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Sensing mechanisms of carbon nanotube based NH$_3$ gas detectors

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1. Introduction

It is well known that the electrical performance of carbon nanotube (CNT) devices is extremely sensitive to chemical environment. Studying the interaction between CNTs and chemical gases could, from fundamental point of view, significantly deepen our understanding on nanoscale device physics. Meanwhile, as large scale integration of CNT devices is still challenging at the current stage, individual electronic devices containing CNTs as their key elements for sensing purpose would be more feasible for practical applications of CNTs. In addition to a small diameter, an extremely large surface to volume ratio makes CNT a suitable material for nanoscale chemical sensing. Since the first CNT gas sensor reported in 2000 (Kong, et al., 2000), many types of CNT-based chemical sensors have been demonstrated. CNT networks (Li, et al., 2003), functionalized CNTs (Qi, et al., 2003), CNT and polymer composites (Wei, et al., 2006), etc, are used as sensing elements. Although tremendous progresses have been achieved in this area, the underlying sensing mechanism still remains unclear. NH$_3$ gas detection represents the most typical argument in CNT based gas sensing area. Previously proposed mechanisms include the indirect interaction through the hydroxyl group on SiO$_2$ substrates (Kong, et al., 2000) or pre-adsorbed water layer (Bradley, et al., 2003), adsorption of gas molecules at the interstitial sites in the CNT bundle (Zhao, et al., 2002), direct charge transfer from the adsorbed gas molecules to the CNT channel (Chang, et al., 2001), and modulation of the SB at CNT/metal contacts (Yamada, 2006), etc. Till now, there is no well recognized sensing mechanisms. Hence in this chapter, we will first review the development of CNT based NH$_3$ gas sensors. After that, we will present a systematic study on the sensing mechanisms through selective Si$_3$N$_4$ passivation, which enables us to truly distinguish the sensing signal from the CNT channel and CNT/metal contacts. By comparing the strikingly distinct sensing performance at various testing conditions, we clearly show that the Schottky barrier modulation at the CNT/metal contacts dominates the sensing performance at room temperature. At higher temperatures, say 150°C or above, NH$_3$ molecules start to adsorb on the CNT wall and the charge transfer from the adsorbed NH$_3$ molecules to the CNTs contributes to the sensing signal. Next, we will demonstrate tunable real-time NH$_3$ sensors with three-terminal CNT field-effect transistors. The room-temperature sensitivity and reversibility of such sensors can be greatly
enchanced by proper gate voltages. Finally, we will conclude the significance achieved so far and give an outlook of the future development of CNT based gas sensors.

2. Literature reviews: Contact Vs Channel

It is well known that most of CNTFETs exhibited p-type characteristics in air, which is commonly attributed the contact SB modulation by environmental oxygen (Derycke, et al., 2002, Heinze, et al., 2002). Will this argument still holds for NH$_3$ gas? On one hand, theoretical calculations predicted limited interaction between NH$_3$ gas and CNT at room temperature (Kong, et al., 2000, Bauschlicher & Ricca, 2004, Peng & Cho, 1999). On the other hand, CNT based sensors showed high sensitivity to chemical gas. It is natural for researchers to consider the role of metal-CNT contacts. In order to differentiate, or separate the effect from CNT channel and metal-CNT contacts, the design of experiments is to protect or cover either of them and then compare the sensing performance against NH$_3$ gas. The first effort belongs to Bradley et al. He and his coworkers used thermally evaporated SiO to passivate a short-channel CNTFETs, as shown Fig. 1. They found a good sensitivity to NH$_3$ after contact passivation. (Bradley, et al., 2003)

Fig. 1. The device structure in Bradley et al’s work

Zhang et al. argued that when the passivation length was comparable to the depletion length in the CNT, the contacts could be indirectly affected, which could be the case in the work above. In their work, polymethylmethacrylate (PMMA) was applied to protect the CNT/metal contacts from NO$_2$ exposure and their devices became insensitive after contact passivation, as shown in Fig. 2. (Zhang, et al., 2006)

Fig. 2. Zhang et al’s sensing results after contact passivation.
Interestingly, Liu et al. also employed PMMA as a passivation layer. They observed changes in the transfer characteristics upon exposure to NH$_3$ and NO$_2$ for both contact-passivated device and channel passivated devices, suggesting that both the CNT channel and the CNT/metal contacts play a role in the detection process (Liu et al., 2005). The obvious ambiguity in those reports could arise from the permeable passivation materials used. Moreover, as the experiments were carried out at room temperature and air ambient only, exclusive identification of the sensing mechanisms is not possible. Next, we will introduce a selective Si$_3$N$_4$ passivation technique, with which the sensing signals from the CNT channel and CNT/metal contacts are truly distinguished. Strikingly distinct sensing performance at various testing conditions is observed.

