

# High Performance Carbon Monoxide Gas Sensor based on Graphene

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**Abstract**— In this paper, a high performance carbon monoxide (CO) gas sensor based on graphene is fabricated using a simple new technique. Graphene layer on flexible Polyethylene Terephthalate (PET) substrate is synthesized by Laser treatment and used as the sensing element of the gas sensor. Graphene Oxide (GO) film deposited on PET substrate is simultaneously patterned and reduced into Laser reduced graphene (LRG) film using a universal Laser system. The CO gas sensor consists of four LRG strips connected together in a Wheatstone bridge circuit. The performance of the sensor is tested at various concentrations of CO gas ranges from 50 to 1000 ppm and under different operating temperatures. The fabricated sensor shows a noticeable decrease in its electrical resistance with CO concentration increase at room temperature with an average sensitivity of (0.1% / ppm) at low CO concentrations up to 50 ppm. At 100 ppm of CO, the sensor shows an average response and recovery times of 70 and 40 s, respectively. This response slightly enhances by increasing the operating temperature up to 80 °C. Besides the merits of fast response and short recovery time; the fabricated sensor shows low power consumption.

**Keywords**— Gas sensor; Carbon monoxide; Graphene synthesis; Laser reduced graphene.

## I. INTRODUCTION

Carbon monoxide (CO) is a colorless, odorless poisonous deadly gas. It is a by-product of incomplete combustion; wherein its sources can include malfunctioning appliances, vehicles exhaust, and industrial activities which depend on burning fossil fuel. The great danger of CO is presented in its attraction to hemoglobin. During breath; CO molecules enter the bloodstream and displace the oxygen found on hemoglobin. This deprives the heart and brain from the necessary oxygen for their functioning. When CO is present in the air, it rapidly accumulates in the blood causing symptoms such as headaches, fatigue and nausea, etc. As levels increase; this leads to loss of consciousness, brain damage and death [1]. Therefore, it is very important to develop sensitive, reliable and low-cost sensors that can be used to monitor CO concentration in closed areas.

Since more than half century, the first solid-state gas sensor was developed by Seiyama, et al. [2]. From this

moment many attempts had been made by several researchers to improve the sensing performance of the gas sensors. For several years, carbon nanotubes (CNTs) had been considered as an attractive sensing material which can detect low concentrations of gases such as NH<sub>3</sub>, H<sub>2</sub>, CO<sub>2</sub> and CO [3 - 6].

More recently, graphene sparked as a promising sensing material due to its exceptional electrical and mechanical properties [7]. Graphene as a two dimensional layer of carbon atoms, has very high electron mobility at room temperature, stability at elevated temperatures, large surface area as well as high capacity to gas-adsorption [8]. Yoon, et al. [9] had used the mechanically exfoliated graphene to detect very small concentrations of CO<sub>2</sub> gas. Also Lu, et al. [10] had used the reduced graphene oxide for gas detection at room temperature. No doubt that the recent improvements which have been made on graphene deposition techniques are contributing in increase the applicability of graphene for device integration. In addition to its planar structure which makes it compatible with standard microfabrication techniques [7].

Till today; the most common gas sensors depend on semiconductor metal oxides as a sensing material [11]. On the other hand; there are many drawbacks associated with this type of sensors such as elevated working temperature, relatively high power consumption, slow response, low stability, and cross sensitivity. Therefore, a new trend has appeared to use graphene and decorated graphene with metal oxides to enhance the characteristics of gas sensors [12, 13].

Graphene could be synthesized using mechanical or chemical techniques. Li, et al. [14] and Yu, et al [15] had synthesized graphene films by CVD on copper and Nickel substrates, respectively. On the other hand; a chemical exfoliation technique was proposed by Hummers and Offeman [16] to produce oxidized or exfoliated graphite. Furthermore, Stankovich, et al. [17] had synthesized reduced graphene oxide sheets by chemical reduction of exfoliated graphite. Also, the femtosecond Laser was used by Chang, et al. [18] to reduce graphene oxide in aqueous solution into graphene. Most of these techniques are complicated, expensive and not suitable for mass production; In addition to the need to use harsh chemicals or elevated synthesis temperatures.

