Oxygen sensors made by monolayer graphene

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abstract

The electrical resistivity of monolayer graphene exhibit significant changes upon expose to different concentration of oxygen (O_2) at room temperature. The monolayer graphene, grown by chemical vapor deposition (CVD) with perfect uniformity within 1cm×1cm will attach O_2 molecules which will act as a p-type dopant and enhance the hole conductivity, make a change of resistivity of graphene thin film. We quantified the change of resistivity of graphene versus different O_2 concentration and the detection limit of the simple O_2 sensor was 1.25% in volume ratio.

Introduction

Oxygen gas (O_2) is widely used in a lot of applications such as medical [1], life support and recreational use [2,3], industrial, and scientific area [4,5]. However, oxygen gas can be toxic at elevated partial pressures, leading to convulsions and other health problems. Oxygen toxicity usually begins to occur at partial pressures more than 50 kilopascals (kPa), or 2.5 times the normal sea-level O_2 partial pressure of about 21 kPa (equal to about 50% oxygen composition at standard pressure). On the other hand, highly concentrated sources of oxygen promote rapid combustion. Fire and explosion hazards exist when concentrated oxidants and fuels are brought into close proximity; however, an ignition event, such as heat or a spark, is needed to

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trigger combustion. Oxygen itself is not the fuel, but the oxidant. Combustion hazards also apply to compounds of oxygen with a high oxidative potential, such as peroxides, chlorates, nitrates, perchlorates, and dichromates because they can donate oxygen to a fire.

Recently, graphene and graphene oxide play important roles in a lot of areas of chemistry, physics, biochemical, and material science because of its excellent electrical and crystal properties [6-10]. As well known, graphene is composed of honeycomb lattice structures of carbon atoms arranged via sp^2 bonds. The delocalizes pi(π) bonds of graphene allow charge carriers to have zero rest mass and high mobility [11,12], which is approximately three one-thousandths of the speed of light. Gas sensing is one of the promising applications for graphene [13-14]. High surface –to- volume ratio in conjunction with high conductivity translates into high sensitivity to molecular disruption on the graphene surface [15].

There were lots of articles published to shown that the potential of graphene and graphene oxide as gas sensors. Graphene oxide reduced by hydrazine was used to detect H_2 and CO by Arsat et al.[16]; NO_2, NH_3, and di-nitro-toluene by Fowler et al.. With mechanically exfoliated graphene[17], Dan et al. detected H_2O, NH_3, octanoic acid, and trimethylamine[18], while Schedin et al. experimented with NO_2, H_2O, I_2, NH_3, CO, and ethanol[19]. Tour et. al using graphene nanoribbons to detect O_2 with very high sensitivity[20].

In this letter, we demonstrate a low cost, easily fabricated of oxygen sensor using a monolayer graphene grown by chemical vapor deposition with simply In ohmic contact in two corner. We quantified the sensitivity, the temporal resolution, and the limit of detection of these sensors for O_2 detection.

Experimental

The monolayer graphene used for the O_2 sensing were grown on 25μm thick copper foil in a quartz tube furnace system using a CVD method involving methane and hydrogen gases. Under vacuum conditions of 10 mtorr, the furnace would be heated with a 2 sccm flow of H_2 present. The growth temperatures was 1000°C. After 40 minutes of heating to allow the copper foil to anneal, a flow of 35 sccm of methane would be introduced for a growth time ranging from 30 seconds to 15 minutes. A quick cooling method was used (~300°C/min) after growth, and the methane and hydrogen gas flows were continued throughout the cooling process. The graphene films on copper were then characterized using scanning electron microscopy (SEM) images. After transferring the films to Si/SiO2 wafers through polymethyl

methacrylate (PMMA) coating and iron (III) nitrate etching, the films would be further analyzed by Hall measurement and Raman spectroscopy.

Results and Discussion

Figure 1 shows the SEM images of graphene on copper foil where the Cu grains are clearly visible. A continuously graphene thin film was observed because we can see clearly the Cu surface steps and graphene wrinkles.

