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Gas sensors based on deposited single-walled carbon nanotube networks for DMMP detection

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Abstract

Sensors based on single-walled carbon nanotube (SWNT) networks were fabricated and their sensitive properties for the nerve agent stimulant dimethyl methylphosphonate (DMMP) vapor were investigated at room temperature. The SWNT networks were deposited on oxidized silicon surface functionalized with 3-aminopropyltrimethysilane (APS). Combining with a traditional silicon process, SWNT-based gas sensors were made at a wafer scale. The effects of the density of deposited SWNTs on the sensor response were studied. The excellent response is obtained under a density of 30–40 tubes $\mu$m$^{-2}$. The sensors exhibit high resistance response, fast response time, rapid recovery and good reproducibility for DMMP vapor. The deposited SWNT sensors will be potentially extended to large-scale fabrication.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Chemical warfare agents (CWAs), especially the nerve agents, are highly toxic and extremely dangerous [1, 2]. Nerve agents can inhibit the activity of the enzyme acetyl cholinesterase (AchE), which leads to the toxic accumulation of the neurotransmitter acetylcholine (Ach). The enzyme inhibition process occurs rapidly and irreversibly, which will cause death [3]. In order to protect human beings, there is a crucial need for high sensitivity and rapid response devices to detect CWAs. The presently reported sensors for nerve agent detection, including electrochemical sensors [4, 5], chemiresistive sensors such as semiconducting metal oxide (SMO) sensors [6–8], microcantilever-based sensors [9, 10], quartz-crystal microbalance (QCM) sensors [11–13] and surface acoustic wave (SAW) sensors [14–18], are usually coated with a thin layer of chemosensitive material.

Carbon nanotubes (CNTs) have been considered as attractive candidates for sensing materials due to their nanoscale size with high aspect ratio, large specific surface area, good chemical stability, and excellent mechanical and electronic properties [19–22]. CNT-based gas sensors generally possess rapid response time, high sensitivity, low operating temperature and small sizes for nanodevice miniaturization. Dai et al [23] first demonstrated that the electrical conductance of CNTs could change significantly upon exposure to NO2 and NH3 gases. CNTs as gas sensors to detect sub-ppm concentrations of NO2, NH3, H2, CO and CH4 have been reported [24–30]. Recently, several groups have made efforts towards developing CNT-based sensors for the detection of CWAs and similar compounds. Strano et al [31] prepared a chemical single-walled carbon nanotube (SWNTs) sensor ordered with alternating-current dielectrophoresis and showed sensitivity to dimethyl methylphosphonate (DMMP) and thionyl chloride (SOCl2). Cattanach et al [32] employed a flexible sensor using network films of bundles of SWNTs on polyethylene terephthalate (PET) substrates for the detection of DMMP and diisopropyl methylphosphonate (DIMP). Snow et al [33, 34] demonstrated the use of SWNTs as both chemiresistors and chemicapacitors for the sensing of various chemical vapors, such as DMMP and dinitrotoluene (DNT).
were ultrasonically dispersed in deionized water for 2 h and investigated at room temperature. The sensing behaviors of the gas sensor to DMMP were then centrifuged at 10 000 g for 20 min. The obtained stable upper suspension was taken for further deposition. The pre-treated silicon substrate modified with an APS monolayer was immersed in the SWNT–water suspension, followed by rinsing with ethanol and deionized water and drying with the aid of nitrogen flow. Zeta potential measurements for the SWNT suspension were done using a zeta plus analyzer (Zetasizer, Malvern, UK). The morphology of the deposited SWNTs was characterized by scanning electron microscopy (SEM, JSM-7401F).

Using standard microfabrication procedures, the SWNT-based gas sensor was fabricated. The interdigitated electrode fingers were made by sputtering 10 nm Cr and 180 nm Au onto a patterned photoresist mold. A lift-off process was further introduced to remove the photoresist. Finally the electrodes were sonicated in ethanol, washed with deionized water thoroughly and then dried by nitrogen flow. Figure 1 shows the schematic diagram of the SWNT deposition process and sensor fabrication.

### 2.3. Sensor testing system

A homemade gas handling system to generate and deliver DMMP vapor is shown in figure 2. Nitrogen was used as the carrier and diluting gas. DMMP vapors were generated by bubbling nitrogen through a glass tube. The carrier gas was passed though the bubbler and the saturated DMMP vapor was carried out of the bubbler. The output flow rate of DMMP vapor, $F_{\text{DMMP}}$, can be described with the bubbler equation [38]:

$$F_{\text{DMMP}} = \left( \frac{P_{\text{DMMP}}}{P_0 - P_{\text{DMMP}}} \right) F_c$$

where $F_c$ (sccm) is the carrier flow rate, $P_0$ is the outlet pressure in the bubbler headspace and $P_{\text{DMMP}}$ (mmHg) is the vapor pressure of the DMMP which is calculated from the Antoine equation [39, 40]:

$$P_{\text{DMMP}} = 2.844 \times 10^8 \times \exp\left(\frac{-11500}{RT}\right)$$

where $T$ (K) is the bubbler temperature of DMMP. The vapor pressure of DMMP at ambient temperature is 112 Pa [41]. Saturation of the DMMP vapor stream in our experimental apparatus was verified by measuring the rate of mass loss of the DMMP liquid in the bubbler [42, 43]. The output of the gas was diluted with nitrogen and controlled by the mass flow controller (MFC). The bubbled DMMP/N2 gas and the diluted N2 were mixed in a stainless steel chamber in order to allow

