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# Flexible $NO_2$ gas sensor using multilayer graphene films by chemical vapor deposition

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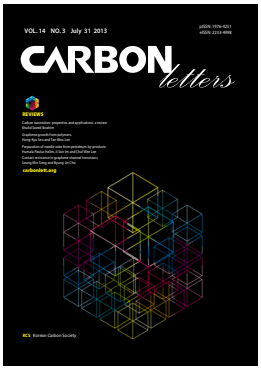


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## Abstract

We report a highly sensitive $NO_2$ gas sensor based on multi-layer graphene (MLG) films synthesized by a chemical vapor deposition method on a microheater-embedded flexible substrate. The MLG could detect low-concentration $NO_2$ even at sub-ppm (<200 ppb) levels. It also exhibited a high resistance change of ~6% when it was exposed to 1 ppm $NO_2$ gas at room temperature for 1 min. The exceptionally high sensitivity could be attributed to the large number of $NO_2$ molecule adsorption sites on the MLG due to its a large surface area and various defect-sites, and to the high mobility of carriers transferred between the MLG films and the adsorbed gas molecules. Although desorption of the $NO_2$ molecules was slow, it could be enhanced by an additional annealing process using an embedded Au microheater. The outstanding mechanical flexibility of the graphene film ensures the stable sensing response of the device under extreme bending stress. Our large-scale and easily reproducible MLG films can provide a proof-of-concept for future flexible $NO_2$ gas sensor devices.

**Key words:** graphene, $NO_2$, gas sensor, chemical vapor deposition

## 1. Introduction

Graphene, a two-dimensional (2D) monoatomic sheet of $sp^2$-hybridized carbons, has attracted tremendous interest from academic and industrial researchers due to its unique thermal, mechanical, and electrical properties. These properties hold particular interest for researchers investigating sensors that can be highly sensitive to the adsorption and desorption of molecules [1-5]. Accordingly, graphene's large available surface area makes it a promising candidate for use as a sensor for chemical and biological detection [6,7]. Recently, a chemical gas sensor using micromechanically exfoliated single-layer graphene showed exceptionally low detection noise levels at room temperature: its high sensitivity resulted from the extremely high mobility of carriers [8]. Although a high response to gas molecules was achieved in that report, the mass producing and integrating of graphene into a real device remained a challenge to be overcome. With that goal in mind, many researchers have developed high-performance $NO_2$ gas sensors using reduced graphene oxide sheets, obtained from high temperature annealing [9] or a chemical conversion with hydrazine [10] and ascorbic acid [11], for application as a low-cost, simple and practical sensor device. More recently, Joshi et al. [12] reported a $NO_2$ gas sensor based on graphene films and ribbons grown on Ni-coated Si substrates using the microwave plasma enhanced chemical vapor deposition (MPECVD) method. In spite of the potential advantages of the CVD-grown graphene films for novel gas sensors, their sensitivity and response time was relatively weak and not yet