Raman spectroscopy was used to evaluate the quality and uniformity of graphene on a SiO2/Si substrate. Figure 2 shows the Raman spectra and maps of the D and 2D bands providing information on the defect density and film thickness. The thickness and uniformity of the graphene films were evaluated via color contrast under optical microscope and Raman spectra. The Raman spectrum in Fig. 2(A) show typical features of monolayer graphene: (i) a ~0.5 G–to–2D intensity ratio and (ii) a symmetric 2D band centered at ~2680 cm^{-1} with a full width at half maximum of ~26 cm^{-1}. As shown in Fig. 2(B) and 2(C), the 2D and the G maps clearly show the presence of more than one layer in the flakes. An analysis of the intensity of the optical image over the whole sample (1 cm by 1 cm) showed that the area with the lightest pink color is more than 95%, and all Raman spectra randomly collected from this area show uniformly monolayer graphene was transferred on SiO_2/Si substrate.

For the O_2 sensing measurement, the sensor was mounted on a carrier and put in a gas chamber filled by N_2 gas. The temperature of chamber was keep at room temperature and a constant forward bias voltage of 500 mV was applied to the ohmic contacts of the sensor. Finally, different amounts of O_2 gas were injected into the chamber. Figure 3 shows the real time O_2 detection with graphene on SiO_2/Si. The current of the sensor showed a rapid increase when the O_2 concentration was changed to 1.25% volume ration in the open cavity with continuous gas flow. A further increase in the current for the sensor was observed when the O_2 concentration increased to 4.7% volume ratio. These abrupt current increases were due to the change in charges in the graphene upon a shift in O_2 concentration. We do believed the sensing mechanism of O_2 on graphene is because when O_2 will attached on the graphene thin films and act as a p-type dopants. As described by Fowler et. al. in ref[17]. Residual epoxide and carboxylic groups expected in chemically produced graphene are electron-withdrawing and promote some holes into the conduction band.

So, when the O_2 was attached on the graphene thin film and enhanced the hole conduction and generate a significant decrease in resistance.

The O_2 sensor showed a good repeatability, as illustrated in Figure 4, the current response of the graphene sensor to O_2 gas flow rate was switching from 0 to 1.25% volume ratio. The change in current for the sensor exposed between 0 ppm to 400 ppm was still considerably larger than the background noise. Thus, graphene sensors could be used to detect small difference in O_2 concentration.

We also test the detach time of O_2 molecule on the graphene thin films, as shown in Figure 5. It was shown that the current between two electrodes will increased suddenly when we turn off the oxygen gas at 400 seconds, which means the oxygen molecule will detached by vacuum dramatically in the very beginning. After few seconds, the current will increased with a slow speed and finally become the initial state within 400 seconds, which show that the current change in different concentration of oxygen ambient comes from the oxygen attachment.

We also think if the current change is because the surface roughness of graphene under different pressure. We use nitrogen instead of oxygen gas, as shown in Figure 6. We can see clearly that the amount of current change from pressure difference is so small that we can clarify the current change of graphene thin film is because of oxygen attachment.

Conclusion

In conclusion, graphene sensor showed rapid change in the current when exposed to different O_2 concentration ambient at room temperature. These results show the potential of graphene for O_2 sensing applications.

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Figure Captions

Figure 1: SEM images of graphene on copper foil

Figure 2 : (a) Raman spectrum of monolayer of graphene.

(b) Raman mapping of 2D band.

(c) Raman mapping of G band.

Figure 3 : Real time O_2 detection with different concentration using graphene on SiO_2/Si substrate.

Figure 4 : Real time O_2 detection with the same concentration using graphene on SiO_2/Si substrate.

Figure 5 : Real time measurement of current change of graphene thin film.

Figure 6 : Real time measurement of current change under nitrogen ambient.