Recently some attempts have been done to synthesis graphene using Laser power. Strong et al. [19] used the Laser of DVD drive to reduce graphene oxide, but the produced graphene has insufficient quality due to incomplete reduction. Gamil et al. [20] also used a CO<sub>2</sub> Laser system to reduce graphene oxide and used it as a strain sensor.

In the present study, we demonstrate the fabrication of CO gas sensor based on graphene resistance change. Universal Laser systems was adopted to simultaneously pattern and reduce graphene oxide (GO) film deposited on flexible Polyethylene Terephthalate (PET) substrate into Laser reduced graphene (LRG) film. The synthesized graphene film was used as the sensing element of the sensor. Finally, the performance of the fabricated gas sensor was evaluated at different CO concentrations and under various operating temperatures.

## II. EXPERIMENT

### A. Graphene Oxide Preparation

Modified Hummer's method was used to oxidize graphite powder to Graphite oxide [16]. A concentration of 5 mg/mL of the prepared graphite oxide in distilled water was sonicated for 2 hours to produce a suspension of exfoliated graphene oxide (GO) sheets. To remove the non-exfoliated graphite oxide; the GO suspension was centrifuged at 5000 rpm for 30 minutes. A final concentration of 3.7 mg/mL of exfoliated GO sheets was obtained as determined from the residual weight of the dried aliquot.

### B. Graphene Film Synthesis

The GO solution was drop-casted at 20 °C on a 100 μm thick PET substrate. The spreaded solution was dried at room temperature for 48 hours. The dried GO film was simultaneously reduced and Patterned into graphene rectangular strips (10 mm × 15 mm) using a universal Laser printing machine (model: Universal Laser Systems VLS2.30) with a focal length of 50 mm, as shown in Fig. 1. This machine uses CO<sub>2</sub> Laser beam with a wavelength of 10.6 μm. The Laser power and patterning resolution were adjusted to 2 Watt and 1000 pulses per inch, respectively. These values were experimentally optimized to produce a fully reduced graphene film with a very good quality.

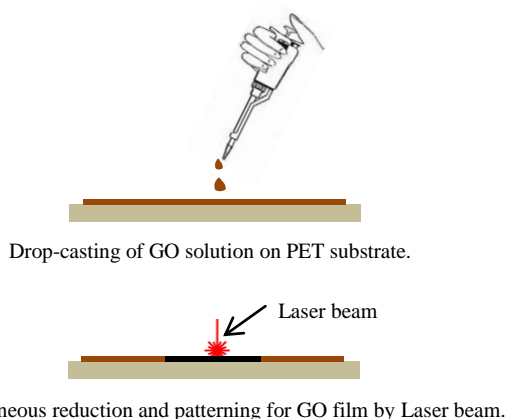


Fig. 1. Synthesis process of the Laser reduced graphene film

### C. Characterization of the Synthesized Graphene Film

The synthesized LRG film was characterized using X-ray diffraction (XRD) (SHIMADZU XRD-6100), Fourier transform infrared spectroscopy (FTIR) (BRUKER VERTEX 70), Raman spectroscopy (HORIBA Jobin Yvon LabRAM HR-800 SSM), 3D Laser scanning microscope (KEYENCE VK-X200) and scanning electron microscopy (SEM) (JEOL JSM-6010 LV).