3. Experimental details

CNTs were aligned between Ti/Au source and drain electrodes predefined on a p-type silicon wafer using an ac DEP technique (Li et al., 2005, Peng et al., 2006), which is simple and cost effective, suitable for CNT sensor fabrications. The CNT suspension is introduced onto the electrodes with an AC voltage across with a frequency of 2-10MHz. The peak-to-peak voltage ranged from 6V to 16V, depending on the electrodes separation. Due to the induced DEP force, the CNTs in the suspension align with the electric field direction and move towards the electrodes surface. The AC voltage was turned off immediately once SWNTs bridged the electrodes, confirmed by monitoring the resistance across electrodes. The number of the SWNTs between the electrodes can be controlled by adjusting the SWNT concentration and the manipulation time. A heavily doped Si with a 200 nm thick thermally

![Fig. 3. Schematics for (a) Device 1: As-prepared CNTFET; (b) Device 1A: the contacts passivated by Si$_3$N$_4$ and (c) Device 2: the central CNT channel passivated by Si$_3$N$_4$.](www.intechopen.com)
grown SiO$_2$ top layer was used as the backgate. Note that the CNTs in this work are on top of Au electrodes and the contact regions are fully accessible to the ambient. These devices are typically the SB-CNTFETs. As illustrated in Fig. 3, three device structures were employed in our experiments: (1) an as-prepared CNTFET with the exposed CNT channel and CNT/Au contacts; (2) only the contacts passivated with 500nm Si$_3$N$_4$ layer and (3) only the channel passivated with 500nm Si$_3$N$_4$ layer. Dry air was used as the background gas with a flow rate of 500sccm in the following experiments unless otherwise stated. NH$_3$ gas was selected as the detecting species to study the sensing mechanisms of the CNT sensors.

4. Results and Discussion

4.1 NH$_3$ sensing at room-temperature

An as-prepared CNTFET (Device 1) showed a sensitive response to small concentrations of NH$_3$ at room temperature (see Fig. 4 (a)). It is seen that, under a positive gate voltage, both the sensitivity and reversibility were much higher than those under a negative one.

Fig. 4. Real-time detection of NH$_3$ at room temperature under various gate voltages (a) before (Device 1) and (b) after the contacts passivation (Device 1A), respectively. Inset: an atomic force microscope (AFM) image of Device 1A after the passivation.

Actually, PMMA was widely employed as a passivation material to protect the CNT/metal contact regions for gas (Zhang, et al., 2006, Liu, et al., 2005) and protein sensing (Heller, et al., 2008). However, two major problems exist due to the polymer nature of PMMA. Firstly, PMMA is not dense enough to fully passivate the contacts. For example, NO$_2$ was found to penetrate the 2.2μm thick SU-8/PMMA layer in 30mins (Zhang, et al., 2006). Thus, the CNT/metal contacts are inevitably affected by the gradual diffusion of the detecting species through the PMMA layer, so that the role of the contact in the detection could not be eliminated. Secondly, PMMA is thermally unstable above 100°C. This is a critical limitation as the adsorptions of some biomolecules and gas molecules on CNTs are enhanced at high temperatures. In contrast, Si$_3$N$_4$ is much denser and it can completely insulate the contacts from chemical environment (Kaminishi, et al., 2005). Meanwhile, its thermal stability allows for high temperature sensing experiments, as shown later.

4.2 NH$_3$ sensing at elevated temperature

The transfer curves of Device 1A before and after exposure to 500ppm NH$_3$ for 1000s are monitored at $T=25^\circ$C, $T=50^\circ$C and $T=100^\circ$C in Fig. 6 (a), (b) and (c), respectively. No
In order to experimentally differentiate whether the sensing responses are from the CNT channel and/or the CNT/Au contacts, we passivated the CNT/Au contacts of Device 1 with a Si₃N₄ thin film, leaving the CNT channel open. After the passivation, we found that the device (Device 1A) did not respond to NH₃ at room temperature, even at a concentration up to 500ppm, as shown in Fig. 4 (b). For comparison, we only passivated the CNT channel with Si₃N₄ thin film in another CNTFET (Device 2), but uncovering the CNT/Au contacts. Interestingly, Device 2 showed a high sensitivity at room temperature (see Fig. 5). Therefore, we can unambiguously conclude that NH₃ gas induced SB modulation is a dominant mechanism for our CNT gas sensors at room temperature.

