# Ammonia sensing properties of centimeter scaled CVD graphene in ambient condition

Juhwan Lim, Rani Anoop, Jong H. Kim, Jaehyuk Yoon, Hye-Rin Ahn, Soonho Song, Yong-Jun Kim, and Seong Chan Jun

Department of Mechanical Engineering, Yonsei University, Seoul, South Korea, scj@yonsei.ac.kr

## ABSTRACT

The present work reports ammonia ($NH_3$) gas sensing properties of Graphene film synthesized by chemical vapor deposition (CVD) in ambient condition. Graphene with a large area as centimeter scale was synthesized on Cu foils by chemical vapor deposition under ambient pressure and has transferred onto Si/SiO$_2$ wafer. By fabricating ohmic contact to both side of graphene layer, we measured DC resistance changes with respect to $NH_3$ gas flow. The gas molecules are absorbed on graphene by chemisorption and causes resistance change of graphene which is increasing by electron injection from ammonia molecules. The sensing characteristics of graphene has been examined by changing the inlet gas flow and the sensor shows better performance with large flow, such as fast response time and high sensitivity.

*Keywords*: CVD graphene, ammonia sensor, ambient condition measurement, gas sensor

## 1 INTRODUCTION

Exraordinary physical properties of graphene such as extremely high electron mobility, optical transparency, thermal property and flexibility encourage various applications of it. [1-4] Epecially, long mean-free path, minimal electron scattering, high electron mobility, crystalinity and extremely large surface-to-volume ratio of this monolayer hexagonal carbon sheet suggest one potential as it can be applied to chemical vapor sensors, and has been highlighted by proving its astonishing sensitivity for future gas sensing material. [5,6] The operational principle of graphene sensing is based on changes in the electrical conductivity induced by the absorbance or desorbance of a gas molecule on the surface. [5-8] This chemisorption mechanism showed its great benefit in gas molecule detection on graphene, one of the most sensitive sp$^2$ carbon sheet, and showed even single molecule level of detection. [5] Currently, not only the detection limit of it as single molecule level but also its promising characteristics as chemical vapor sensor in abmbient condition has been reported. [7,8] This reasonable sensing characteristics of graphene, which has better performance than carbon nanotube (CNT) in ambient condition, suggest high possibilities for applying it to future gas sensing material. Especially, its higher surface-to-volume ratio and signal-to-noise ratio than CNT presents its novelty in gas detection as future carbon material. [8] Currently, one of the most benefits of graphene in electric device application can be found on its high productivity, which reported that it can be grown in large scale by chemical vapor deposition (CVD) process. [9-11] In the view of graphene growth by CVD, current study suggested the possibilities for growing it in large scale as much as 30-inch with metal catalyst film such as Cu or Ni. [10] Also, many studies relating graphene growth on airbitrary substrate and more reliable transfer technology accelerates its possibility for relizing graphene into real device. In this concept, it is essential to study interaction between CVD graphene with chemical vapor molecules and its application to gas sensor.
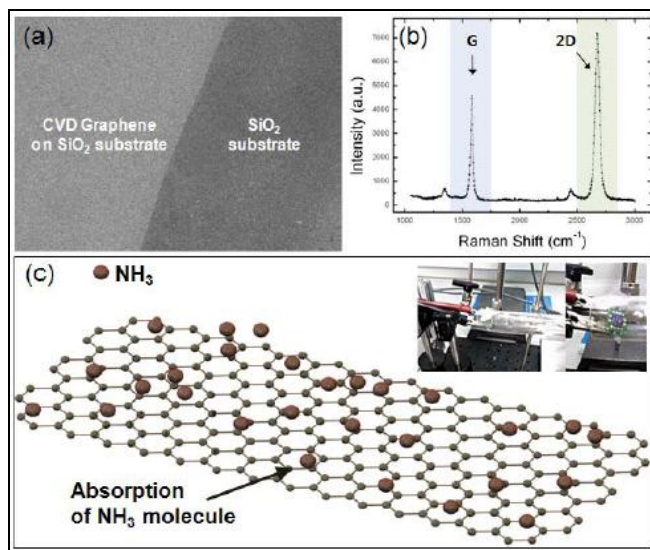


Figure 1: Graphene growth by CVD and schematics of sensing mechanism (a) A SEM image of a CVD-growth graphene, which was transferred on Si/SiO$_2$ wafer. (b) A Raman spectroscopy of mono layer graphene. (c) A schematic of sensing mechanism, $NH_3$ absorption. The inset figure 1(c) shows the measurement system of ambient condition.