### D. Gas Sensor Fabrication

Four rectangular LRG strips (10 mm × 15 mm) on PET substrate were used as the sensing elements in the gas sensor. The four graphene strips were connected in a typical Wheatstone bridge circuit, as shown in Fig. 2. Two of the graphene strips (on two different branches of Wheatstone bridge – R<sub>1</sub> and R<sub>3</sub>) were exposed to CO gas; while the other two strips (R<sub>2</sub> and R<sub>4</sub>) were prevented from the exposure to gas stream. This connection sequence of the graphene strips is eliminating the effect of temperature and other parameters on graphene resistance change, and as a consequence; the change in the output voltage (V<sub>o</sub>) of Wheatstone bridge circuit will be only due to the change in the electrical resistance of graphene strips after the exposure to CO gas. The sensor was designed to eliminate the flow effect on graphene resistance change by exposing the two graphene strips (R<sub>1</sub> and R<sub>3</sub>) to CO gas through a perforated cover with tiny holes.

### E. Test Rig Preparation

In order to evaluate the performance of the fabricated gas sensor; a typical gas sensor testing setup was used, as shown in Fig. 3. The setup consists of a controlled temperature/humidity chamber. This chamber could be evacuated through a vacuum pump. CO gas cylinder was used as a source of CO gas, also a Nitrogen (N<sub>2</sub>) cylinder was used as a N<sub>2</sub> source to compose a mixture with different concentrations of CO. Mass flow controllers were used to control the concentration of CO gas in the mixture. Nano-voltmeter (Keithley 2182A) was used to measure the change in the output voltage (V<sub>o</sub>) of Wheatstone bridge circuit after the exposure to different concentrations of CO gas.

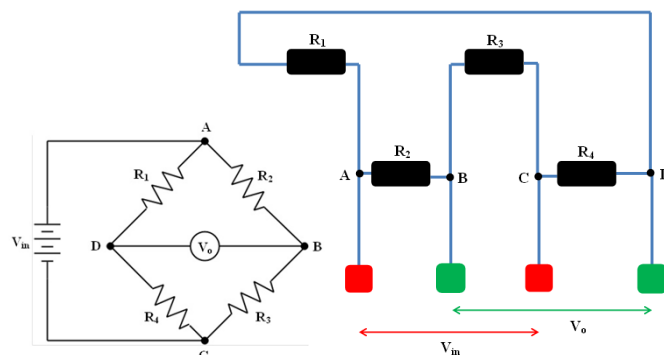


Fig. 2. Schematic representation of the gas sensor

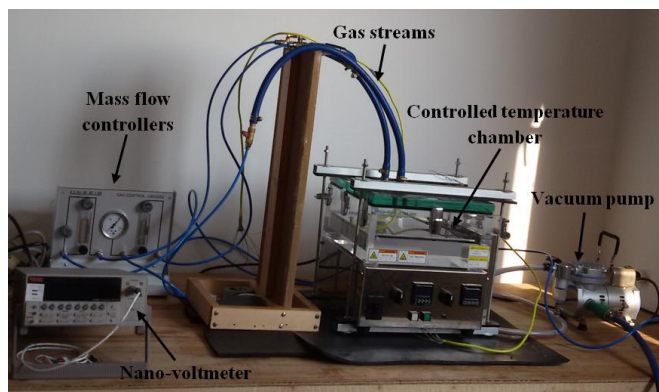


Fig. 3. Experimental setup for performance evaluation of the gas sensor

### III. RESULTS AND DISCUSSION

#### A. Characterization of the Laser Reduced Graphene Film

The transformation of graphene oxide into Laser reduced graphene, and the efficiency of the Laser treatment process were confirmed using various characterization techniques. The FT-IR spectrum presents an evidence on the transformation of GO to LRG, as shown in Fig. 4. The FT-IR spectrum of GO shows the existence of different function groups due to the chemical exfoliation process by means of Modified Hammer's method. (O-H) group absorption causes the peak at  $3400\text{ cm}^{-1}$ , and the (C=O) group gives a peak at  $1720\text{ cm}^{-1}$ . Also stretching vibration peaks due to various deformations are observed at  $1220\text{ cm}^{-1}$ , and  $1060\text{ cm}^{-1}$  due to (C-OH), and (C-O) groups; respectively. The existing peak at  $1600\text{ cm}^{-1}$  is due to unoxidized graphitic domains of in-plane C=C bonds and the skeletal vibration of the graphene sheets. On the other hand, the FT-IR spectrum for the LRG indicates that the Laser treatment process removes (C=O), (C-OH), and (C-O) groups; While (O-H) stretching vibrations observed at  $3400\text{ cm}^{-1}$  decreased due to deoxygenation, and carbon-carbon bonding is restored. The remnants of hydroxyl groups were reported to be related to water molecules intercalated among graphene layers [21, 22].