Fig. 5. Sensing response of Device 2 at room temperature. Inset: AFM image of Device 2 with central channel passivated.

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4.2 NH₃ sensing at elevated temperature
The transfer curves of Device 1A before and after exposure to 500ppm NH₃ for 1000s are monitored at T=25°C, T=50°C and T=100°C in Fig. 6 (a), (b) and (c), respectively. No
significant change in $V_{TH}$ curves was observed. We suggest that, the adsorption of NH$_3$ on the CNT is not favored at this temperature range.

Fig. 6. Transfer characteristics of Device 1A with contacts passivated before and after exposure to NH$_3$ at (a) $T=25^\circ$C, (b) $T=50^\circ$C and (c) $T=100^\circ$C respectively.

Fig. 7. The transfer characteristics for Device 1A with the contacts passivated before and after exposure to NH$_3$ at (a) $T=150^\circ$C and (b) $T=200^\circ$C, respectively.

The transfer curve started to shift towards negative gate voltage after NH$_3$ exposure at $150^\circ$C and above, see Fig. 7 (a). Since the contacts were fully isolated from NH$_3$, this parallel shift in the transfer curve suggests that NH$_3$ could adsorb on the CNT wall and donate electrons to the CNT. Consequently, the Fermi level of the CNT moves towards the conduction band edge so that the threshold voltage $V_{TH}$ becomes more negative. When the testing temperature reached $200^\circ$C, this phenomenon became more prominent. Progressive shift of the transfer curve in accordance with NH$_3$ concentrations is shown in Fig. 7 (b).
The transfer curve started to shift towards negative gate voltage after NH$_3$ exposure at 150°C and above, see Fig. 7 (a). Since the contacts were fully isolated from NH$_3$, this parallel shift in the transfer curve suggests that NH$_3$ could adsorb on the CNT wall and donate electrons to the CNT. Consequently, the Fermi level of the CNT moves towards the conduction band edge so that the threshold voltage $V_{\text{TH}}$ becomes more negative. When the testing temperature reached 200°C, this phenomenon became more prominent. Progressive shift of the transfer curve in accordance with NH$_3$ concentrations is shown in Fig. 7 (b).
Under a first order estimation, the total charge transferred $\Delta Q = C_G \Delta V_{TH}$, where the gate capacitance $C_G = \frac{2 \pi \epsilon \epsilon_0 L}{\cosh^{-1}(h/r)}$, the SiO$_2$ dielectric constant $\epsilon=3.9$ and thickness $h=200\text{nm}$.

For a SWNT bundle with a length $L \sim 5\mu\text{m}$ and a radius $r \sim 5\text{nm}$, $C_G \approx 0.25\text{fF}$. Thus, $\Delta Q$ is approximately $0.625\text{fC}$ or about 4000 electrons, at 200°C with $\Delta V_{TH} = 2.5V$ for 500ppm NH$_3$. If the cross-sectional area of NH$_3$ $A \sim 0.13\text{nm}^2$, the length of the exposed CNT channel $L' \sim 3\mu\text{m}$, the coverage $\theta \sim 0.07$ (interpolated from the Langmuir plot for 500ppm NH$_3$ on CNT (Bradley, et al., 2003)), the charge transfer rate $f \approx \Delta QA / q \theta \pi L'$ is about 0.02 electron. This value is reasonably consistent with typical theoretical predictions.

![Graph](Fig. 8) Extracted sensitivities for (a) Device 1 and Device 1A at $T=25$°C; (b) Device 2 and Device 1A at $T=150$°C, respectively.

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The extracted sensitivity $S = \Delta R / R_0$ of Device 1 and Device 1A under three gate voltages at T=25°C are shown in Fig. 8 (a). For Device 1, a very high sensitivity and significant gate modulation were observed. When the gate voltage is varied from negative to positive, the dominant carrier injection process changes from tunneling to thermionic emission, and the source-drain current becomes very sensitive to the SB height. A small change in the contact SB height due to NH$_3$ adsorption will be prominently reflected in the source-drain current. Our device structure with a CNT on top of metal electrodes could also enhance the SB modulation effect. Once the contacts passivation is carried out in Device 1A, it essentially does not respond to NH$_3$, implying that the CNT channel is not active to NH$_3$ at room temperature. Fig. 8 (b) compares the sensitivities for Device 1A and Device 2 at T=150°C. At small NH$_3$ concentrations, a low coverage of NH$_3$ on the CNT channel and poor charge transfer efficiency result in a small sensitivity in Device 1A. When the NH$_3$ concentration is increased, the sensitivity for Device 2 becomes saturated, probably due to limited interaction area in the CNT/Au contacts.