In this study, we presents interaction between $NH_3$ vapor molecule and the surface of graphene which is actively enough to be applied to future gas sensor by interact each other and changes charge carrier concentration of graphene. The $NH_3$ molecules act as donor and increased the resistance of graphene. Previous studies shows well about intrinsic response of graphene from mechanical exfoliation to gas molecules. However, for its real approach to gas sensor, it is essential to confirm the gas sensing charateristics of graphene growth by CVD in ambient condition, which describes real atmospheric pressure, temperature and with air compounds. This study will suggest to how graphene growth by CVD absorbs $NH_3$ vapor molecules and performs as a real chemical vapor sensor.

## 2  FABRICATION AND MEASUREMENT

We synthesized graphene of 1.5 cm x1.5.cm scale and transferred it on $Si/SiO_2$ as shown in Fig. 1(a). The graphene confirmed its quality by Scanning electron microscope (SEM) and Raman spectroscopy for distinguishing it as a monolayer as shown in Fig. 1(b). Fig. 1(c) shows the schematic process and mechanism of sensor, that $NH_3$ gas flow and absorption of each molecules to the graphene surface. The inset of Fig. 1(c) shows the measurement system, which opened on both sides for ensuring ambient condition such as atmospheric temperature and pressure.
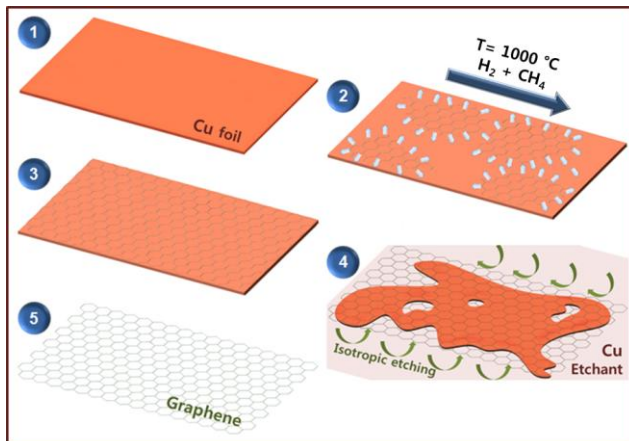
### 2.1  Graphene growth and characterization



Figure 2: Schematic of graphene growth process by chemical vapor deposition (CVD)

Graphene was growth by CVD process and transferred on $Si/SiO_2$ substrate following processes presented in Fig. 2, schematically. We grew graphene on Cu foils of 50μm thickness at temperatures of 1000°C with carbon from mixture of methane ($CH_4$) and hydrogen ($H_2$) gas and

transferred it on $Si/SiO_2$ with polymetylmethacrylate (PMMA) and Cu etchant.

Copper foil with dimensions about 20cm loaded in reactor of 2-inch-wide quartz tube and temperature increased to 1,000°C with $H_2$ condition of 90 mtorr pressure for 30 min. After reaching 1,000°C, the sample is annealed for 30 min with sustaning flow rate and pressure of $H_2$ gas. This heat-treatment of copper foils ensure enough grain size for higher-quality graphene films, as presented by Li et.al. [12] After 30 minutes of annealing, $CH_4$ gas flows with $H_2$ with matching total pressure as about 440 mtorr for 30 min. By this step, carbon from methane diffused into coppor foil. Finally, the process is terminating with far rapid cooling to room temperature with flowing only $H_2$ under a pressure of 90 mtorr. From the rapid cooling, carbon diffused into coppor went out to the surface and form monolayer carbon hexagonal film, the graphene.

