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Sensitivity Study of Graphene Nanoribbon with NH_3 at Room Temperature

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ABSTRACT

This study presents the sensitivity of graphene nanoribbon (GNR) when exposed to ammonia gas at room temperature. Alumina were used as a substrate and coated with GNR as sensing film for ammonia gas detection. Four different concentration of GNR in the category of maximum, high, low, and minimum were prepared. Each category of GNR will be dispersed on alumina substrate with area of $1cm^2$ and $4cm^2$. 30nm of gold contacts are sputtered on both ends of the sensing film. The ammonia gas can be detected by measuring the changes in resistance. The GNR as ammonia sensor shows good responses at room temperature. In repeatability test, maximum GNR shows least variation when exposed to ammonia with the value of 1.01% ($4cm^2$) and 2.12% ($1cm^2$). In a sensitivity test, 0.25% to 1.00% of ammonia gas was used and tested on maximum GNR. Maximum GNR on $4cm^2$ substrate shows higher sensitivity as compared to $1cm^2$. Reaction time of GNR on ammonia gas decreased as the concentration of ammonia increased. Larger surface area of sensing element required lesser reaction time.

Keywords: GNR, alumina substrate, ammonia, sensitivity

INTRODUCTION

Concerns over air pollution which directly affects the health of human beings and animals have led to increased demands for low power consumption, low temperature operation, and smaller size sensors that are highly sensitive in detecting pollution (Somov et al. 2015). Recent researches on nanotechnologies gas sensors have shown good responses on the targeted chemical gas such as polymer fibres for hydrogen gas (Chen et al,. 2014), polymer dispersed liquid crystal doped with carbon nanotube for acetone gas (Lai et al., 2013), and carbon nanotube for carbon dioxide detection (Wang et al., 2014). Ammonia gas, NH_3 is a toxic gas which is harmful to the

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environment and living beings. Long periods of exposure to NH_3 will cause severe irritation to the skin, harm the respiratory systems and damage the internal organs. Hence a high sensitivity and fast response ammonia gas detector is needed to curb these problems.

Graphene with excellent electronic properties had received attention in the sensor field. Its properties are suitable for sensing with high mobility at room temperature, high current densities, and high thermal conductivity (Kara et al., 2013). The two-dimensional honeycomb-like structure of graphene also helps in promoting gas sensing sensitivity exposing large areas to the targeted gas (Huang et al., 2012). Many researches on ammonia gas sensor have been reported using graphene as sensing elements which basically can be divided into: graphene with polymers (Wu et al., 2013) and graphene with oxide (Huang et al., 2012) which shows good response. There is not much research on the sensitivity of GNR coated on alumina substrate. This paper aims to study the sensitivity of GNR coated on alumina substrate with ammonia gas at room temperature.

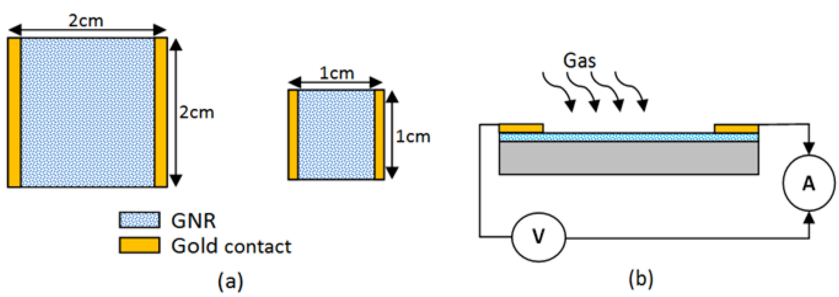

Figure 1. Schematic diagram of (a) sensor with different surface area; (b) measurement design when sensor exposed to gas

Table 1
Category of different amount of GNR on type I and type II substrate

Alumina Substrate	Label for GNR coated	GNR coated on substrate (cm/Ω)
Type I	Maximum	4.03 x 10^{-4}
2cm x 2cm	High	3.16 x10^{-4}
	Middle	1.02 x 10^{-4}
	Low	0.73 x 10^{-4}
Type II	Maximum’	3.92 x 10^{-4}
1cm x 1cm	High’	2.39 x 10^{-4}
	Middle’	1.27 x 10^{-4}
	Low’	1.63 x 10^{-4}

EXPERIMENT DETAILS

Figure 1(a) shows the schematic diagram of the sensing part. Alumina is used as the substrate for the sensing part. GNR is prepared and coated in Kyutech, Kyushu Institute of Technology. Double walled carbon nanotube was used to obtain single layered GNR. The method of preparation is adopted from (Tanaka et al. 2015).

