

## تأثیر دما بر حسگری اکسیژن توسط گرافن

ذاکری، فهیمه؛ توبه ئیها، نفیسه؛ استواری، فاطمه؛

یزد، صفایه، دانشگاه یزد، دانشکده فیزیک

چکیده-گرافن با استفاده از روش هامر سنتز و سپس ترانزیستوری با پوشش نانو صفحات گرافن بر روی زیرلایه  $\text{SiO}_2/\text{Si}$  ساخته شد. جریان عبوری از افزاره ساخته شده هنگامی که در معرض گاز اکسیژن در شرایط محیطی و در دماهای مختلف مورد بررسی قرار گرفت. این نسبت به مولکولهای اکسیژن پاسخ  $p$ -type را در دمای اتاق نشان داد. بنابراین جذب مولکولهای اکسیژن بر روی حسگر تراکم حاملهای بار را کاهش می دهد و موجب کاهش جریان الکتریکی می شود. اما افزایش دما بطور چشمگیری منجر به افزایش جریان و افزایش قدرت حسگری آن می شود. همچنین در این مطالعه میزان حساسیت حسگر ساخته شده نیز اندازه گیری و تأثیر جذب اکسیژن بر مقدار جریان الکتریکی نشان داده شده است.

کلید واژه- سنسور اکسیژن، گرافن، حساسیت، شرایط محیطی، افزایش دما

## The Effect of Temperature on the Oxygen Sensing by Graphen

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**Abstract-** We have synthesized graphene using Hammers' method. Then the Oxygen sensor is fabricated with qualified graphene nanosheets covered  $\text{SiO}_2/\text{Si}$  wafer and Ohmic contact in tow corners. Finally, we investigate the sensitivity of it when exposed to Oxygen at ambient condition in air and at different temperatures.

A resistive graphene-based gas sensor prepared in this way revealed  $p$ -type oxygen response at room temperature. So the absorption of Oxygen molecules on it increases the carrier density and cause to increase the electrical current across it. The variations of electrical current across the sensor, when exposed to Oxygen flow, get increased by increasing temperature.

**Keywords:** Oxygen sensor, graphene, sensitivity, ambient condition

## 1 Introduction

Graphene, a two-dimensional (2D)  $sp^2$  carbon network, has attracted a wide range of interest due to its fascinating electronic, mechanical and thermal properties after its empirical discovery in 2004 [1]. The extremely high carrier mobility, mechanical flexibility, optical transparency and chemical stability of graphene provide a great opportunity for the development of high-performance electronic and optoelectronic devices [2–11].

Among other applications, the exceptional surface-to volume ratio and high electron mobility in room temperature entitles graphene as a promising candidate for gas sensing applications. In this regard, the ultimate single-molecule sensitivity of graphene devices has been reported in recent years [12,13]. In addition to sensitivity and selectivity, sensor response is important in environmental conditions and under the interaction with surrounding atmospheric gases.

Although Oxygen ( $O_2$ ) is very important for life and industrial use, it can lead to combustion at high concentrations. Some researches show the ability of graphene to sense  $O_2$  with very high sensitivity. In this work, we have used graphene for the fabrication of an  $O_2$  sensor at ambient condition in air when exposed to  $O_2$  gas and at different temperatures.

So, Hummers' method was utilized to oxidize natural graphite powder then the chemically oxidized graphite is cleaved to obtain graphene oxide nanosheets. Graphene nanosheets can be achieved by an additional reduction step. As-prepared sheets were characterized by the field emission scanning electron microscope (FESEM), FTIR spectrum and Raman scattering analysis. Then the  $O_2$  sensor is fabricated with qualified graphene nanosheets covered  $SiO_2/Si$  wafer and Ohmic contact in tow corners. Finally, we investigate the sensitivity of it at ambient condition in air and under  $O_2$  flow and at different temperatures.

## 2 Materials and method

In order to synthesize the graphite oxide, Hummers' method was utilized to oxidize natural graphite powder.