The graphene film growth on Cu film then transferred on $Si/SiO_2$ substrate with using PMMA. We coated PMMA on graphene-Cu foil and cut it with proper size and shape following substrate size. PMMA coated graphene-Cu foil then floated on Cu etchant (C100). The isotropic wet etching removes Cu and some graphene residue at the bottom surface of the Cu foil. The remaining PMMA-graphene film then rinse with DI with one or two days for ensuring there is no Cu etchant residue on its surface and transferred carefully on $Si/SiO_2$ substrate.

The substrate then go through acetone cleaning and annealing with high vacuume and temperature condition for removing PMMA adhision. Finally, we make sure the pure graphene film on $Si/SiO_2$ substrate with measuring SEM as Fig. 1(a), Raman spectroscopy as Fig. 1(b) and other versatile characterization as electrical resistance or optical transmittance in visible region. The SEM image of Fig. 1(a) shows uniform deposition of graphene on substrate and Raman spectroscopy in Fig. 2(b) presents the quality of CVD graphene, by $I_{2D}/I_G$ ratio and we can confirmed it as monolayer graphene.

### 2.2  Measurement

We used silver paste for making ohmic contact electrode on both side of grahene with few-centimiter size. The sample was insearted in the test chamber which the quartz tube used in measurement was 2 inch- diameter and 50-cm long, and the volume of test-cell is about 1012.9 $cm^3$. Variations in resistance from electrical reaction from absored gas molecule and conductance change of the sensors were measured using a semiconductor parameter analyzer (Keithley 4200-SCS).

Gas flow was controlled by a mass flow controller (MFC), and we used NH3 gas with a purity of 99.999% as react gas and 99% $NO_2$ as purging gas. We used $N_2$ as purging gas that it is well known gas which doesn't reacts with graphene and also occupy high portion in air concentration. All the measurements were carried out in air

condition with open the both end of quartz tube but changing inlet gas flow rate.

## 3 RESULT AND DISCUSSION

Fig. 1 (c) presents mechamism of the sensor, schematically. The resistance remained constant in the presence of $N_2$, but increased when ammonia gas molecule go through the chamber and simply absorbed on the surface of graphene.

In the presence of $NH_3$ as the target gas, the resistance changed rapidly due to absorption onto the graphene [13]. Upon exposure to $NH_3$, the gas acted as an electron donor, shifting the valence band of graphene away from the Fermi level, resulting in hole depletion and increased resistance. The observed response could be effected from the presence of other molecules in air even though we used high purity gases. At the same time, this measurement process can be considered as the response of sensor is reliable in open, ambient condition which contains large different sorts of gas molecules which can react with graphene. We believe that if we measure the sensor in the vacuum condition, the sensor would show higher and better response than the present results, such as higher sensitivity and lower noise, but still study it in ambient condition suggests broad application of it for real gas sensor area.
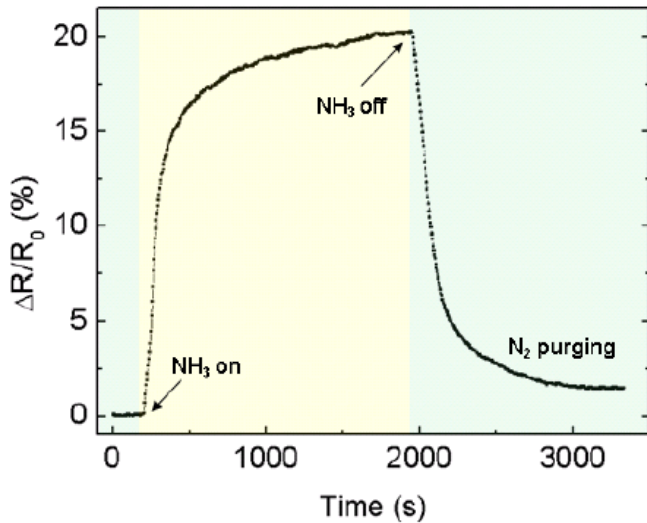
$$Sensitivity(\%) = (R_{max} - R_0)/R_0 * 100 \quad (1)$$

and response time was defined as R reach to 63.2% of maxium resistance of $R_0$, following the response curve of $R=R_0*[1-\exp(-t/\tau)]$. In response curve for $t= \tau$, the sensor response level reach to 63.2% of initial resistance. As shown in Fig. 3, it is obvious from the sensor's response that $NH_3$ molecules reacts with graphene surface and change its electrical conductance.

