DETECTION OF NH₃ & CO₂ USING CARBON NANOTUBES AT ROOM TEMPERATURE

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ABSTRACT

Gas sensors have attracted intense research interest due to the demand of sensitivity, fast response, and stable sensors for industry, environmental monitoring, biomedical, and so forth. Conventional metal oxide gas sensors lack flexibility with poor response times and operate at elevated temperature (200-500°C), which implies that power is required. The development of nanotechnology has created huge potential to build highly sensitive, low cost, portable sensors with low power consumption. The extremely high surface-to-volume ratio and hollow structure of nanomaterials is ideal for the adsorption of gas molecules. Particularly, the advent of carbon nanotubes (CNTs) has fuelled the inventions of gas sensors that exploit CNTs' unique geometry, morphology, and material properties. Upon exposure to certain gases (alkalis, halogens and other gases at room temperature), the electrical resistance of CNT’s drastically changes. Hence, carbon nanotubes have the potential to be a better chemical sensor. The gases used in this study were ammonia (NH₃), carbon dioxide (CO₂), hydrogen (H₂) and etc. Gas sensing properties of carbon nanotube was studied; the presence of gas is detected by changing of its electrical resistivity.

KEYWORDS: Carbon Nanotubes, Electrical Resistance, Gas Sensor, CVD

INTRODUCTION

Gas sensors, or chemical sensors, are attracting tremendous interest because of their widespread applications in industry, environmental monitoring, space exploration, biomedical and pharmaceutics. Gas sensors with high sensitivity and selectivity are required for leakage detections of explosive gases such as hydrogen, and for real-time detections of toxic or pathogenic gases in industries. There is also a strong demand for the ability to monitor and control our ambient environment, especially with the increasing concern of the global warming. Researchers from the national aeronautics and space administration (NASA) are seeking the use of high-performance gas sensors for the identification of atmospheric components of various planets. In addition, nerve agent sensing for homeland security is also at the center of public concern. Generally, there are several basic criteria for good and efficient gas sensing systems: (i) high sensitivity and selectivity; (ii) fast response time and recovery time; (iii) low analyt consumption; (iv) low operating temperature and temperature independence; (v) stability in performances. Commonly used gas sensing materials include vapor-sensitive polymers, semiconductor metal oxides (such as tin oxide, zinc oxide, titanium oxide and aluminum oxide.), and other porous structured materials such as porous silicon. Since the most common gas sensing principle is the adsorption and desorption of gas molecules in sensing materials, it is quite understandable that by increasing the contact interfaces between the analysts and sensing materials, the sensitivity can be significantly enhanced. The recent development of nanotechnology has created huge potential to build highly sensitive, low cost, portable sensors with low power consumption. The extremely high surface-to-volume ratio and hollow structure of nanomaterials is ideal for gas molecules adsorption and storage. Therefore, gas sensors based on nanomaterials, such as carbon nanotubes (CNTs), nanowires, nanofibers, and nanoparticles, have been investigated widely.
CNTs are new carbon materials discovered recently. They are cylindrical carbon molecules with properties such as low density, high tensile strength and elastic modulus. Metallic CNTs have a high electric current density, and all of these properties make CNTs potentially useful in extremely small-scale electronic and mechanical application. There are two main types of nanotubes; single walled carbon nanotubes (SWNTs) and multi walled carbon nanotubes (MWNTs). SWNTs can be considered as a sheet of graphene that has been rolled up into a seamless cylinder, while MWNTs consist of nested coaxial arrays of SWNT constituents. Their structures are unique, only a few nanometers in diameter, but up to hundreds of microns long. CNTs possess very unique characteristics due to their hollow center, nanometer size and large surface area, and are able to change their electrical resistance drastically when exposed to alkalis, halogens and other gases at room temperature. Hence, they have the potential to be a better chemical sensor. This study is carried out to investigate the potential application of carbon nanotubes as a gas sensor by measuring the change of electrical resistance of the carbon nanotubes upon gas absorption. The gases used in this study were carbon dioxide (CO$_2$), ammonia (NH$_3$) and hydrogen (H$_2$).

**CNTs PREPARING TECHNIQUES**

Three main techniques to prepare CNTs are as follows

- arc-discharge technique
- laser ablation technique
- chemical vapor deposition (CVD) technique.

The carbon arc-discharge method is the first technique that was used to grow CNTs. The process is carried out in a vacuum chamber with two carbon electrodes as carbon source. Inert gas (typically helium) is supplied to increase the speed of carbon deposition. When high DC voltage is applied between the carbon anode and cathode, plasma of the inert gas is generated to evaporate the carbon atoms.

The ejected carbon atoms are then deposited on the negative electrode to form CNTs. Both SWNTs and MWNTs can be grown by this method, while the growth of SWNTs requires catalysts. It is the principal method to produce high quality CNTs with nearly perfect structures.

In the laser ablation technique, a carbon target is ablated by intense laser pulses in a furnace in the presence of an inert gas and a catalyst. CNTs are formed and collected on a cold substrate. Both the arc-discharge and laser-ablation methods require high growth temperature, which is about 3000–4000°C for the evaporation of carbon atoms from solid carbon source.