In this process, in a 250 mL flask 1 g of graphite and 1.5 g  $NaNO_3$  were added to 25 mL of  $H_2SO_4$ . The flask was then placed in an ice bath for 15 min to cool it down to 0 °C. After that, 3 g of potassium permanganate ( $KMnO_4$ ) was added slowly to the flask. The obtained suspension was then stirred

continuously for 2 h. The temperature in this step was kept at 35°C. Subsequently, it was diluted by 200 mL of deionized (DI) water at the temperature less than 60°C.  $H_2O_2$  solution was then added to flask over which the residual permanganate was reduced to soluble manganese ions. The obtained product was then isolated by filtration, washed copiously with DI water and dried at 60°C for 24 h to obtain brownish graphite oxide powder. In order to form a stable colloidal dispersion, a 10 mg portion of graphite oxide powder was dispersed in 10 mL of DI water by magnetic stirring for 1 h and sonication for 2 h [14, 15].

As a substrate for deposition of G sheets, (1 0 0) oriented silicon wafer was used. A 100 nm thickness of  $SiO_2$  layer was then thermally grown on silicon substrate to electrically isolate the contacting electrodes from the substrate.

The Raman spectroscopy was used for characterization of the reduced sheets. Raman spectra were obtained at room temperature using a Nicolet Almega XR Dispersive Raman spectrometer equipped with second harmonic frequency of a Nd:YLF laser operating at 532 nm. Fourier transform infrared spectroscopy (FT-IR) was obtained using Bruker Tensor 27 Spectrometer to characterize the oxidized sheets. Morphological study of the samples was performed by a Hitachi 4160 FESEM at an electron accelerating voltage of 15 kV.

## 3 Results and Discussion

To characterize the surface topography of the prepared sheets by FESEM, graphene sheets were coated on the  $Si/SiO_2$  substrate. Figures 1 show FESEM images of the prepared graphene sheets. Images present some partially overlapped sheets deposited on the substrate. As can be seen from Figures 2 and 3, the dimension of the majority of the sheets was found to be a few micrometers.

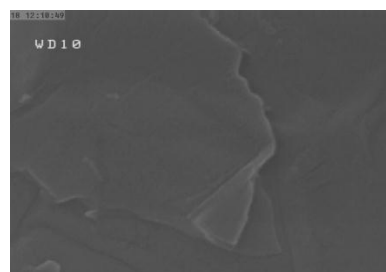


Figure 1: FESEM images of the prepared G sheets on  $SiO_2/Si$  substrate.

Raman spectroscopy is a widely used tool for the characterization of carbon-based structures. The Raman spectra of graphene sheets exhibit two important peaks called D, G and 2D bands around

1331, 1590 and 2898  $\text{cm}^{-1}$ . The G band shows the presence of  $\text{sp}^2$  carbon-type structures within the sample and the D band is associated with the presence of defects in the hexagonal graphitic layers [16–18].

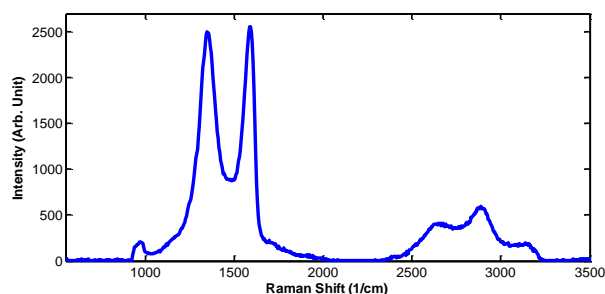


Figure 2: Raman spectroscopy of the prepared graphene sheets on  $\text{SiO}_2/\text{Si}$  substrate.

To identify the bonds between C and O, FTIR analysis was carried out for graphene sheets on  $\text{SiO}_2/\text{Si}$  and Graphite Oxide powder prepared by Hammers' method. The FTIR spectra show the presence of C-H, C-O, C-O-C, C-C and C=O at 900, 1020, 1123, 1583 and 1710  $\text{cm}^{-1}$  respectively in Figure 3. The intensity of peaks is different for graphene layers and Graphite Oxide powder. Spatially, the appearance of a spread peak in the region of 3000 to 3600  $\text{cm}^{-1}$  is seen in FTIR of Graphite Oxide powder that is related to the tensile vibration of the O-H bond [19, 20].