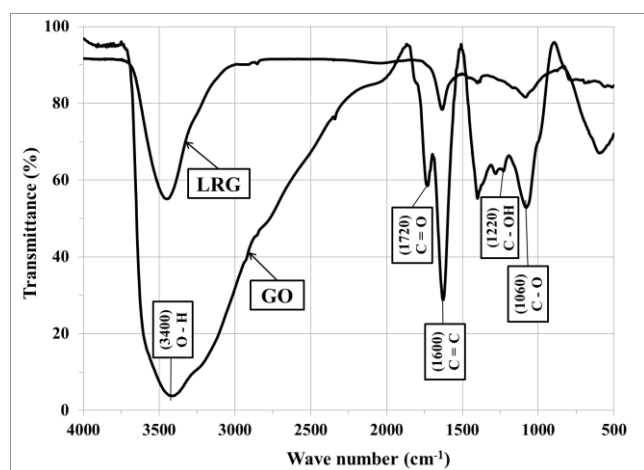


Fig. 4. FT-IR spectrum for GO and LRG

The XRD technique indicates the remarkable peak of GO at  $10.8^\circ$  with an interlayer distance of  $8.14\text{ \AA}$  due to the oxidation of graphite into graphene oxide, as shown in Fig. 5. By applying the Laser treatment; a graphene film with an estimated interlayer distance of  $3.43\text{ \AA}$  was formed with a characteristic halo peak of amorphous carbon at  $25.9^\circ$ . This decrease in interlayer distance is due to the removal of oxygen functional groups and water molecules from the interlayer spacing of GO film upon Laser reduction process.

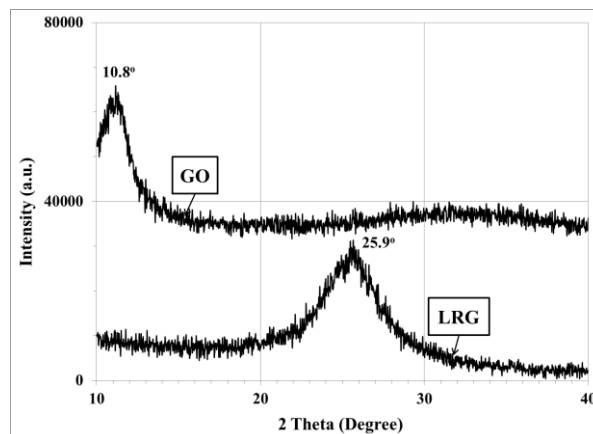


Fig. 5. XRD patterns for GO and LRG

Raman spectrum as a powerful tool for characterization was used to identify the graphene formation by Laser treatment and its characteristics. Fig. 6 shows the Raman spectrum for the synthesized graphene film. Three predominant peaks in this spectrum could be noticed; the 2D band at  $2700\text{ cm}^{-1}$ , G band at  $1580\text{ cm}^{-1}$ , and the disorder-induced D band at  $1360\text{ cm}^{-1}$ . The G-band and the 2D-band are characteristic of the  $sp^2$ -hybridized carbon-carbon bonds in graphene [23 – 27]. The D-band (at  $1360\text{ cm}^{-1}$ ) indicates the presence of structural imperfections induced by the attachment of oxygen functional groups on the carbon basal plane [26]. Fig. 6 shows an intensity of Lorentzian G peak about three times as the D peak; this indicates that the synthesized graphene film is disordered graphene. Also it could be noticed that the 2D peak is symmetric with an intensity half of that of the G peak, and this gives evidence for the formation of multilayer graphene film [27].