In a CVD system, a gas hydrocarbon source (usually methane, acetylene or ethylene) flows into the reaction chamber. The hydrocarbon molecules are broken into reactive species at the temperature range of 550–1000°C. The reactive species react in the presence of catalysts (usually metal particles such as Ni, Fe or Co) that are coated on the substrate, leading to the formation of CNTs. Compared with the first two techniques; CNTs can be synthesized at relatively low temperature using CVD method.

Therefore, this technique is more efficient and allows scaling up the growth of SWCNTs. By modification and calculated control of the growth parameters, vertically aligned MWCNTs growth can be achieved by CVD technique. This enhances CNTs electronic properties in different applications. High-quality SWCNTs can also be obtained by the optimization of the catalysts.
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EXPERIMENTAL

Growth of CNTs

A silicon substrate is coated with a Ni metal which act as a catalyst for CNT growth using thermal evaporation method. The coated samples are placed onto a heating plate in the center of the PECVD reactor, which is then pumped down to a low base pressure (~1mTorr) to evacuate atmospheric gasses. Then the substrate is heated to a temperature shown to produce carbon nanotubes (450 to 700°C depending on process and chemistry).

Gas Sensing Procedure

Gas sensing experiments were carried out by placing CNTs synthesized on a quartz substrate in a sealed Plexiglas test chamber with an electrical feed-trough. At first, the chamber was purged continuously with pure argon gas about 1 hour. Then, diluted CO$_2$ or NH$_3$ in the argon as a carrier gas was injected into the chamber at room temperature of 25°C.

Sensor resistance was measured at intervals of 10 seconds with a digital Multimeter connected to a computer using an RS232 interface that was fully automated and logged by a program. We repeated each test for two times to obtain the exact results. A schematic of the apparatus used for gas detection is shown in Fig. 1.

RESULTS AND DISCUSSIONS

Structure Characterization

The samples were characterized by using Scanning Electron Microscopy (SEM). SEM micrographs have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample. Fig. 2.a. Shows the SEM image of pristine sample which is taken after deposition of 100Å thin layer of Ni metal on Si substrate by evaporation technique.
And Fig. 2.b. Shows the SEM image of CNTs after CVD-Process (PECVD without plasma) using a mixture of \( \text{NH}_3 \) (15sccm) and \( \text{C}_2\text{H}_2 \) (15sccm) at Reaction temperature of 730\(^\circ\)C. From this it is clear that the growth of CNTs produced is tip-growth, where the nanotube lifts the catalyst from the substrate during the growth, as the nanotube nucleates and grows below the catalyst.

Figure 2.b: SEM image of CNTs after PECVD without Plasma/CVD

Gas Sensing Characterization

Ammonia Absorption

The results obtained indicate that the carbon nanotubes grown were sensitive to ammonia. Upon exposure to ammonia, the resistance of carbon nanotubes increased significantly at room temperature of 25\(^\circ\)C.

Figure. 3. Shows the results of the samples for 2 repetitions. The maximum resistance detected is 159.8 milliohm which is more than the resistance recorded in argon.

From the graph, it can be seen that the first repetition, R1 has a lower value compared to R2. This indicates that the absorbed ammonia gas had interacted with carbon nanotube molecules and did not desorbed immediately.

R2 has a higher reading due to accumulated ammonia gas in the sample.

This result indicates that CNTs have a high affinity for ammonia due to ammonia being a polar molecule with a dipole moment of 1.5 debye. When the samples are exposed to \( \text{NH}_3 \) gas, electrons are transferred from \( \text{NH}_3 \) to CNTs. \( \text{NH}_3 \) molecules donate electrons to the valence band of the CNTs, decreasing the number of holes, thereby increasing the separation between the conduction band and the valence band.

This forms a space charge region at the surface of the semiconducting CNTs, increasing the electrical resistance. The increase in resistance proves that the CNTs are a p-type semiconductor.

From results even we can say that, upon exposure to \( \text{NH}_3 \) gas, the resistance of the CNTs based sensor increased with an increase in gas concentration.

It is noted that \( \text{NH}_3 \) absorbed into CNTs by replacing pre-adsorbed oxygen within the carbon atoms. Oxygen, an oxidizing gas, increases the conductivity of p-type carbon nanotubes as it increases the hole concentration; hence the replacement of oxygen by ammonia should reduce the conductivity.
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![Graph showing electrical resistance variation of CNTs grown sample upon injection of NH₃ gas](image)

**Figure 3: Electrical Resistance Variation of CNTs Grown Sample upon Injection of NH₃ Gas**

**Carbon Dioxide Absorption**

The results of carbon dioxide absorption into CNTs grown sample indicated that injection of carbon dioxide gas had a similar effect as in ammonia absorption. This trend is shown in the Figure 4. Whereby there are significant increments in the resistance when CO₂ gas is injected into the system. The same pattern was obtained for both the two repetitions indicated by R1 and R2.

Carbon dioxide is a reducing gas and its absorption resulted in injection of electrons to the CNTs and reduced number of holes in the material. Holes are the main charge carrier for p-type semiconductor, holes depletion will result in increase resistivity or decrease the conductivity of the sample.