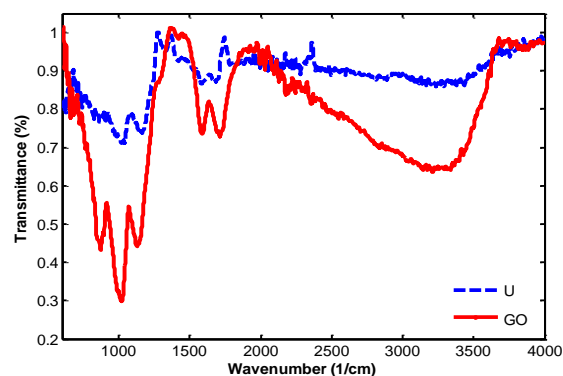


Figure 3: FTIR spectra of the prepared graphene sheets on  $\text{SiO}_2/\text{Si}$  substrate.

To test the applicability of the fabricated structure as  $\text{O}_2$  sensor, the electrical current variation during exposure of  $\text{O}_2$  at different temperatures were studied at ambient conditions in air. For this purpose, the current across the fabricated structure have been investigated versus the source-drain voltage before and after gas absorption at different temperatures. Then the differences between them are plotted at different temperatures versus source-drain voltage (Fig. 4).

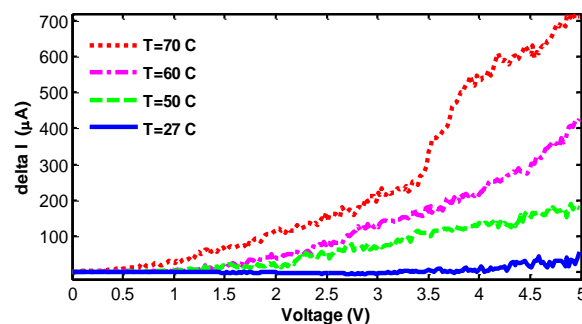


Figure 4: Variations of electrical current across the sensor, when exposed to Oxygen flow at different temperature.

The current of the sensor showed an increase when exposed to the  $\text{O}_2$  flow at ambient condition and room temperature. These current increases were due to the absorption of  $\text{O}_2$  molecules on graphene surface. They act as p-type dopants and enhanced the hole conduction and generate a significant increase in current. At higher temperature, the absorption rate of  $\text{O}_2$  on the surface of graphene increases and so the response of sensor to  $\text{O}_2$  flow becomes stronger.

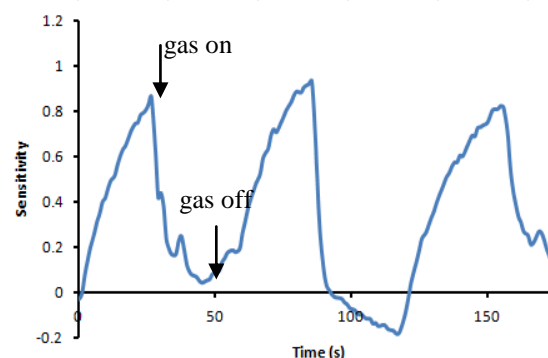


Figure 5: Sensitivity of the graphene to Oxygen at 60°C.

Fig. 5 presents the achieved electrochemical sensitivity ( $\Delta I/I$ ) of the graphene based sensor, in response to Oxygen gas at 60°C. One can see that electrical conductivity of graphene is highly depended on the gas adsorption on this two dimensional carbon lattice.  $\text{Sp}^2$  orbitals in graphene, behave as active sites which adsorb molecular gases and can lead to variation of conductivity according to the electron affinity of the Oxygen molecules.

In conclusion, the current that is passing from the graphene sensor changes when expose to the  $\text{O}_2$  flow at ambient condition. By increasing temperature the sensitivity of graphene for  $\text{O}_2$  sensing gets increased.