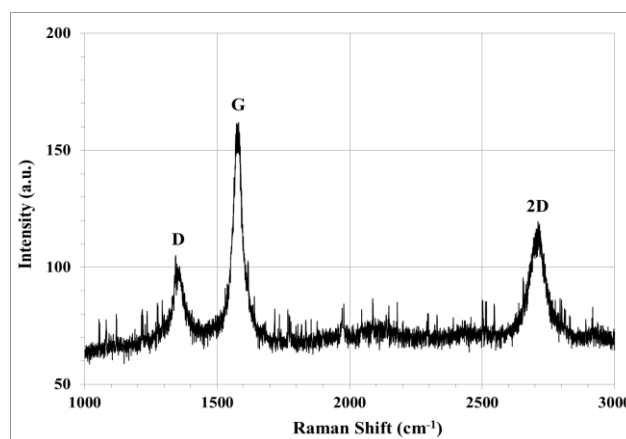


Fig. 6. Raman spectra for LRG film



The thickness and surface topography of the synthesized LRG film were estimated by using a 3D Laser microscope. Fig. 7 shows the formation of a crack free rough surface with an average thickness of 3  $\mu\text{m}$ . This indicates that the structure integrity of the synthesized LRG film is maintained after the Laser reduction process.

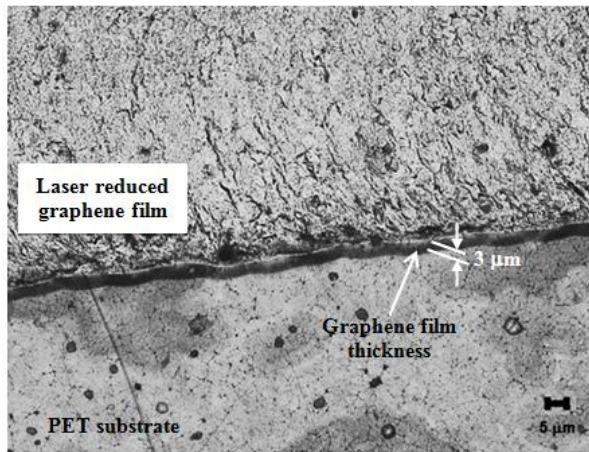


Fig. 7. Thickness of the LRG film on PET substrate using 3D scanning Laser microscopy

The microstructure of the LRG film is presented using SEM images at various magnifications, as shown in Fig. 8. Figs. 8(a) and 8(b) clearly illustrate the existence of overlapped graphene flakes structure. The overlapped flakes connect together by means of electrostatic forces (Van der Waals forces) to form a continuous and conductive network [28].

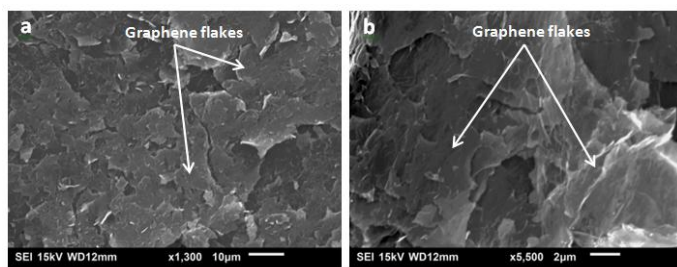


Fig. 8. SEM images of LRG film at various magnifications

### B. Performance Evaluation of the Fabricated Gas Sensor

The performance of the fabricated graphene-based gas sensor was evaluated by measuring the change in its electrical conductivity upon the exposure to different concentrations of CO gas inside the prescribed test rig, as shown in Fig. 3. The concentration of the CO gas in the mixture was varied from 50 to 1000 ppm. The change in the output voltage of Wheatstone bridge circuit was used to indicate that change in electrical resistance, and was recorded using nano-voltmeter (Keithley 2182A). The effect of the operating temperature on the response of the fabricated sensor was studied up to 80  $^{\circ}\text{C}$ .

