High Performance Nitrogen Dioxide Sensors with Sulfur Doped Graphene And Micro-Hotplatform

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***Abstract*—Nitrogen dioxide sensors with ppb level sensitivity and fast response and recovery were developed by integrating sulfur doped graphene with micro-hotplatform. Sulfur was doped in graphene after its transfer onto the micro-hotplatform through chemical vapor deposition at 500°C. The sensors were sensitive to 5 ppb nitrogen dioxide at room temperature. With the help of heater integrated in MHP, the sulfur doped graphene sensors could quickly recover to the baseline within 5 min. The sensors described here were very promising for practical applications.**

Keywords—sulfur-doped graphene, nitrogen dioxide sensor, ultra-sensitive, micro-hotplatform

I. INTRODUCTION

Graphene, a single or a few layers of sp^2 bonded carbon atoms, has attracted widely attention and research in many areas ranging from academic research to industrial applications since it was found in 2004 due to its unique physical, photonic, and electronic properties [1-4]. Because of their ultra-high specific surface area, high conductivity, and low Johnson noise, graphene materials have been widely explored for the fabrication of gas sensors [5-7]. After the pioneer work reported by Novoselov and co-workers [6], graphene becomes a highly attractive sensing candidate for NO_2, which is a notoriously hazardous gas that can cause not only acid rain but also severe damage to human respiration systems and lung tissues even at ppb level. Therefore, it's imperative to develop ultra-sensitive sensors to detect NO_2 at ppb level or even lower.

Different types of NO_2 sensors using various methods such as thermally reduced graphene oxide, hydrazine-reduced graphene oxide and epitaxially grown graphene have been developed. Lu et al. obtained partially reduced graphene oxide sheets through low-temperature step annealing and the detection limit of the as-fabricated sensors was only 2 ppm [8]. Pearce et al. utilized epitaxially grown graphene and the corresponding sensor devices showed detection limit of 2.5 ppm [9]. Moreover, all these techniques involve complex fabrication process such as troublesome transfer steps. And the recovery time of graphene-based NO_2 sensors was usually as long as tens of minutes or even a few hours.

In this article, we propose an in-situ fabrication method to prepare S-doped graphene NO_2 sensors integrated with micro-hotplatform (MHP). In this method, there is only one transfer process and sulfur is in-situ doped in graphene at 500°C, which eliminates possible defects introduced by multiple transfer and simplifies the fabrication process to the most extent. The as-prepared sensors showed ppb-level sensitivity to NO_2 and could quickly recover to the baseline within 5 min with the help of MHP. The simple and low-cost manufacturing process and the wide availability of chemical vapor deposition (CVD) graphene could lead to cost-effective, practical implementation of graphene sensors.

II. EXPERIMENTAL DETAILS

Micro-hotplatforms (MHPs), in this article, are used as substrates to fabricate sulfur doped graphene gas sensors. MHPs are microelectromechanical systems (MEMS) devices that are fabricated in wafer runs using standard MEMS technology. MHPs have been described elsewhere [10, 11]. Due to their low thermal mass, these devices can be heated at rates up to 10^5 to 10^6 °C/s, which make it suitable as a heating substrate for gas sensors.

After synthesized by CVD, the graphene films were transferred to a MHP using widely used polymethylmethacrylate (PMMA) as support material. We do not directly dope graphene on copper substrate because copper could react with hydrogen sulfide at high temperature. The PMMA was coated onto graphene-copper surface by spinning. After wet-etching of the underlying copper foil by $FeCl_3$ solution, the product PMMA/graphene film was rinsed in deionization water, and then transferred to the MHP. The PMMA was dissolved with acetone. Afterwards, the pristine graphene with MHP was put into CVD system for in-situ sulfur doping. A mixed gas flow of 1000 sccm argon, 40 sccm hydrogen and 20 sccm hydrogen sulfide was introduced into the CVD chamber to dope sulfur in graphene at 500°C which is relatively low compared to traditional annealing temperatures. The doping time was 20 min. After doping, the system was cooled to room temperature with a gas flow of argon. Finally, the sulfur-doped graphene (SG) sensors were fabricated. The fabrication process was shown in Fig. 1.