This sensor showed comparable sensitivity and response time, but some defects on recovery performance about 3~4% of residue. The reason for the failure of complete recovery may be due to the factors such PMMA contamination to graphene, other gas contamination and experimental errors. First of all, PMMA contamination of graphene is the main reason that reduces the recovery performance. It is not solved yet, how to remove the contamination while obstacle issues in CVD graphene research community. We believe that after resolving this issue, this device may recover fairly as same as the initial state. Since the experiment was carried out in atmosphere condition, the presence of some other gases can also affect the results. There are some gas molecules that absorbes on graphene and reacts as donor or acceptor, such as $CO_2$ or $NO_2$. This molecules may exists in the ambient condition chamber and seem to degraded the recovery performance .



Figure 3 Sensing response of CVD graphene on Si/SiO$_2$ to NH$_3$ gas with inlet of 100ml/min.

Fig. 3 shows the response of the sensor, by showing resistance change with inlet of 100ml/min of $NH_3$ gas flow. The resistance increases by gas injection and decreases to initial state by purging with $N_2$ gas. The sensitivity of 18% is found to be better than that from micron-size graphene from mechanical cleavage, [7,8] but shows a slower response time. The sensitivity is calculated by equation (1) in below,
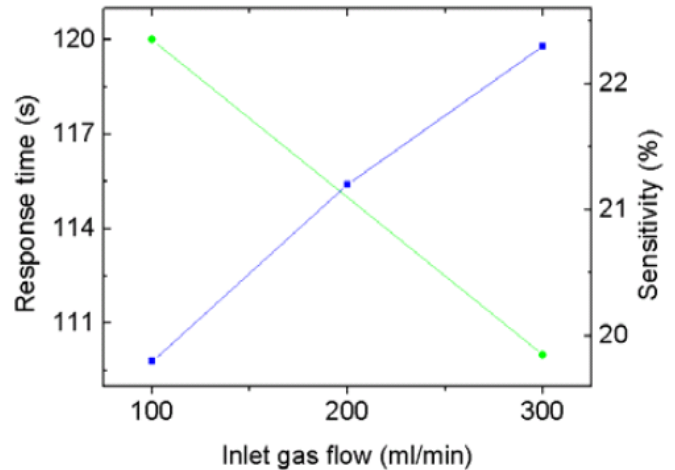


Figure 4 Sensing performance change by changing inlet gas flow. Green line indicates response time decreases and blue line shows sensitivity increases as flow increase.

Fig. 4 shows sensor's sensitivity and response time with different flow rate of react gas. In higher flow rates, more gas molecules with higher concentration is existing in the chamber that chemisorptoin rate would be increased and causes intense and fase response of the material. Our sensor showed reasonable response time and sensitivity in this concept, that sensitivity increased from 19% to 23% due to increased inlet gas flow and response gets fast from 120s to 107s with repect to increasing gas flow. Our sensor showed

comparable sensitivity and response time than graphene exfoliated by mechanical tapping method, which implied higher potential of commertial CVD graphene to be applied to chemical vapor sensor.

## 4 CONCLUSION

Highly sensitive $NH_3$ gas sensors were fabricated using CVD graphene films grown by chemical vapor deposition. We prepared graphene by CVD process and transferred it on $Si/SiO_2$ substrate using Cu etchant and PMMA adhision. The sensors prepared with mono layer graphene showed satisfactory sensing characteristics for $NH_3$ gas with simple chemisorption mechanism. The sensor shows high sensitivity, fast response and recovery. Our preliminary findings are a promising starting point to investigate this material as a suitable candidate for gas sensing at room temperature.

## 5 ACKNOWLEDGEMENTS

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