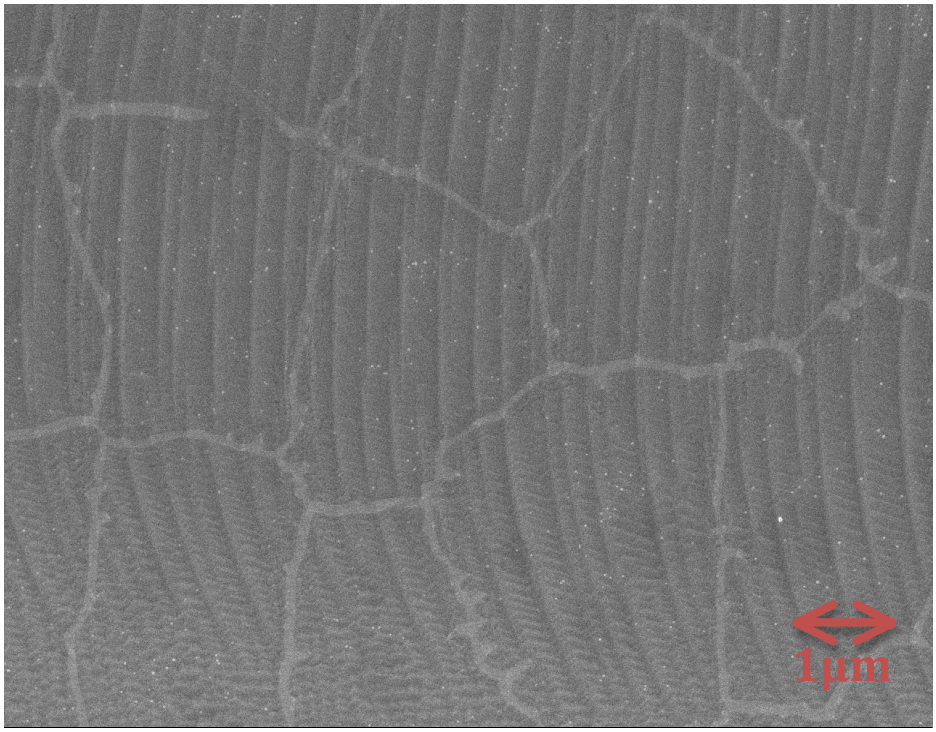

Figure 1. SEM images of graphene on copper foil

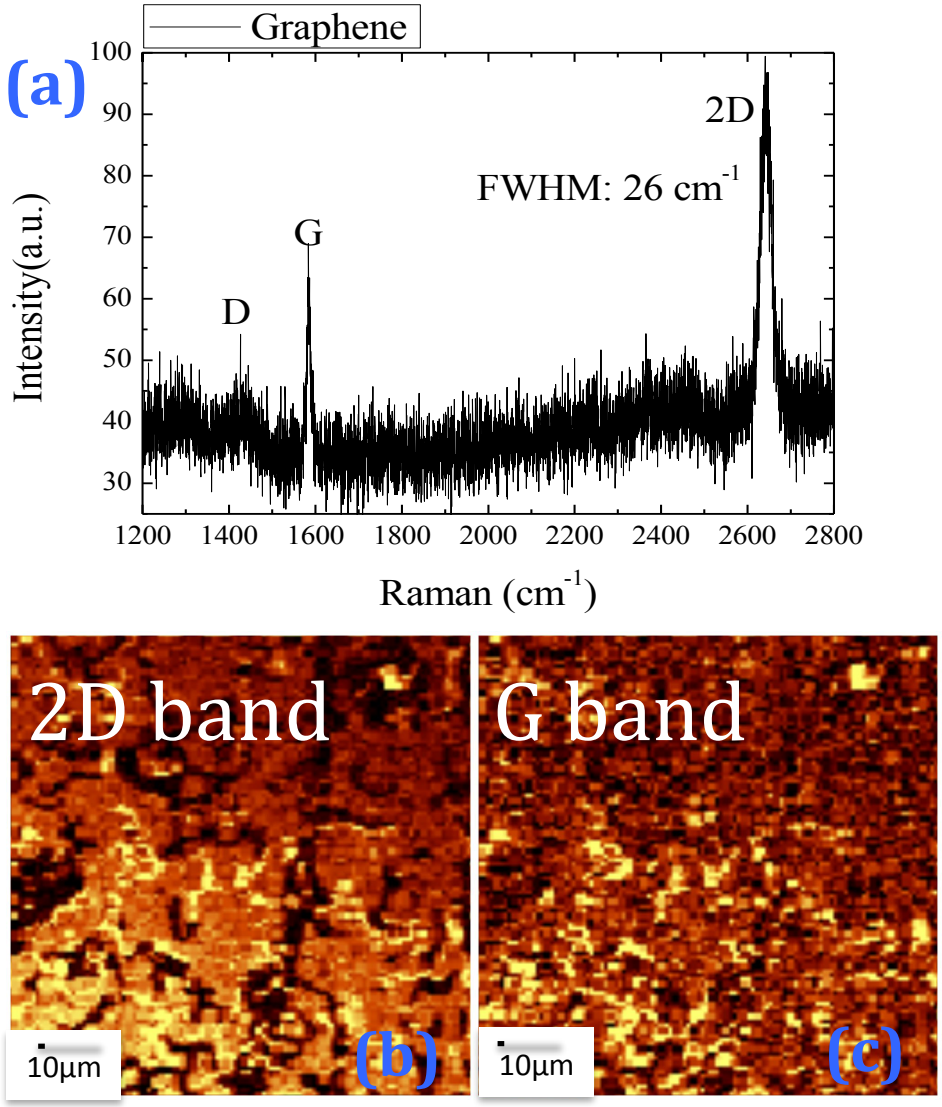

Figure 2. (a) Raman spectrum of monolayer of graphene. (b) Raman mapping of 2D band. (c) Raman mapping of G band.