Raman spectrum and high-resolution transmission electron microscopy (TEM) were used to characterize the morphologies and properties of our S-doped graphene samples. The Raman spectrum was RenishawinVia with a laser wavelength of 532nm and the high-resolution TEM was performed with JEM-2100F operating at 200 kV.

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III. Results And Discussion

After S-doping process, TEM was carried out on a JEM-2100F field emission transmission electron microscope. The S-doped graphene film was transferred to TEM lacey carbon coated grids. As shown in Fig. 2a, the sample consisted of few layer graphene. And there were lots of dark dots appeared after sulfur doping process. The dark dots were S-condensed area resulting from the reaction between hydrogen sulfide with graphene.

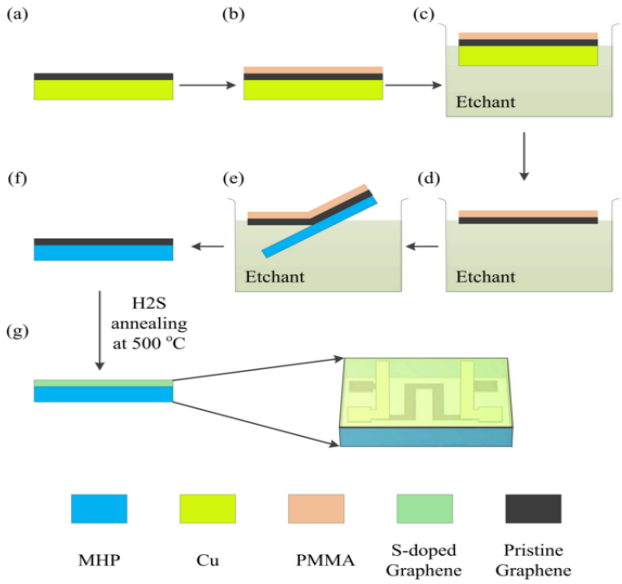

Figure 1: Fabrication process of S-doped graphene sensor integrated with MHP.

The quality of S-doped graphene film was also characterized by Raman spectroscopy in Fig. 2 (b). Raman spectrum is the most effective way to confirm the quality of graphene, which provides a quick and facile structural characterization of graphene [12]. As shown in Fig. 2 (b), without doping the low intensity D band located at 1353 cm^{-1} which indicated that there were fewer defects in graphene lattice. The sharp G band showed good organization of in-plane carbon atoms in the graphene sample. The 2D band around 2690cm^{-1}, a double resonance of D band, was sensitive to the number of graphene layers and the quality of graphene by its intensity and shape. The broader, lower 2D band in Raman spectrum implied that it was few-layer graphene which was in agreement with the TEM results. In S-doped graphene, the strong D band indicated that defects appeared after H_2S annealing which was in agreement with TEM results.

The performances of the gas sensors were evaluated by their resistance decrease upon exposure to NO_2 with a controlled concentration. The response is defined as $\Delta R/R_0$ where ΔR is resistance change and R0 is the resistance of the sensing layer recorded in an atmosphere of N_2. Fig. 3 showed repeated experiments for SG sensors towards 5 ppm NO_2. The sensors worked at RT when exposed to NO_2 and after 10 min exposure, the sensors were heated to 200°C through MHP to recover to the baseline with NO_2 off and N_2 on. Traditionally, graphene based gas sensors had to be annealed at high temperature or illuminated by ultraviolet light to recover to the baseline due to long recovery time [6, 13, 14]. These steps were tedious and time-consuming during a continuous testing. In our work, the SG sensors quickly recover to the baseline through MHP heating. Moreover, no baseline drift was observed for SG sensors during multiple cycling processes. SG sensors described here exhibited good repeatability and quickly recover to the baseline which is a big improvement compared to previous work.