## References

- [1] A. K. S. Novoselov<sup>1</sup>, B. A. K. Geim<sup>2</sup>, C. S. V. Morozov<sup>3</sup>, D. D. Jiang<sup>4</sup>, E. Y. Zhang<sup>5</sup>, F. S. V. Dubonos<sup>6</sup>, G. I. V. Grigorieva<sup>7</sup>, H. A. A. Firsov<sup>8</sup>, *Electric Field Effect in Atomically Thin Carbon Films*, Science 306, 666 (2004)
- [2] A. Sasha Stankovich<sup>1</sup>, B. Dmitriy A. Dikin<sup>2</sup>, C. Richard D. Piner<sup>3</sup>, D. Kevin A. Kohlhaas<sup>4</sup>, E. Alfred Kleinhammes<sup>5</sup>, F. Yuanyuan Jia<sup>6</sup>, G. Yue Wu<sup>7</sup>, H. SonBinh T. Nguyen<sup>8</sup>, I. Rodney S. Ruoff<sup>9</sup>, *Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide*, Carbon 45, 1558 (2007).
- [3] A. Ostovari, Fatemeh<sup>1</sup>, B. Abdi, Yaser<sup>2</sup>, C. Ghasemi, Foad<sup>3</sup>, "Controllable formation of graphene and graphene oxide sheets using photocatalytic reduction and oxygen plasma treatment". Eur. Phys. J. Appl. Phys. (2012) 60: 30401.
- [4] A. Ostovari, Fatemeh<sup>1</sup>, and B. Abdi, Yaser<sup>2</sup>, *Magnetic field enhanced hydrophilicity of Fe-TiO<sub>2</sub> nanostructures*. Eur. Phys. J. Appl. Phys. (2012) 58: 30402.
- [5] A. Robinson, Jeremy<sup>1</sup>, B. Perkins, Keith<sup>2</sup>, C. Snow, Eric<sup>3</sup>, D. Wei, Zhongqing<sup>4</sup>, E. Sheehan, Paul<sup>6</sup>, *Reduced Graphene Oxide Molecular Sensors*. Nano Lett. 8, 3137 (2008).
- [6] A. Das, Sriya<sup>1</sup>, B. Irin, Fahmida<sup>2</sup>, C. Ahmed, Tanvir<sup>3</sup>, D. Abel, Cortinas<sup>4</sup>, E. Ahmed, Cortinas<sup>5</sup>, F. Wajid Ahmed<sup>6</sup>, G. Parviz, Dorsa<sup>7</sup>, H. Jankowski, Alan<sup>8</sup>, I. Kato, Masaru<sup>8</sup>, J. Green, Micah<sup>9</sup>. *Non-covalent functionalization of pristine few layer graphene using triphenylene derivatives for conductive poly (vinyl alcohol) composites*. Polymer 53, 2485 (2012) .
- [7] A. Ostovari, Fatemeh<sup>1</sup>. and B. Farshi, Moravvej<sup>2</sup>, *Photodetectors with armchair graphene nanoribbons and asymmetric source and drain contacts*. Appl. Surf. Sci. 318, 108–112, (2014)
- [8] A. Ostovari, Fatemeh<sup>1</sup>, and B. Farshi, Moravvej<sup>2</sup>, *Photodetectors with zigzag and armchair graphene nanoribbon channels and asymmetric source and drain contacts: Detectors for visible and solar blind applications*. J. Appl. Phys. 120, 144505 (2016).
- [9] A. Stampfer, C<sup>1</sup>, B. Schurtenberger, E<sup>2</sup>, 3. Molitor, F<sup>3</sup>, D. G'uttinger, J<sup>4</sup>, E. Ihn, T<sup>5</sup>, F. Ensslin, K<sup>6</sup>, *Tunable Graphene Single Electron Transistor*, Nano Lett. 8, 2378 (2008)
- [10] A. Ostovari, Fatemeh<sup>1</sup>, and B. Farshi, Moravvej<sup>2</sup>, *Dual function armchair graphene nanoribbon-based spin-photodetector: Optical spin-valve and light helicity detector*, Appl. Phys. Lett, 105, 072407, (2014).