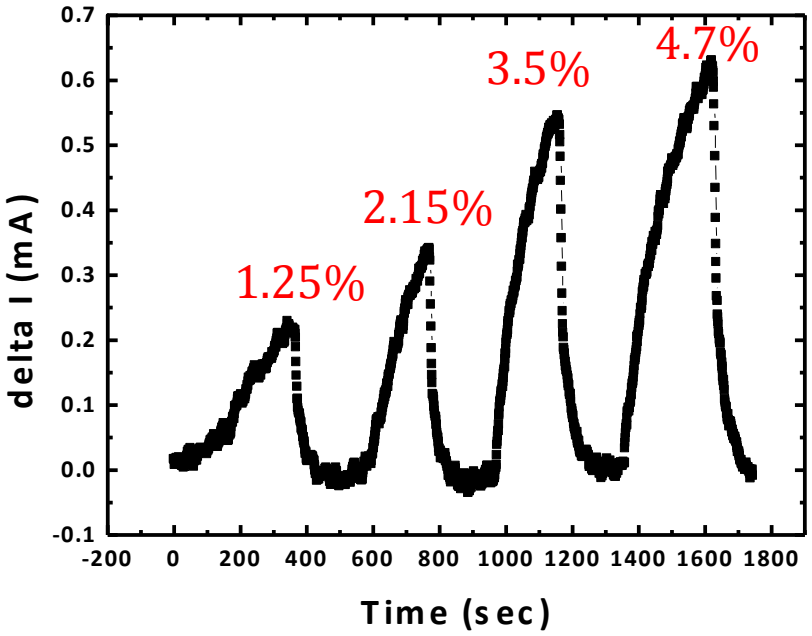

Figure 3. Real time O_2 detection with different concentration using graphene on SiO_2/Si substrate.

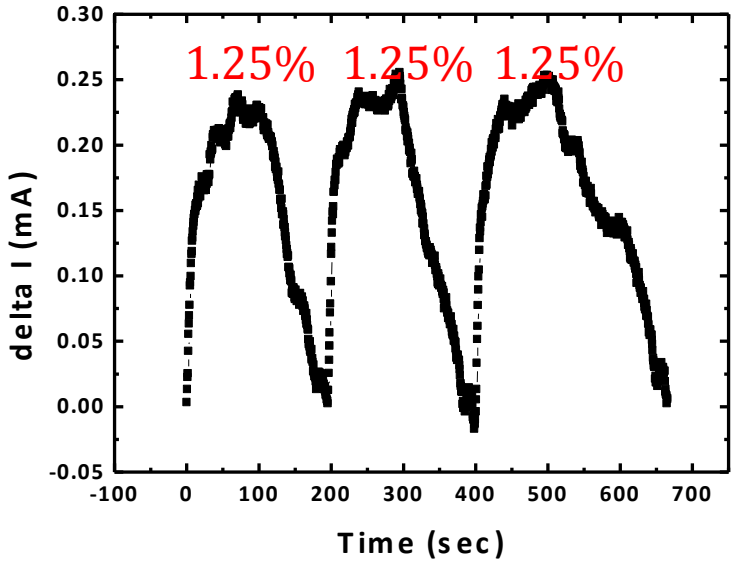

Figure 4. Real time O_2 detection with the same concentration using graphene on SiO_2/Si substrate.

