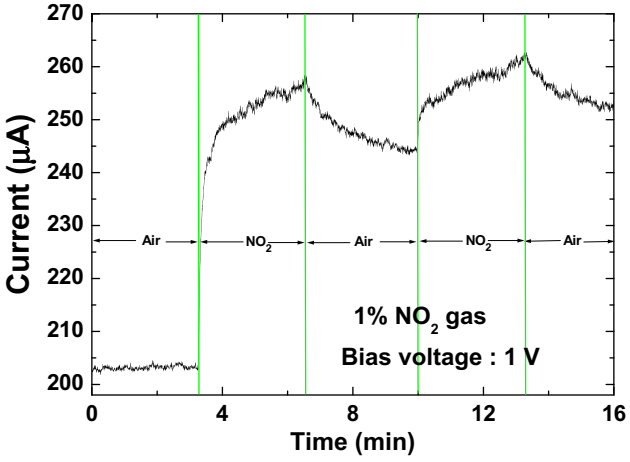

Fig. 4. The reversibility when alternate gas molecules were used.

lower NO_2 concentrations (100 ppm and 500 ppm) (Fig. 5). The sensitivity can be defined by

$$S(\%) = \frac{R_{Air} - R_{NO_2}}{R_{Air}} \times 100\% \quad (1)$$

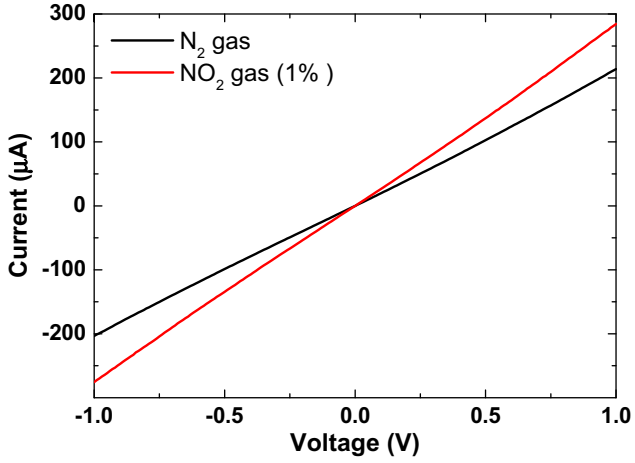

Fig. 2. The current–voltage characteristics under N_2 and NO_2 gas ambients at room temperature.

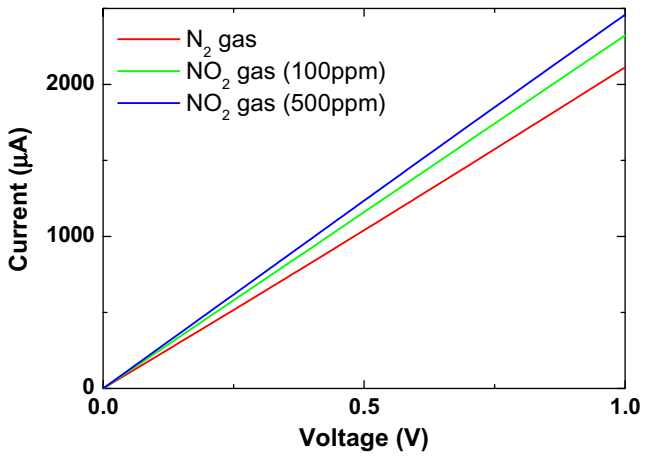

Fig. 5. The current–voltage characteristics when N_2 and NO_2 gas (100 ppm and 500 ppm) ambients were used at room temperature.

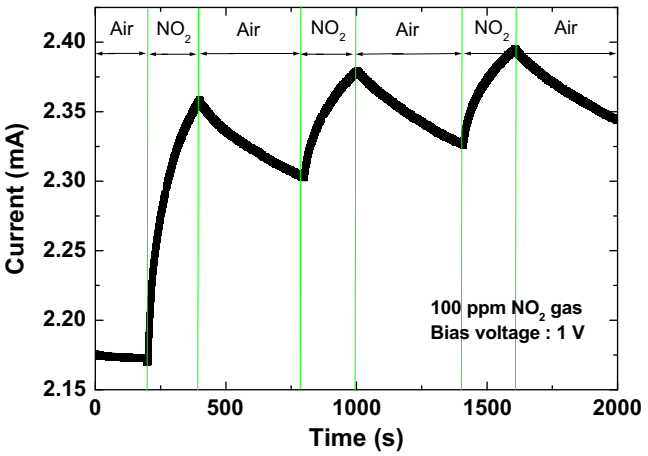

Fig. 6. The reversibility when alternate gas molecules were used under 100 ppm NO_2 gas.

where R_{Air} and R_{NO_2} are the resistances of graphene in air and ambient NO_2, respectively [13]. In this experiment, the S under exposure to 100 ppm and 500 ppm NO_2 gas was 9% and 14%, respectively, without optimization. Fig. 6 shows the response of our graphene-based gas detector under 100 ppm NO_2 gas. Based on these results, the graphene layer has great potential for ultra-sensitive gas detector by the optimization of device structure. The detection of a single gas molecule can be achieved by using graphene-based gas detector because the change in the conductivity of the graphene is quantized in response to NO_2 molecule [10]. In addition, the sensitivity can be also enhanced by using the noble metal [15].

Graphene is a very attractive material for use in gas sensors because half of its entire surface area is exposed to ambient air when a single layer of graphene is used. In addition, it is flexible, transparent and conductive. Furthermore, the air-bridge design, where the entire carbon atoms are exposed to the ambient air, can be used to increase the detection limit of graphene-based gas sensors. Graphene-based devices can be easily integrated with advanced Silicon microelectronics. The selectivity for various gas mixtures can also be improved by using rare-earth metals, which were used in CNT-based gas sensors. By optimizing UV light-emitting diodes (LEDs) with graphene devices, there is a huge potential for the development of fast response/recovery portable graphene-based NO_2 sensor that can detect gases at concentrations as low as 1 part per billion [10].

4. Conclusion

The applicability of graphene-based gas sensors was demonstrated by exploiting the charge transfer mechanism between NO_2 molecules and graphene. The selectivity was tested under air and NO_2 gas ambients. In addition, this novel graphene-based gas sensor displayed good reproducibility when the ambient was alternated. The adsorption rate was much faster than the desorption rate due to the reaction occurred on the graphene surface. The sensitivity was 9% at 100 ppm NO_2 gas, which can be further improved by optimization of the sensor structure and by using a single layer of graphene.

Acknowledgements

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