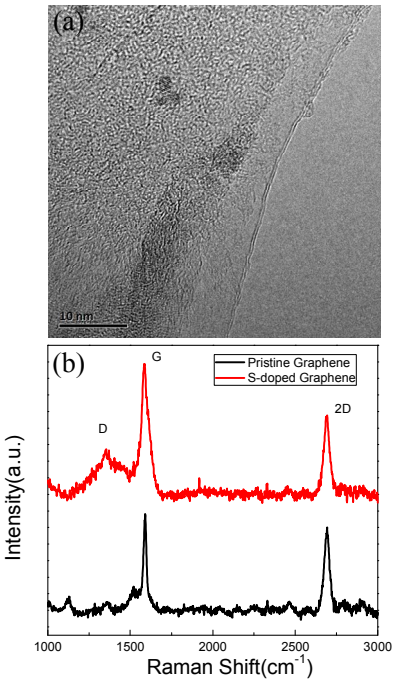

Figure 2: (a) High resolution TEM showing the sample consisting of few layer of graphene; (b) Raman spectra of pristine graphene and S-doped graphene showing D band appeared after sulfur doping indicating the defects mainly caused by doped S atoms.

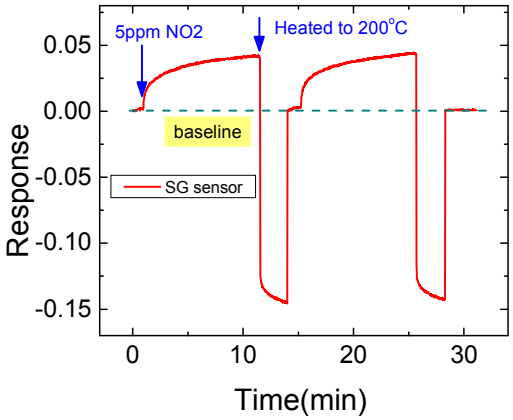

Figure 3: Repeated response of SG sensor to 5 ppm NO_2 through heating to recover to the initial state.

Furthermore, the sensor response to various concentrations ranging from 5 ppb~5 ppm was conducted under the same measurement condition. As shown in Fig. 4, the sensors were

exposed to different concentrations of NO_2 with the same exposure time (10 min) and showed different response to different concentrations of NO_2. The sensors were sensitive to 5 ppb NO_2 with response about 0.00824 indicating ultra-sensitive characteristic of the as-prepared sensors. Due to excellent signal to noise ratio (SNR) shown in Fig. 4, the response to 5 ppb NO_2 is easy to be recorded by data acquisition system. Because of the limit of the measurement system, 5 ppb NO_2 was the lowest concentration that was tested in this work. Due to the excellent SNR displayed in the response curve in Fig. 4, it is feasible to predict that the SG sensors are sensitive to NO_2 concentrations lower than 5 ppb.

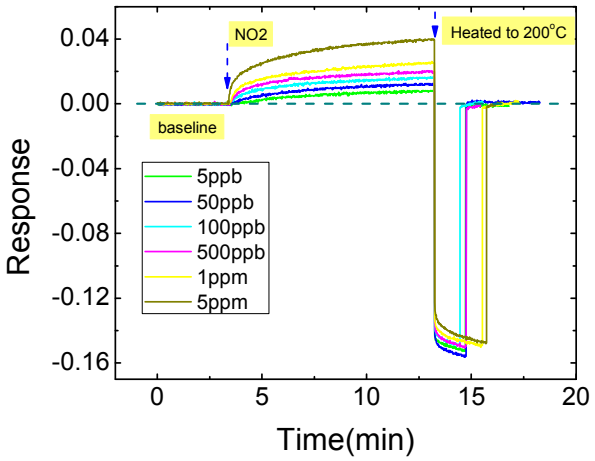

Figure 4: Response of SG sensor to various NO_2 concentrations ranging from 5ppb to 5 ppm.