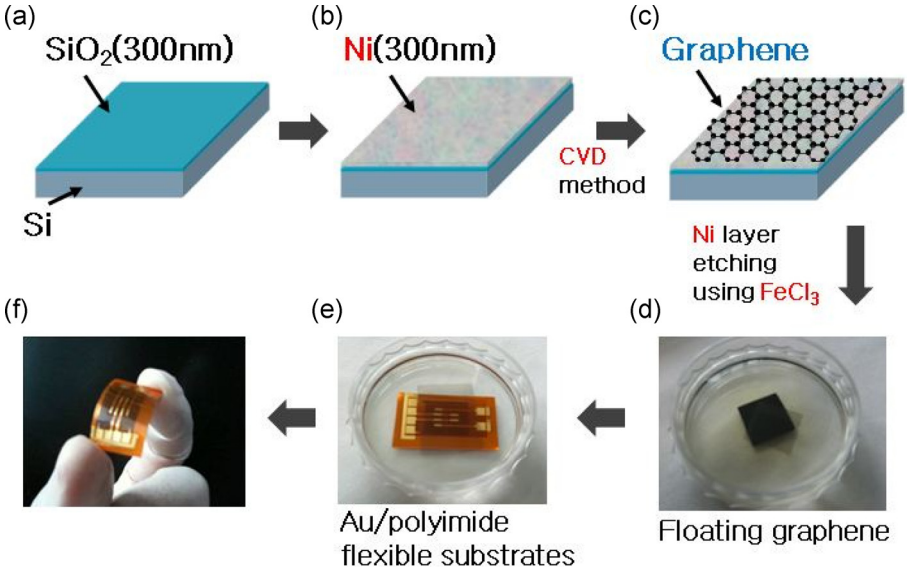


**Fig. 1.** Schematic diagrams of the fabrication process for the gas sensor based on chemical vapor deposition (CVD) graphene. (a) $SiO_2$/Si substrate. (b) Ni (300 nm) deposition on $SiO_2$/Si by e-beam evaporation process. (c) multi-layer graphene (MLG) growth on Ni/$SiO_2$/Si using chemical vapor deposition process. (d) Floating graphene on DI-water for rinsing after etching Ni layer using $FeCl_3$. (e) Floating graphene on DI-water for transferring to Au/polyimide substrates. (f) Transferred MLG on Au/polyimide substrates.

satisfactory for high performance sensing applications.

Here we report the fabrication and characterization of a gas sensing system based on multi-layer graphene (MLG) films synthesized by the CVD method. The gas sensor uses relatively simple fabrication processes and graphene, producing a remarkably improved gas sensing performance which is retained even in an extreme bending state [13]. This was achieved because of the high surface sensitivity of MLG films and their strong mechanical flexibility.

## 2. Experimental

Fig. 1 schematically shows a procedure for fabricating our flexible $NO_2$ gas sensor based on CVD graphene films [14,15]. An electron-beam evaporator was used to deposit a 300 nm thick Ni layer on a dielectric substrate ($SiO_2$/Si). The crystallinity of the Ni layer was controlled by its thickness, annealing, and the nature of the substrate [16]. Then, the Ni/ $SiO_2$/Si substrate was heated up to 1000°C inside a quartz tube under an argon atmosphere, followed by injection of the reaction gas mixture (Ar : $H_2$ : $CH_4$ = 500 : 160 : 125 sccm) for a few minutes. While cooling to room temperature, MLG was grown on the Ni substrate with a thickness range of 7 to 15 nm, depending on annealing time, reaction time, gas mixture and cooling rate. To transfer the MLG to an arbitrary substrate, the Ni layer was etched with a $FeCl_3$ (Iron III chloride) solution [17]. The isolated MLG was rinsed with DI-water several times over 30 min to remove $FeCl_3$ residue. The rinsed MLG was transferred to Au/polyimide flexible substrates and baked at 60-90°C for a few minutes in order to increase the adhesion between the MLG and Au/polyimide substrate. As shown in Fig 1f , the $NO_2$ gas sensor device shows mechanical flexibility.

The gas sensing properties of the device were measured using a digital multi-meter (HP 3458A) and a dc power supply (HP E3610A). $N_2$/$NO_2$ gas mixtures at a fixed flow rate of 1000 sccm were introduced into a glass chamber using mass flow controllers, and all data were recorded on a desktop computer. Raman spectra were measured by Raman microscope (CRM 200 Wi-tech, 532 nm laser wavelength). High resolution transmission electron microscopy (HRTEM) images were taken using a JEOL JEM-2100F operating at an accelerating voltage of 200 kV.

## 3. Result and Discussion

Fig. 2a shows the schematic illustration of our flexible $NO_2$ gas sensor based on MLG, which consisted of a polyimide flexible substrate, Au electrodes (1 mm width), a Ni/Cu microheater, and MLG film. The cross-section HRTEM image, shown in Fig. 2b, clearly confirms the MLG grown with 7-8 layers on Ni metal substrate. Raman spectra of the graphene film as transferred to the surface of an oxidized Si wafer are shown in Fig. 2d.. Two spectra taken at different positions marked in the optical image of Fig. 2c indicate that the film mostly consists of a few layers of graphene with a high G to 2D peak ratio. [18-,19]

Fig. 3a shows a typical $NO_2$ sensor response from the MLG film operated at room temperature. The gas sensitivity (S) was defined as $S = \Delta R / R_0$, where $R_0$ is the initial resistance when exposed to pure $N_2$, and $\Delta R$ is the change in resistance measured in the presence of the $N_2$/$NO_2$ gas mixture. The variation in resistance was measured upon exposure to $NO_2$ concentrations ranging from 0.2 to 5 ppm in dry nitrogen for 30 min. An initial drop of resistance at the beginning of $NO_2$ exposure was observed. This can be explained by the hole conduction mechanism induced by an electron-withdrawing oxidizer, such as $NO_2$, which has been well reported by Schedin et al. [8] The degree of resistance decrease at 0.2, 0.5, 1, 2, and 5 ppm was calculated to be 11.5, 15.5, 19.5, 26.3, and 38.7%, respectively.