Alumina substrate can be divided into two categories: type I and type II. Type I and Type 11 indicate the substrate with area of $4cm^2$ and $1cm^2$ respectively. A thin layer of GNR is coated on the alumina substrate (Tanaka et al., 2015). Two strips of gold contact are sputter coated on top of GNR at both ends. Thickness of the gold contact is 30nm. Gold is used as contact for two reasons: its resistance to corrosion and it does not produce any chemical reaction with ammonia gas. Table 1 shows the preparation of the sensing part with different amount of GNR on type I and type II substrate. The amount of GNR is obtained from the resistivity equation (1).

$$R = pl/A \tag{1}$$

Figure 1(b) shows the electrical connection to the sensing part. A constant voltage supply of 1.5V is connected to the sensing part throughout the experiment. Resistance of the GNR can be obtained by measuring the current as shown in Figure 1(b). Fluke 289 True RMS Multimeter is used for current measurement. Chemical gas flowed in and out are indicated as gassing and degassing respectively.

Sensing part is placed into the airtight stainless steel gas chamber with the connection of gas inlet, gas outlet, and measuring probe to the power supply and multimeter. The gas flow is controlled by computerised Aalborg Gas Controller Module. Amount of gas flow into the chamber can be observed through the Aalborg Command Module.

Repeatability Test

The sensing element was stabilised during the pre-experiment stage whereby 15 minutes of air is flowed in to stabilise the GNR. Ammonia gas with concentration of 0.5% was used during repeatability test. Duration of ammonia gassing and degassing was 10 minutes for each session and both were repeated for two cycles.

Repeatability of the sensing element can be determined by observing the difference (variation) between the first and the second gassing response as stated in Table 2. Equation (2) and (3) show the mathematical calculation to determine the variation and consistency. Maximum concentration shows the least variation followed by high, middle and low concentration. Low variation indicates high consistency.

$$Variation\ (\%) = \frac{Second\ peak - First\ peak}{First\ peak}\ x\ 100\% \tag{2}$$

$$Consistency = \frac{1}{Variation} \tag{3}$$

Table 2
GNR with different concentrations towards 0.5% ammonia gas for type I and type II

	Type I	Type II
Concentration of GNR	Variation (%)	Variation (%)
Maximum	1.01	2.12
High	2.81	2.18
Middle	4.61	2.23
Low	4.77	3.44

Sensitivity Test

GNR with maximum concentrations for type I and type II were used to further the experiment on sensitivity test. The sensing part was stabilised before gassing. Ammonia gas with 0.25%, 0.5%, 0.75% and 1% concentrations respectively were gassed into the chamber alternately with air in between. The sensing element sensitivity in this experiment is measured and expressed:

$$Sensitivity\ (\%) = \frac{R_g - R_o}{R_o} \cdot 100 \quad (4)$$

where R_g and R_o are the resistance of GNR exposed to ammonia gas and air respectively.

RESULT AND DISCUSSION

Repeatability Test

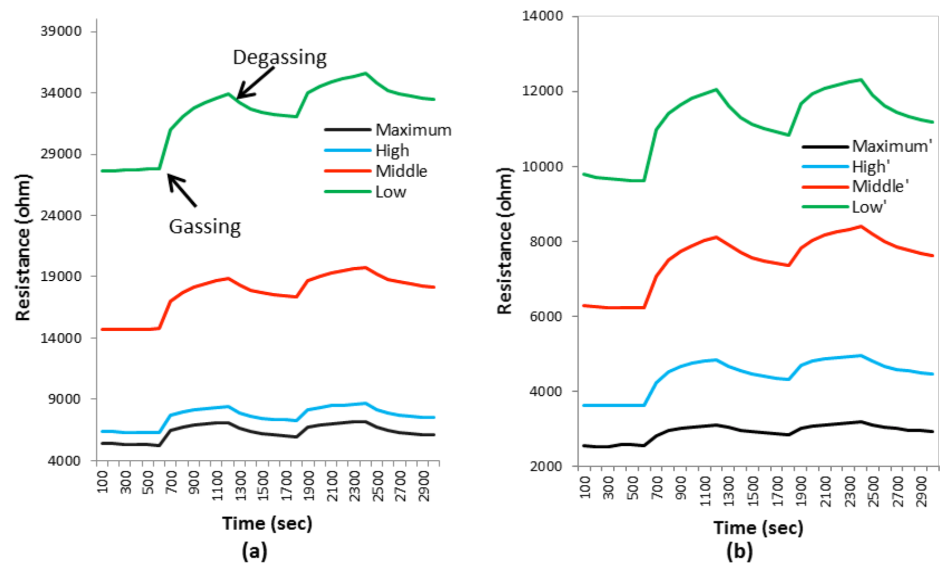

Figure 2. Response of ammonia gas on sensing part (a) Type I (b) Type II

Responses for the repeatability test were shown in Figure 2. Adsorption of ammonia gas on the GNR surface will alter the conductivity of the GNR. Significant changes can be observed from the response of the sensor. Resistance of the GNR increased when ammonia gas is introduced to the sensing element.