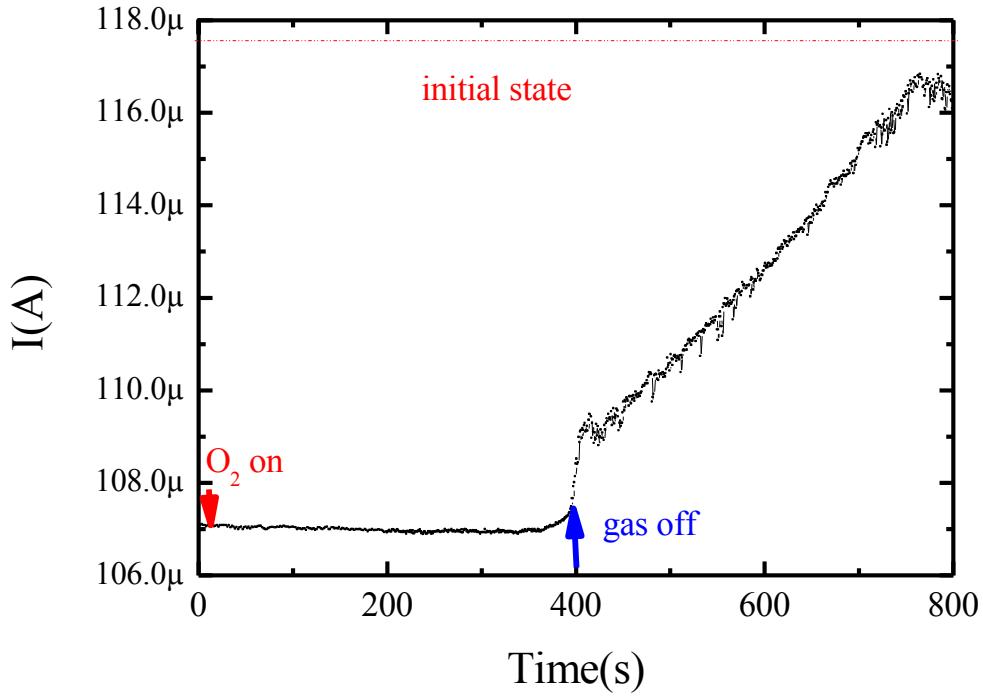

Figure 5 : Real time measurement of current change of graphene thin film.

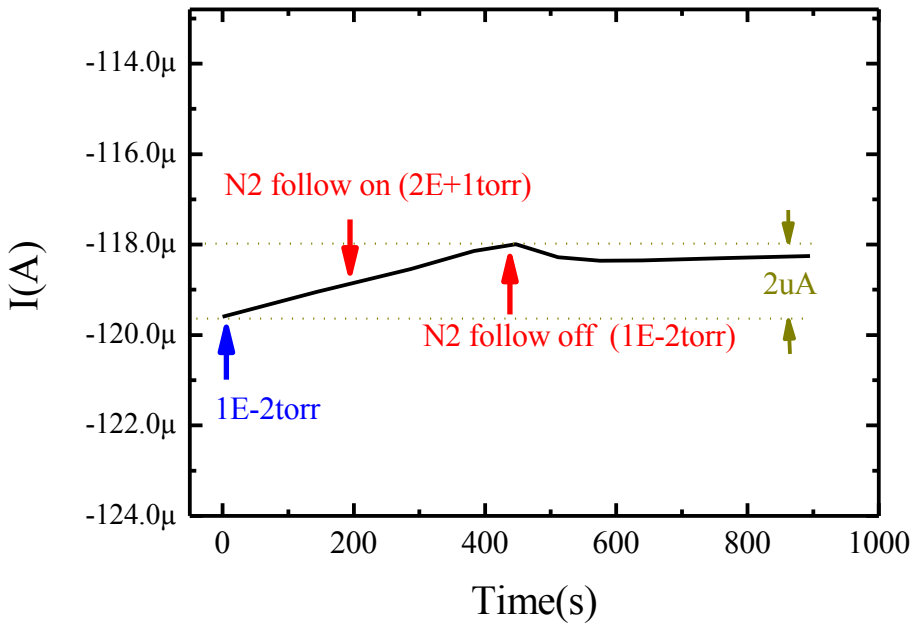

Figure 6 : Real time measurement of current change under nitrogen ambient.