- [11] A. Ostovari, Fatemeh<sup>1</sup>, B. Abdi, Yaser<sup>2</sup>, C. Darbari, S<sup>3</sup>, D. Ghasemi, Foad<sup>4</sup>, *Effects of electromechanical resonance on photocatalytic reduction of the free-hanging graphene oxide sheets*, J Nanopart Res (2013) 15:1551
- [12] A. Rumyantsev<sup>1</sup>, B. S, Liu<sup>2</sup>, C. G, Shur<sup>3</sup>, D. M.S, Potyailo<sup>4</sup>, E. R.A, Balandin<sup>5</sup>, *Selective gas sensing with a single pristine graphene transistor*, Nano Lett, 12 (5) (2012) 2294e2298.
- [13] A. Jebreil Khadem<sup>1</sup>, B. Abdi, Y<sup>2</sup>, C. Darbari, S<sup>3</sup>, D. Ostovari, F<sup>4</sup>, *Investigating the effect of gas absorption on the electromechanical and electrochemical behavior of graphene/ZnO structure, suitable for highly selective and sensitive gas sensors*, Current Applied Physics, 14, 1498-1503, (2014).
- [14] A. Sasha Stankovich<sup>1</sup>, B. Dikin, Dmitriy A<sup>2</sup>, C. Piner, Richard D<sup>3</sup>, D. Kohlhaas, Kevin A<sup>4</sup>, E. Kleinhammes, Alfred<sup>5</sup>, F. Jia, Yuanyuan<sup>6</sup>, G. Wu, Yue<sup>7</sup>, H. Nguyen, SonBinh T<sup>8</sup>, J. Ruoff, Rodney S<sup>8</sup>, *Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide*. Carbon 45, 1558 (2007)
- [15] A. Bing, Li<sup>1</sup>, B. Xintong, Zhang<sup>2</sup>, C. Xinghua, Li, Lei, Wang, Runyuan, Han, Bingbing, Liu, Weitao, Zheng, Xinglin, Li, Yichun, Liua. *Photo-assisted preparation and patterning of large-area reduced graphene oxide-TiO<sub>2</sub> conductive thin film* Chem, Commun. 46, 3499 (2010)
- [16] A. Tuinstra, F<sup>1</sup>, B. Koenig, J<sup>2</sup>, C. L, Chem J<sup>3</sup>, *Raman Spectrum of Graphite*, Phys. 53, 1126 (1970)
- [17] A. Ferrari, A<sup>1</sup>, B. C, Robertson, J<sup>2</sup>, *Interpretation of Raman spectra of disordered and amorphous carbon*, Phys. Rev. B 61, 14095 (2000)
- [18] A. Graf<sup>1</sup>, B. D, Molitor<sup>2</sup>, C. F, Ensslin<sup>3</sup>, D. K, Stampfer<sup>4</sup>, E. C, Jungen<sup>5</sup>, F. A, Hierold<sup>6</sup> G. Wirtz, L<sup>7</sup>, *Spatially Resolved Raman Spectroscopy of Single- and Few-Layer Graphene*, Nano Lett. 7, 238 (2007)
- [19] A. Eun-Young Choi<sup>1</sup>, B. Tae Hee Han<sup>2</sup>, C. Jihyun Hong<sup>3</sup>, D. Ji Eun Kim<sup>4</sup>, E. Sun Hwa Lee<sup>5</sup>, F. Hyun Wook Kim<sup>6</sup>, G. Sang Ouk KiM<sup>7</sup>, *Noncovalent functionalization of graphene with end-functional polymers*, Journal of Materials Chemistry, 20, (2010) 1907-1912.
- [20] A. Tessy Theres, Baby<sup>1</sup>, and B. Ramaprabhu, S<sup>2</sup>, *Investigation of thermal and electrical conductivity of graphene based nanofluids*, Journal of Applied Physics 108, (2010) 124308.