It is notable that our MLG $NO_2$ gas sensor exhibited a higher

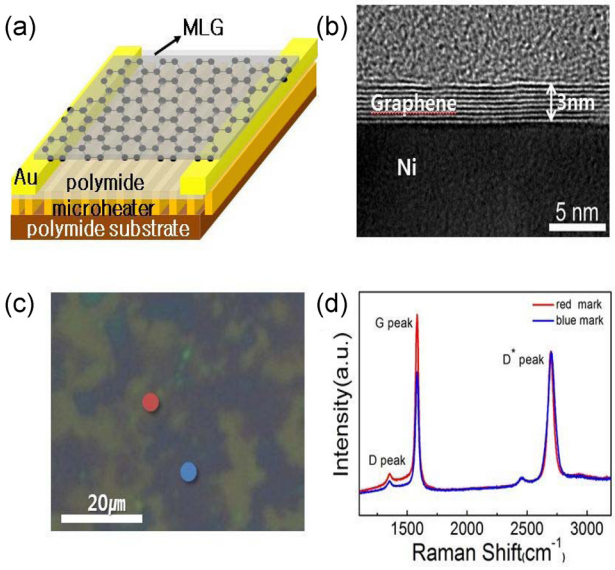


**Fig. 2.** (a) A schematic of chemical vapor deposition graphene sensor device. (b) Transmission electron microscopy image of graphene/Ni films (3 nm graphene thickness). (c) Optical microscope image of the graphene (two different color marks with contrast). (d) Raman spectra obtained from two color spot in (c) (532-nm laser wavelength). MLG: multi-layer grapheme.

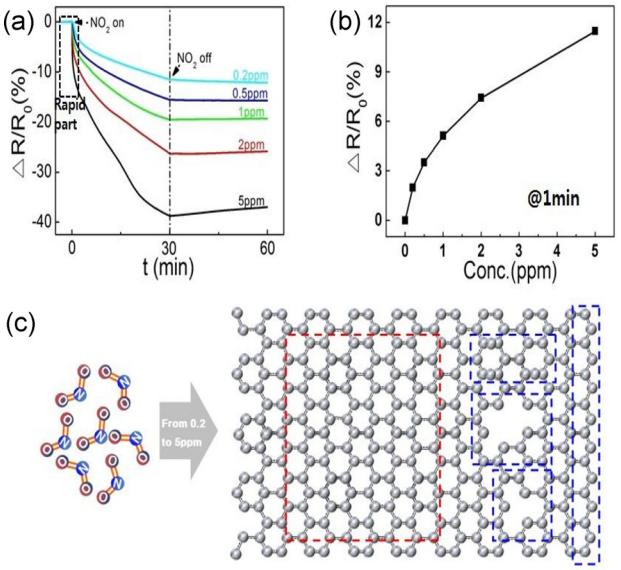


**Fig. 3.** (a) Room temperature $NO_2$ sensing behavior of chemical vapor deposition graphene devices at $NO_2$ concentrations from 0.2 to 5 ppm. (b) Resistance response of multi-layer graphene $NO_2$ gas sensor measured after exposure to $NO_2$ at various concentrations for 1 min. (c) Schematic of graphene sheet consisting of sp2-bonded carbon (red dotted mark), structural defects, vacancies, and edge (blue dotted mark) for reaction with $NO_2$ gas.

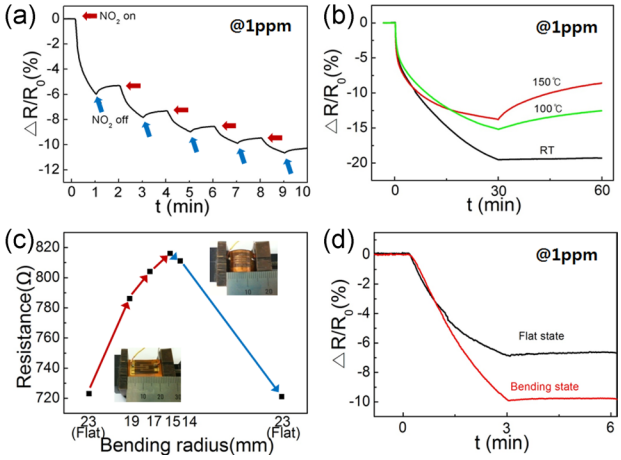


**Fig. 4.** (a) Resistance variation in chemical vapor deposition (CVD) graphene sensor to 1 ppm $NO_2$ every 1 min. (b) Resistance variation in CVD graphene sensor to 1 ppm $NO_2$ from 20 to 150°C. (c) Resistance variation in CVD graphene sensor device as a function of bending radius. (d) Resistance variation of flat and bending states to 1 ppm $NO_2$ gas exposure for 3 min.

