Potential Application of Y-tip Graphitic Nanoribbons to Gas Sensing

Z. Yunusa, M.N. Hamidon, S. A.Rashid and I. Ismail

Abstract— In this paper, we report the application of Graphitic Nanoribbons (GNR) as gas sensor. Bulk Y-tip GNR was directly synthesized using Alcohol Catalytic Chemical Vapor Deposition (ACCVD) on a sensing platform which consists of gallium orthophosphate, platinum and zirconium. The novel material was deployed for gas sensing application by monitoring resistances changes upon gas injection. The sensor was exposed to both hydrogen and ammonia gases respectively. Results obtained showed no sensitivity to hydrogen gas between 1% to 1.75% and good response to ammonia gas from 1250 ppm to 10,000 ppm. The sensor also showed good repeatability with good response and recovery times.

1 Introduction

Carbon nanomaterials have proven to be good sensing materials when employed for gas sensing application [1].Different techniques of coating the sensing material for gas sensing which includes spin coating [2], drop casting [3] , spray painting [4], langmuirr Blodgett [5] and direct synthesis techniques [6], [7] have been reported . However, based on literature it has been reported that sensors that are developed based on direct synthesis of the sensing material have better adhesion which leads to improved sensitivity as well as improved stability [8]. Another advantage of this technique is that it involves a single step process which saves time for sensor preparation.

Past researches involving direct synthesis of CNT for ammonia sensing application have used SiO_2 [11] and Pt-Alumina substrates [6], [7] which showed that it has affinity to pristine carbon nanomaterials as reported in literature [9]

In this paper, synthesis of GNR was carried out directly on the sensing platform which comprises of $GaPO_4$ substrate and a layer of zirconium and platinum. Similarly, the same substrate was used as a sensing platform for the detection of hydrogen using surface acoustic wave resonator [10]. Detailed procedure of the synthesis process could be found in our previous paper [11], [12]. In this paper, the directly synthesized GNR will be deployed as a sensing material so as to explore its potential application in the sensor industry.

As a new material, selectivity test will be done towards both hydrogen and ammonia gases. Hydrogen gas is colourless, odorless and could be used as a clean fuel [13]. However, 4% of hydrogen in air will cause explosion [14]. Therefore, a sensor is required to monitor its concentration in air so as to avoid accidents. In this paper, the sensor will be exposed to hydrogen gas between 1% to 1.75%.

Ammonia gas was also chosen as the second target gas due to its high toxicity. Humans exposed to low concentrations of ammonia ranging from 25 ppm to 1000 ppm have health complications such as eye, nose and throat irritation as well as breathing problems, while long exposure to high concentrations greater than 1700 ppm might lead to death [15]. Therefore, monitoring of ammonia gas becomes critical. However, in this paper the interest was on sensing ammonia at high concentrations from 1250 ppm to 10,000 ppm.

- *Zainab Yunusa Institute of Advanced Technology Universiti PutraMalaysia 43400 Serdang Selangor, Malaysia*
- *Mohd Nizar Hamidon Institute of Advanced Technology Universiti PutraMalaysia 43400 Serdang Selangor, Malaysia*
- *Suraya Abdul Rashid Institute of Advanced Technology Universiti PutraMalaysia 43400 Serdang Selangor, Malaysia*
- *Ismayadi Ismail Institute of Advanced Technology Universiti PutraMalaysia 43400 Serdang Selangor, Malaysia*

2 MATERIALS AND METHODS

2.1 Fabrication of sensing platform

The platform that was used for the synthesis comprises of 3 layers; gallium orthophosphate ($GaPO_4$) which is a piezoelectric material, zirconium under layer which is between the $GaPO_4$ and the platinum to promote adhesion.Figure 1 shows the cross section of the sensing platform.

2.2 Gas sensing application of GNR

The GNR was made into a sensor without any post treatment by directly connecting two gold wires to the platinum pads on an alumina substrate. These wires were then connected to a fluke 289 multimeter. The gas sensing set-up is as shown in Figure 2 and it consists of two Aalborg mass flow controllers which are fed with air and ammonia gases respectively. These were connected to a command module which is connected to a computer and controlled using labview program. The gas was introduced into the chamber via the inlet from the mass flow controllers. The output of the sensor was data logged with the aid of fluke-view form software via the computer. The sensor was tested towards ammonia gas with different concentrations from 0.25 % to 1 %. Measurements were carried out at room temperature. Ammonia gas was purged in for a period of 5 minutes and synthetic air was used as for recovery for 15 minutes.

2.3 GNR for Hydrogen and AmmoniaSensing

After synthesis, the sample was made into a sensor by mounting it on an alumina substrate and connecting two gold wires for electrical connections. Subsequently, the sensor was put into the gas chamber and immediately deployed for gas sensing measurements. Air was first purged into the chamber so as to stabilize the system for 30 minutes and then 1% hydrogen gas concentration was introduced into the chamber for 5 minutes. The same process of gas adsorption was repeated with different concentrations of hydrogen of 1.25%, 1.5% and 1.75% respectively and air was used for recovery. All measurements were carried out at room temperature. The gas chamber of Figure 2 was modified to house a heater and a thermocouple for measuring temperature. The sensor was heated to 60^0C and then measurements were repeated with different hydrogen concentrations from 1% to 1.75% with the same timing for gas adsorption and desorption as that of room temperature. The output of the sensor was monitored by a Flukeview 289 Multimeter by taking resistance measurements which was retrieved via a data logger connected to a personal computer. The response of the sensor was calculated based on the equation.