Finally the absorption of carbon dioxide gas had a significant effect on the resistance of CNTs. The sample resistance showed an increment upon exposure to carbon dioxide gas.

![Graph showing electrical resistance variation of CNTs grown sample upon injection of CO₂ gas](image)

**Figure 4: Electrical Resistance Variation of CNTs Grown Sample upon Injection of CO₂ Gas**

**Hydrogen Absorption**

Hydrogen is the lightest and most abundant element in the universe. At standard pressure and temperature, it occurs as diatomic gas. Hydrogen absorption into CNTs samples at room temperature had no significant change in the resistance of CNTs. The CNTs need to be doped with other atoms or operated at higher temperature for them to be a good gas sensor for hydrogen.

The results from this study on the effect of hydrogen absorption in the carbon nanotubes sample is plotted in Figure 5. Wong et al., 2003 reported that gas sensor utilizing CNTs in a thin layer Pd/CNTs/n+-Si structure has a high sensitivity to hydrogen over a wide temperature range. It is concluded that raw and palladium doped CNTs sensors do not detect hydrogen at room temperature. Sayago et al., 2005 discovered that the sensing activity of raw CNTs started at temperatures higher than 200°C.
The finding by Wong et al., 2003 and Sayago et al., 2005 are relevant with the result obtained in this study. It is confirmed that pure CNTs unable to detect hydrogen gas at room temperature.

**Figure 5: Effect of H₂ Absorption on CNTs**

**Effect of Gases on Carbon Nanotubes Samples**

Graphs of testing gas absorption into CNTs samples were plotted as samples electrical resistance in a milliohm against tested gas as shown in Figure 6. The graph shows that ammonia recorded the highest increment of electrical resistance followed by carbon dioxide. This indicates that CNTs have a higher affinity for ammonia due to ammonia being a polar molecule with a dipole moment of 1.5 debye.

The other tested gases are non-polar molecule with a zero dipole moment. However, carbon dioxide showed a significant increment in the resistance, but not hydrogen. This is due to the reason that carbon dioxide possesses rich electron site in their molecules. Carbon dioxide has two sets of lone pairs contributing by two oxygen atoms, whereas hydrogen is non-polar molecules and had none electronegative atoms in the molecules which can contribute to the electron rich site within the molecules.

**Figure 6: Overall Results of Gas Absorption into CNTs Grown Samples**

Sensitivity of the CNTs sample is estimated by Varghese et al., 2001 using the following equation,

\[ S = \left( \frac{R_{\text{gas}} - R_{\text{argon}}}{R_{\text{argon}}} \right) \times 100 \]

Where, \( S \) = Sensitivity

\( R_{\text{gas}} \) = Resistance of sample in testing gas

\( R_{\text{argon}} \) = Resistance of sample in argon gas

The sensitivity of the sample upon exposure of these gases is tabulated in Table 1. From the table, it can be concluded that ammonia has the highest sensitivity.
Finally, from the results obtained, it can be concluded that CNTs has a potential application for gas sensing technology operated at room temperature for ammonia and carbon dioxide. For hydrogen, modifications had to be done to the CNTs to make it more sensitive towards the gas.

### Table 1: Sensitivity of Carbon Nanotubes Sample in Ammonia and Carbon Dioxide

<table>
<thead>
<tr>
<th>Time T(Seconds)</th>
<th>Resistance of Ammonia $R_{NH3}$ (mΩ)</th>
<th>Resistance of Carbon Dioxide $R_{CO2}$ (mΩ)</th>
<th>Resistance of Argon $R_{Ar}$ (mΩ)</th>
<th>Sensitivity of Ammonia $S_{NH3}$ (%)</th>
<th>Sensitivity of Carbon Dioxide $S_{CO2}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>158</td>
<td>157.705</td>
<td>146</td>
<td>8.219</td>
<td>8.017</td>
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<td>80</td>
<td>158.5</td>
<td>157.61</td>
<td>146</td>
<td>8.561</td>
<td>7.952</td>
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<tr>
<td>120</td>
<td>158.35</td>
<td>157.94</td>
<td>146</td>
<td>8.458</td>
<td>8.178</td>
</tr>
<tr>
<td>180</td>
<td>158.95</td>
<td>157.79</td>
<td>146</td>
<td>8.869</td>
<td>8.0753</td>
</tr>
<tr>
<td>Average:</td>
<td>158.45 mΩ</td>
<td>157.76 mΩ</td>
<td>146 mΩ</td>
<td>8.52%</td>
<td>8.05%</td>
</tr>
</tbody>
</table>

### CONCLUSIONS
The aim of this study was to investigate the electronic sensor application of CNTs upon absorption of ammonia, carbon dioxide and hydrogen. Based on the experimental results, it was proven that the CNTs have the capability to detect ammonia and carbon dioxide at room temperature. Therefore, it can be concluded that the gas sensing characteristics carried out in this work has shown that CNTs have potential to be an excellent ammonia and carbon dioxide sensor material at room temperature.

### REFERENCES