Fig. 9 shows the temperature effect on graphene film resistance. A decrease in graphene electrical resistance could be noticed due to excitation of electrons with temperature increase.

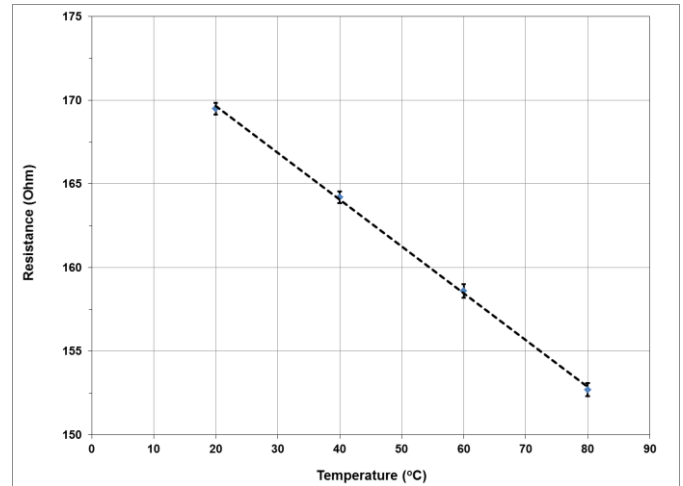


Fig. 9. Electrical resistance change of the LRG at different temperatures

The change in the ratio of output voltage ( $V_o$ ) to input voltage ( $V_i$ ) at various concentrations of CO at 20  $^{\circ}\text{C}$  is shown in Fig. 10. As the concentration of CO gas increases; an increase of the ( $V_o/V_i$ ) ratio is observed due to the decrease in the electrical resistance of the two graphene strips which exposed to CO gas. By increasing the concentration of CO from 50 to 250 ppm; the ratio of ( $V_o/V_i$ ) increases from 4.7 % to 9.5 %; while at 1000 ppm this ratio exceeds 12 %. On the other hand; the sensor shows a sensitivity of (0.1% / ppm) at low concentrations of CO up to 50 ppm; on contrary this sensitivity decreases at higher concentrations due to saturation effect.

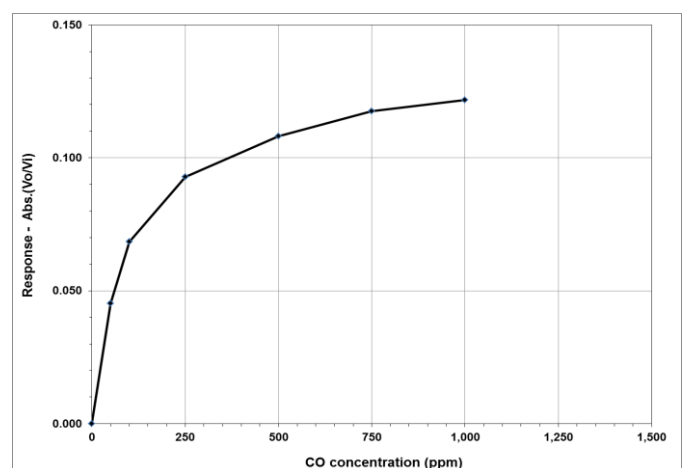


Fig. 10. Sensor response at different concentrations of CO gas at 20  $^{\circ}\text{C}$

The time response of the fabricated CO gas sensor is presented in Fig. 11 at concentrations of 100, 500 and 1000 ppm of CO at 20  $^{\circ}\text{C}$ . Once the sensor is exposed to CO gas; a sudden steep decrease in its electrical resistance can be observed and that reflects on the ratio of ( $V_o/V_i$ ). After a certain time the sensor reaches the steady state condition. The fabricated sensor shows a short response time of 70 s and fast recovery within 40 s at CO concentration of 100 ppm. These times slightly increase with the increase of CO concentration to reach an average response time of 80 s and recovery time of 60 s at 1000 ppm.