Similarly, after complete recovery for 1 day, the same sensor was deployed for ammonia gas testing using the same set up of Figure 2 at room temperature. Ammonia gas was purged with a concentration of 1250 ppm for 5 minutes while air was used for recovery for a period of 15 minutes. Different concentrations of ammonia gas of 2500 ppm, 5000 ppm, 7500 ppm and 10,000 ppm were further purged into the gas chamber all at room temperature for adsorption and then air introduced for desorption. The output of the sensor which was measured as a change of resistance of the GNR was measured using a fluke 289 multimeter

$$Sensitivity = \frac{\Delta R}{R}\ (\%) \qquad \text{eqn.1}$$

3 RESULTS AND DISCUSSIONS

Resistance changes obtained were plotted as shown in Figure 3 and Figure 4. Figure 3 showed resistance change when the sensor was exposed to hydrogen at room temperature and it could be noticed that there are no significant changes for all the hydrogen gas concentrations. Similarly, when the sensor was heated at 60 ^{0} C the resistance changes were as plotted in Figure 4. This also showed that the resistance changes do not increase proportionately with increase in gas concentrations from 1% to 1.75%. This is in conformity with the results shown by Jayatissa et al, that pristine carbon based materials are not good sensing materials at room temperature but require elevated temperatures [16]. Pristine carbon materials need to be functionalized with acids [17], metal

nanoparticles [18]–[20] and oxides [21] to present good sensitivity towards hydrogen gas.

The sensitivity of the sensor was obtained based on equation 1 and the results are plotted as shown in Figure 5(a). It could be observed that the sensitivity increases with increasing gas concentrations. The minimum sensitivity of the sensor at 1250 ppm concentration is 4.5% while the maximum sensitivity for 10000 ppm concentration is 6%. This shows that the pristine GNR based sensor has affinity towards ammonia gas as in CNT based ammonia gas sensors. In order to test the sensor for repeatability, it was tested repeatedly for 1250 ppm gas concentration for four cycles and the response obtained which is plotted in Figure 5 (b). The results showed good repeatability and also recovery to baseline without any annealing or heating treatment requirement. It could also be observed that the sensitivity increases as a result of increase in gas concentration which is in agreement with work done by other researchers [6], [7], [22], [23] .

The sensitivity of the sensor towards ammonia was plotted for different concentrations from 1250 ppm to 10000 ppm as shown in Figure 6 and it shows a linearity behavior with each increase in gas concentration. Response and recovery times were also observed and recorded. The response times were calculated based on the time it took for the sensor to reach 90 % of its steady state value. Figure 7(a) shows plot of the response time versus gas concentration which shows that the response time becomes faster with increasing gas concentration. The response time is seen to slow down from 4.5 minutes for 1250 ppm ammonia gas concentrations to 1 minute in case of 10000 ppm gas concentration. Recovery times were computed based on the time it took for the sensor to attain 90 % of the baseline. A plot of the recovery time versus gas concentrations is shown in Figure 7(b).which shows that recovery time increases with increase in gas concentration due to the high concentration of the gas species adsorbed by the GNR which therefore required a longer time to recover to baseline. It could be observed that the recovery time increases from 8 minutes in the case of low gas concentration to 12 minutes for full gas concentration.

Since there are no reports of a similar GNR structure in literature, the response of ammonia gas to the GNR could be compared with that of CNT which has already been established. Based on our results the sensing mechanism is similar to ammonia gas sensors based on CNT. As shown by [19]–[22] when ammonia gas is exposed to ammonia gas it donates electrons to the CNT because ammonia is an electron donor. The injection of ammonia gas causes increase in the separation between the valence band and the conduction band; as a result the number of holes becomes depleted due to the donating electrons. This depletion causes a space charge region at the surface of the semiconducting CNTs and thereby results in increased electrical resistance which makes the CNT to behave like a p-type semiconductor.

4 CONCLUSION

The synthesis of bulk GNR directly on a piezoelectric substrate using the ACCVD and its potential application was reported. The GNR based sensor was exposed to different concentrations of hydrogen and ammonia gases respectively so as to determine selectivity. Based on the sensor response it was observed that the sensor did not show sensitivity towards hydrogen gas at room temperature and at 60^0C. However, the sensor showed good response to ammonia gas even at room temperature the sensitivity of the sensor was 4.5% at 1250 ppm. Response time was also calculated to be 4.5 minutes at 1250 ppm while it was 1.5 minutes at full concentration of 10000 ppm. Similarly, the sensor showed good recovery with a recovery time of 6 minutes at 0.125% and 12 minutes at 1% without any heating. Good repeatability was also observed at 0.125%. Based on these results, it could be deduced that the pristine novel GNR could be a potential sensing material for ammonia gas sensor. Future works need to focus on how to enhance the sensitivity by functionalization with metal nanoparticles, composites and polymers.

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