The resistance of the GNR was obtained by measuring the current change with constant voltage supply of 1.5V throughout the experiment. The response of GNR towards ammonia can be explained based on the chemical adsorption between sensing element and the targeted gas. Ammonia gas tends to be a donor of electron (Yunusa et al. 2015). Resistance of the GNR increased due to the space charge region on the surface. This region appears due to the donating electrons which eventually depletes the holes and increases the distance between the conduction band and valence band.

Repeatability test on GNR could be observed through the injection of 0.5% of ammonia gas. Variation of each concentration of GNR is shown in Table 2. Variation of the response increased for the Low concentration of GNR. Maximum concentration of GNR shows lowest variation (type I: 1.01% and type II: 2.12%) which means the response for the second gassing session has little changes compared with the first gassing session (higher consistency).

Sensitivity Test

The same sample of GNR with maximum concentration from repeatability test was used for sensitivity test. Responses from type I and type II with maximum concentration of GNR exposed to different concentration of ammonia gas are shown in Figure 3. Ammonia with concentration of 0.25%, 0.50%, 0.75%, and 1.00% respectively were injected and the response is recorded. The experiment is carried out at room temperature and with the supply of 1.5V throughout the experiment. These have satisfied the aim of target for sensors: response at room temperature and low power consumption (Giselle et al., 2007).

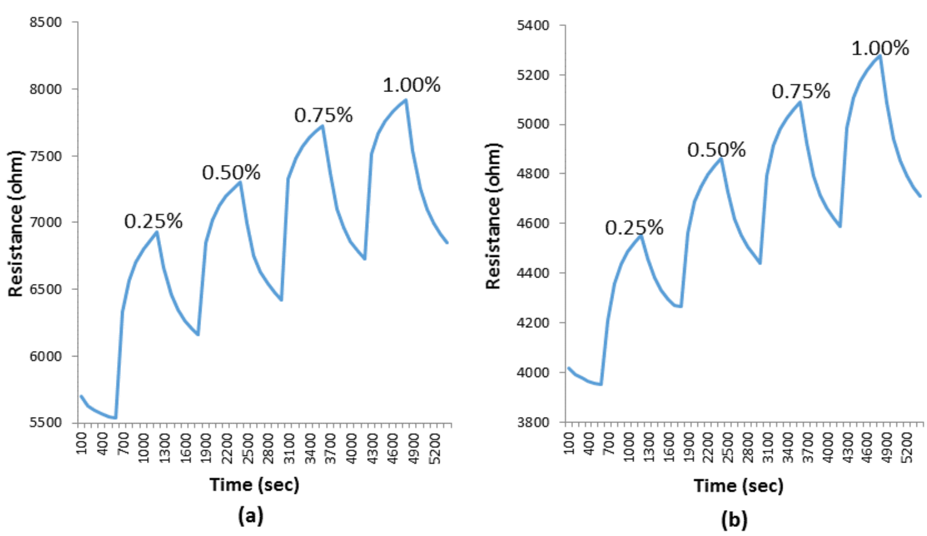

Figure 3. Response of GNR maximum (a) Type I (b) Type II on variation of ammonia concentration

Table 3 shows the reaction time and sensitivity for type I and type II in sensitivity test. Sensitivity of type I is higher than type II. Larger surface area caused larger surface of GNR exposed to ammonia gas; hence, higher sensitivity and lower reaction time for type I compared with type II. Reaction time refers to the time taken for the GNR response during injection of ammonia gas.

Table 3
Reaction time and sensitivity of sensing part with different ammonia concentration

Concentration of NH_3 (%)	Reaction Time *(sec)*		Sensitivity *(%)*	
	Type I	Type II	Type I	Type II
0.25	22	28	25.21	15.27
0.50	20	23	32.03	23.15
0.75	15	20	39.61	28.87
1.00	13	16	43.12	33.64

CONCLUSION

Ammonia gas sensor with GNR as sensing element shows good responses at room temperature. Sensing elements with surface area of $4cm^2$ and $1cm^2$ were studied. Repeatability test using 0.5% ammonia gas were tested on all type I and type II GNR. Maximum concentration of GNR shows least variation when exposed to ammonia at room temperature with the value of 1.01% and 2.12% for type I and type II respectively. Maximum concentration of GNR shows highest consistency compared with lower concentration of GNR. Sensitivity tests were performed on GNR with maximum concentration. An experiment was carried out by injecting variation of ammonia gas with concentration of 0.25% to 1.00%. The sensitivity of GNR towards ammonia increased as concentration of ammonia increased. Type I which has a bigger area, $4cm^2$, shows higher sensitivity compared with type II with an area of $1cm^2$. Time for GNR to react with ammonia gas decreased as the concentration of ammonia increased. Larger surface area of sensing element required lesser reaction time. Graphene with excellent electrical properties have shown responses with 1.5V of supply throughout the experiment.

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