4.3 Effect of oxygen on NH$_3$ sensing

Theoretical studies suggest that, NH$_3$ interacts weakly with pristine CNTs with little charge transfer (Kong, et al., 2000, Bauschlicher & Ricca, 2004, Peng & Cho, 1999). Existence of a large activation barrier prevents adsorption of NH$_3$ on perfect CNTs even at high temperatures. However, the adsorption of the gas molecules on defective CNTs could be much easier (Feng, et al., 2005, Robinson, et al., 2007). In addition, the adsorption barrier of NH$_3$ on a defective CNT can be further lowered by pre-dissociated oxygen atoms, leading to an enchanted charge transfer rate, as pointed out by Andzelm et al (Andzelm, et al., 2006).

In order to study the influences of oxygen on NH$_3$ adsorption onto the CNT wall, we changed the background gas from dry air to N$_2$. Device 1A was first annealed in N$_2$ environment at 350°C for 2 hrs to degas the adsorbed oxygen. Note that during the high-temperature annealing, remaining oxygen molecules at the contacts can be further desorbed and the device became more n-type. The transfer curves before and after exposure to 500ppm NH$_3$ for 1000s from T=25°C to T=150°C were shown in Fig. 9, and real-time sensing results at T=200°C are shown in Fig. 10. No detectable changes due to NH$_3$ exposure were observed. Comparing with the sensing response observed in dry air environment, we can confirm that the adsorption of NH$_3$ is facilitated by environmental oxygen. It was also found that the sensitivity was restored after the background was changed to dry air again. Our results are consistent with Andzelm et al’s predictions. NH$_3$ could preferentially attach to the defect sites on CNT with pre-dissociated oxygen, as illustrated in Fig. 11.
Fig. 9. Transfer characteristics of Device 1A in N\textsubscript{2} before and after exposure to NH\textsubscript{3} at (a) T=25\textdegree C, (b) T=50\textdegree C, (c) T=100\textdegree C and (d) T=150\textdegree C respectively.

Fig. 10. Response of I\textsubscript{SD} to various concentrations of NH\textsubscript{3} in N\textsubscript{2} at T=200\textdegree C for Device 1A.
4.4 Comparisons of the sensing mechanisms in CNT based gas sensors

From our results, we are able to rule out several possibilities of indirect interactions between NH$_3$ and CNT. Firstly, as the testing environment was totally dry, NH$_3$ adsorption through water layer is not applicable here. Secondly, If NH$_3$ could interact through the SiO$_2$ substrate or adsorb inside the CNT bundles, a reduced sensitivity should have been observed after contacts passivation. However, our observation that Device 1A is totally insensitive to NH$_3$ at room temperature does not support this hypothesis. In fact, charge transfer and the SB modulation are the two mechanisms in our CNT sensors.

At room temperature, the weak adsorption of NH$_3$ on the CNT wall does not induce any measurable effect on the source-drain current. The sensing signal mainly arises from the contacts. When NH$_3$ molecules are adsorbed on the CNT/Au interface, the work function of the Au electrode is reduced (Bilic, et al., 2002) and/or the electrostatic charge balance between the CNT and Au is disturbed by the dipoles of NH$_3$ molecules,(Yamada, 2006) leading to an increased SB for hole injection. The sensitivity reflected in the source-drain current are, however, gate voltage dependant. As illustrated in Figure 12 (b), when a negative gate voltage bends the energy band of the CNT upwards, the SB width becomes very narrow and holes could tunnel through the barrier, even when the SB height is increased by NH$_3$. In contrast, at a positive gate voltage, the SB width is too thick for tunneling process. Thus, hole injection is only through thermionic emission over the SB height. The source-drain current is then expressed as:(Appenzeller, et al., 2004) $I_{DS} \sim T^2 \exp(-q\phi_B / K_BT)$, where $\phi_B$ is the Schottky barrier height, $K_BT$ is the
Boltzmann’s constant and T is the temperature in Kelvin. In this case, the sensitivity for the SB modulation is \( S = \Delta R / R_0 \approx \exp(q\Delta\phi_B / K_B T) - 1 \). Owing to the exponential dependence on the SB height change \( \Delta\phi_B \), extremely high sensitivity can be achieved. Our results are consistent with Yamada’s theoretical prediction that the SB modulation is most significant when CNT is operating in the depletion mode. (Yamada, 2006)