IV. Conclusion

In this work, nitrogen dioxide sensors with ppb level sensitivity and fast response and recovery were developed by integrating sulfur doped graphene with micro-hotplatform. Sulfur was doped in graphene after its transfer onto the micro-hotplatform through chemical vapor deposition at 500°C. The sensors were sensitive to 5 ppb nitrogen dioxide at room temperature. With the help of heater integrated in MHP, the sulfur doped graphene sensors could quickly recover to the baseline within 5 min. which is a big improve compared to current reported graphene-based NO_2 sensors. The simple and low-cost manufacturing process and the wide availability of CVD graphene and MEMS-based MHP could lead to cost-effective, practical implementation of graphene-based NO_2 sensors.

References

[1] K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, et al., "Electric field effect in atomically thin carbon films," Science, vol. 306, pp. 666-669, Oct 22 2004.

[2] S. Stankovich, D. A. Dikin, G. H. B. Dommett, K. M. Kohlhaas, E. J. Zimney, E. A. Stach, et al., "Graphene-based composite materials," Nature, vol. 442, pp. 282-286, Jul 20 2006.

[3] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, et al., "Large-scale pattern growth of graphene films for stretchable transparent electrodes," Nature, vol. 457, pp. 706-710, Feb 5 2009.

[4] Z. M. He, H. Phan, J. Liu, T. Q. Nguyen, and T. T. Y. Tan, "Understanding TiO2 Size-Dependent Electron Transport Properties of a Graphene-TiO2 Photoanode in Dye-Sensitized Solar Cells Using Conducting Atomic Force Microscopy," Advanced Materials, vol. 25, pp. 6900-6904, Dec 2013.

[5] A. K. Geim and K. S. Novoselov, "The rise of graphene," Nature Materials, vol. 6, pp. 183-191, Mar 2007.

[6] F. Schedin, A. K. Geim, S. V. Morozov, E. W. Hill, P. Blake, M. I. Katsnelson, et al., "Detection of individual gas molecules adsorbed on graphene," Nature Materials, vol. 6, pp. 652-655, Sep 2007.

[7] W. J. Yuan, A. R. Liu, L. Huang, C. Li, and G. Q. Shi, "High-Performance NO2 Sensors Based on Chemically Modified Graphene," Advanced Materials, vol. 25, pp. 766-771, Feb 6 2013.

[8] G. H. Lu, L. E. Ocola, and J. H. Chen, "Gas detection using low-temperature reduced graphene oxide sheets," Applied Physics Letters, vol. 94, Feb 23 2009.

[9] R. Pearce, T. Iakimov, M. Andersson, L. Hultman, A. L. Spetz, and R. Yakimova, "Epitaxially grown graphene based gas sensors for ultra sensitive NO2 detection," Sensors and Actuators B-Chemical, vol. 155, pp. 451-455, Jul 20 2011.

[10] L. Xu, T. Li, X. L. Gao, and Y. L. Wang, "Development of a Reliable Micro-Hotplate With Low Power Consumption," Ieee Sensors Journal, vol. 11, pp. 913-919, Apr 2011.

[11] L. Xu, T. Li, R. Zheng, L. Xie, L. C. Lee, J. W. Jiao, et al., "An Ultra Low Power Consumption Methane Gas Detector Based on an Optimized Suspended Membrane Microhotplate," Sensor Letters, vol. 9, pp. 717-720, Apr 2011.

[12] A. C. Ferrari, J. C. Meyer, V. Scardaci, C. Casiraghi, M. Lazzeri, F. Mauri, et al., "Raman spectrum of graphene and graphene layers," Physical Review Letters, vol. 97, Nov 3 2006.

[13] S. Rumyantsev, G. X. Liu, M. S. Shur, R. A. Potyrailo, and A. A. Balandin, "Selective Gas Sensing with a Single Pristine Graphene Transistor," Nano Letters, vol. 12, pp. 2294-2298, May 2012.

[14] M. G. Chung, D. H. Kim, H. M. Lee, T. Kim, J. H. Choi, D. K. Seo, et al., "Highly sensitive NO2 gas sensor based on ozone treated graphene," Sensors and Actuators B-Chemical, vol. 166, pp. 172-176, May 20 2012.