sensitivity than other graphene-based $NO_2$ gas sensors [6,9,10, 20]. Furthermore, the maximum response of our MLG device to 5 ppm is 38.7%, about 2.7 times higher than the CNTs/reduced graphene hybrid gas sensor previously reported by our group [13]. The exceptional sensitivity achieved here is deeply related to the unique properties of 2D graphene, with its high surface energy and various defect sites, compared to carbon nanotubes. The response curve, as seen in Fig. 3a, after exposure to $NO_2$ gas for 30 min, can be divided into two parts; a first rapid response and subsequent slow response. The rapid part can be understood to result from molecular adsorption onto low-energy binding sites, such as $sp^2$-bonded carbon, and the slow response is due to molecular interactions with higher-energy binding sites (illustrated in Fig. 3c), such as vacancies, structural defects, and oxygen functional groups, as has been well explained by Robinson et al. Two different types of binding sites also induce the nonlinear behavior seen as a function of $NO_2$ concentration (from 0.2 to 5 ppm), shown in the sensing response graph in Fig. 3b. Clean graphene surfaces respond sensitively to the variation of $NO_2$ concentration, while defect sites react slowly to $NO_2$ concentration. The higher energy binding sites could lead to the enhanced sensing response by providing more binding sites for $NO_2$ adsorption; however, they could delay recovery due to the high binding force between defect sites and $NO_2$ molecules, as is clearly shown in the $NO_2$-off region of Fig. 3a.

Furthermore, as shown in Fig. 4a, when we investigated the variation of resistance of the MLG $NO_2$ gas sensor at 1 ppm of $NO_2$, measured every 1 min, a remarkable resistance response of 5.9% was obtained. However, the desorption of $NO_2$ at room temperature shows a poor response: the resistance signal is unrecovered from the baseline signal. In addition, the pair of adsorption and desorption curves decrease with increasing $NO_2$ exposure time. Since a slow recovery is unfavorable for practical sensor devices, an additional process, such as thermal annealing or Joule heating needs to be introduced. Therefore, we investigated a response that is temperature-dependent at 1 ppm $NO_2$, with temperature increasing from room temperature to 150°C. Fig. 4b shows that the resistance response time at room temperature is faster than at 150°C, whereas the recovery time is slower. Since the thermal treatment removes $NO_2$ lodged within vacancies, structural defects and oxygen functional groups, it can increase the recovery time. On the other hand, this thermal treatment creates an obstacle by preventing to bind higher-ener-

gy binding sites for resistance response. The effective operation of the $NO_2$ gas sensor is therefore performed in two parts, which are, adsorption at room temperature and desorption at 150°C.

The attractive mechanical properties of our MLG $NO_2$ gas sensor allow it to be applied in conditions where flexibility is required. In order to demonstrate its flexibility, the resistance of the MLG $NO_2$ gas sensor was measured under a bending radius from 23 mm (flat state) to 14 mm (bent state) without any injection of gas. As shown in Fig. 4c, as the bending radius decreases from 23 mm to 14 mm, resistance starts to increase from 725 Ω to 813 Ω. Following this, as the bending radius reaches the flat state, resistance almost completely recovers. Fig. 4d shows the variation in resistance for flat and bending states measured at 1 ppm $NO_2$ for 3 min. The resistance response for the bent state demonstrates as good performance as the flat state.

## 4. Conclusions

In conclusion, we have demonstrated a flexible $NO_2$ gas sensor based on CVD-grown MLG, which is the most promising and attractive active material for detecting gas adsorption down to the single-molecule level. Our MLG $NO_2$ gas sensor detected in the sub ppm scale, and has a superior mechanical property that allows it to be bent extremely and still function, which is an asset for various applications. The flexible MLG $NO_2$ gas sensor has outstanding sensitivity (a resistance response of 6.9% and 19.5% for 1 and 30 min, respectively), compared to other graphene-based gas sensors. Solving the major obstacle, namely its slow desorption property related to the vacancies, structural defects and oxygen functional groups of graphene, still remains as a challenge to be addressed, to realize a more practical device.

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