One disadvantage of the SB dominated sensors is a typical long recovery process at room temperature. Once the operating temperature is increased, the sensitivity degrades sharply due to its exponential dependence with \( 1/T \). The nanoscale CNT/metal contacts could also be prone to subtle environmental noises, causing fluctuations during detection. In contrast, using the CNT channel as a sensing element can avoid the problems. In addition, the large surface to volume ratio of CNT offers another merit. At \( T > 150 \)°C, when the adsorption barrier is further lowered by oxygen, NH\(_3\) adsorption on the defect sites of the CNT becomes favored. Upon the consequent charge transfer, the Fermi level of the exposed central CNT channel moves upwards and the energy band shifts downwards with respect to those passivated parts, a potential barrier is therefore created and impedes the current flow, see Fig. 12 (d). Here, we would like to emphasize that, the charge transfer effect can be studied only when the contacts are fully protected. Otherwise, as temperature increases, the sensitivity enhancement from the charge transfer effect and the degradation due to SB modulation counteract each other.

![Fig. 12. Schematic energy band diagram for: Device 1 (a) before and (b) after the NH\(_3\) exposure (An intrinsic CNT is considered. The work function of the source/drain electrodes is initially near the valence band edge of the CNT and is reduced after NH\(_3\) exposure); Device 1A (c) before and (d) after the NH\(_3\) exposure (After passivation, the work function of electrodes aligns near the midgap of CNT. The Fermi level of the exposed central CNT channel shifts upwards due to electron-doping from NH\(_3\)). Legend: Red dotted for \( V_{GS}<0 \); Green solid for \( V_{GS}=0 \); Blue dashed for \( V_{GS}>0 \).](image-url)
Table 1 compares the SB modulation and charge transfer mechanisms. The sensors with the SB modulation usually demonstrate a high sensitivity at room temperature. Their sensing performance can be adjusted through the gate voltages. In contrast, the sensors under the charge transfer mechanism require high working temperatures, showing a good reversibility.

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>SB modulation</th>
<th>Charge transfer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity</td>
<td>Extremely high in depletion</td>
<td>Low</td>
</tr>
<tr>
<td>Gate dependence</td>
<td>Strong</td>
<td>Weak</td>
</tr>
<tr>
<td>Operating</td>
<td>Room temperature</td>
<td>T&gt;150°C</td>
</tr>
<tr>
<td>Temperature</td>
<td>Low, can be improved at</td>
<td>Good</td>
</tr>
<tr>
<td>Reversibility</td>
<td>positive gate voltage</td>
<td></td>
</tr>
</tbody>
</table>

Table 1. Comparisons between sensors operated by SB modulation and charge transfer.

5. Conclusions and Future Work

In this chapter, we discussed in details the sensing mechanisms of CNT based NH₃ detection. By selective Si₃N₄ passivation, We clearly show that the SB modulation at the CNT/metal contacts dominates the sensing performance at room temperature, and the sensor exhibits high sensitivity and good tunability under appropriate gate voltages. At higher temperatures, say 150°C or above, NH₃ molecules start to adsorb on the CNT wall and the charge transfer process from the adsorbed NH₃ molecules to the CNTs contributes to the sensing signal. As the mechanisms are identified, the next step is how to improve the sensing performance, and more challenging, how to differentiate between different gas species. One promising way could be functionalization method (Feng, et al., 2005, Qi, et al., 2003). For example, using metal catalysts in the form of nanoparticles to decorate CNT, which promotes the interaction with specific gas species. With a combination of several metal nanoparticles, the sensing performance to various gas molecules could be compared and contrasted.

6. Reference


This book has been outlined as follows: A review on the literature and increasing research interests in the field of carbon nanotubes. Fabrication techniques followed by an analysis on the physical properties of carbon nanotubes. The device physics of implemented carbon nanotubes applications along with proposed models in an effort to describe their behavior in circuits and interconnects. And ultimately, the book pursues a significant amount of work in applications of carbon nanotubes in sensors, nanoparticles and nanostructures, and biotechnology. Readers of this book should have a strong background on physical electronics and semiconductor device physics. Philanthropists and readers with strong background in quantum transport physics and semiconductors materials could definitely benefit from the results presented in the chapters of this book. Especially, those with research interests in the areas of nanoparticles and nanotechnology.

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