The physically adsorbed CO molecules on the graphene film induce a decrease in its electrical resistance; wherein these molecules act as a donor of electrons. The charge carriers' transfer between CO molecules and graphene film is the basic phenomenon of the sensing mechanism [29, 30]. The short recovery time is mainly due to the weak physical interaction between CO molecules and graphene film. This interaction does not need long time annealing at elevated temperature to remove the adsorbed gas molecules on graphene surface [8].

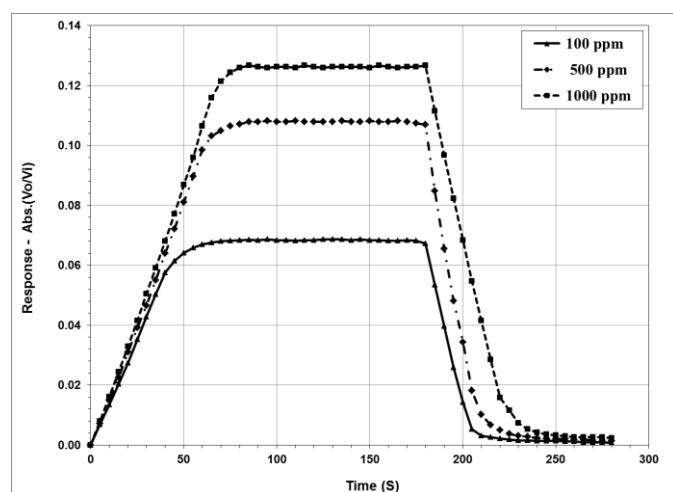


Fig. 11. Time response of gas sensor at 100, 500 and 1000 ppm of CO at 20 °C

The fabricated gas sensor did not show any sensitivity enhancement with temperature increase up to 80 °C; but a slight decrease in response and recovery times could be observed. At 80 °C, the sensor shows an average response and recovery times of 65 and 30 s, respectively at 100 ppm of CO. This slight enhancement is mainly due to electrons' excitation with temperature increase.

It is worth mentioning that the effect of temperature on graphene resistance change is eliminated by using the proposed design of the gas sensor as prescribed in section 2.4.

The experimental results of the fabricated gas sensor with the proposed technique show the efficiency of the synthesized graphene film by Laser reduction to be used as a sensing material for CO gas. Also the proposed design of the gas sensor shows a good approach to fabricate a high performance CO gas sensor with a productive and low cost technique.

#### IV. CONCLUSIONS

A carbon monoxide gas sensor based on graphene was fabricated with a new technique. Graphene film was synthesized using a printing Laser system. The Laser beam was used to simultaneously reduce and pattern a graphene oxide film on flexible PET substrate into a LRG film. The synthesized graphene film was characterized by XRD, FT-IR, Raman spectroscopy and SEM techniques. A proposed design for the gas sensor based on Wheatstone bridge circuit was introduced to eliminate the effect of temperature on graphene resistance change. The performance of the fabricated gas sensor was studied at various concentrations of CO gas up to 1000 ppm and at different operating temperatures. At 100 ppm

of CO, the sensor showed an average response and recovery times of 70 and 40 s, respectively at 20 °C. These times were slightly enhanced at an operating temperature of 80 °C; wherein the sensor showed an average response and recovery times of 65 and 30 s, respectively. Furthermore, the fabricated sensor showed an average sensitivity of (0.1% / ppm) at low concentrations of CO gas up to 50 ppm at 20 °C with no recognized enhancement with temperature increase.

Based on the presented experimental results of the fabricated CO gas sensor; it could be concluded that the proposed technique offers a new low cost and productive fabrication method for flexible and high performance gas sensors based on graphene.

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