<table>
<thead>
<tr>
<th>CNT type</th>
<th>CNT deposition method</th>
<th>Detection limit</th>
<th>Response time (s)</th>
<th>Reversibility</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare SWNTs</td>
<td>CVD</td>
<td>&lt;1 ppb</td>
<td>1000</td>
<td>Reversible</td>
<td>[36]</td>
</tr>
<tr>
<td>Metallic SWNTs</td>
<td>Dielectrophoresis</td>
<td>50 ppm</td>
<td>10</td>
<td>Irreversible</td>
<td>[31]</td>
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<tr>
<td>Polymer-functionalized SWNTs</td>
<td>Dip coating</td>
<td>25–50 ppm</td>
<td>1200</td>
<td>Reversible</td>
<td>[32]</td>
</tr>
<tr>
<td>DNA-functionalized SWNTs</td>
<td>CVD</td>
<td>25 ppm</td>
<td>50</td>
<td>Reversible</td>
<td>[37]</td>
</tr>
</tbody>
</table>

Currently, two main methods have been reported for depositing SWNTs across electrodes for the fabrication of gas sensors [35]. One is to directly grow CNTs on the sensor platform via chemical vapor deposition (CVD). This method involves high temperature, complex processes and low yields. The other is to drop-cast an SWNT solution onto the prefabricated electrode surface. Solution-casting techniques, such as microsyringes and dielectrophoresis, are more reproducible, less expensive and have higher yields. But they often result in poor electrical contact between nanotubes and electrodes. Table 1 summarizes the sensing performance of SWNT sensors for detecting DMMP vapor reported in the literature.

In this study, a facile and controllable method has been developed for deposition of SWNT networks. The advantage of this method is that it can be used for the fabrication of sensors at a wafer scale. The deposited SWNTs can be absorbed firmly on the amino-terminated Si/SiO2 wafer substrate resulting in good electrical contact between SWNTs and Au electrodes. Combined with conditional lithography and lift-off processes, SWNT-based gas sensors were made. The sensing behaviors of the gas sensor to DMMP were investigated at room temperature.

### 2. Experimental details

#### 2.1. Materials

SWNTs synthesized by the arc discharge method were used in this present work. SWNTs were purified by air oxidation at 365 °C for 30 min, followed by refluxing with a 3:1 mixture of concentrated sulfuric acid and nitric acid at 80 °C for 30 min. The final purified SWNTs have a purity of about 95%. DMMP and 3-aminopropyltrimethysilane (APS) were purchased from Sigma-Aldrich. Deionized water (18 MΩ cm) was used throughout all processes. All reagents were analytical grade and were used without further purification.

#### 2.2. SWNT network deposition and sensor preparation

The Si/SiO2 wafer substrate was ultrasonically rinsed in turn with toluene, acetone, ethanol and deionized water, followed by cleaning with a Piranha solution (3:1 H2SO4:H2O2). The pre-treated substrate was immersed in a 1 mM APS aqueous solution for 2 h and then kept in a vacuum evaporator at 120 °C for 1 h to form the amino-terminated monolayer on the surface of the Si/SiO2 substrate. The purified SWNTs were ultrasonically dispersed in deionized water for 2 h and then centrifuged at 10 000 g for 20 min. The obtained stable upper suspension was taken for further deposition. The pre-treated silicon substrate modified with an APS monolayer was immersed in the SWNT–water suspension, followed by rinsing with ethanol and deionized water and drying with the aid of nitrogen flow. Zeta potential measurements for the SWNT suspension were done using a zeta plus analyzer (Zetasizer, Malvern, UK). The morphology of the deposited SWNTs was characterized by scanning electron microscopy (SEM, JSM-7401F).

### Table 1. Some SWNT-based sensors for detecting DMMP vapor.

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Figure 1. Schematic diagram of SWNT deposition process and sensor fabrication: (a) Si/SiO₂ wafer substrate cleaning, (b) APS modification, (c) SWNT deposition, (d) photoresist patterning, (e) sputtering Au electrode and (f) removing the photoresist.

Figure 2. Schematic diagram of the apparatus for SWNT-based gas sensing test.

the gas to blend homogeneously. The mixture was delivered at a flow rate of 1 l min⁻¹ to the testing chamber. The detection chamber has a volume of about 15 cm³, in which the sensor is attached on the top and an inlet pipe and an outlet pipe are connected to both sides, respectively. The resultant DMMP concentration, \( C_{DMMP} \) (ppm), was calculated from \( F_{DMMP} \) and the dilution ratio \[44\]:

\[
C_{DMMP} (\text{ppm}) = \frac{10^6 F_{DMMP}}{F_d + F_c + F_{DMMP}} \tag{3}
\]

where \( F_d \) (sccm) is the dilution flow rate. The sensor was illuminated with an IR lamp and the testing chamber was evacuated to desorb the DMMP from the SWNT surface after each testing cycle. All the gas sensing tests were carried out at room temperature. The resistance variation during testing was monitored using a precision semiconductor parameter analyzer (Agilent 4156C). The sensor response was evaluated by the resistance change at a sampling voltage of 300 mV.

3. Results and discussion

3.1. The morphology of the deposited SWNT networks

Zeta potential of SWNT–water suspension is measured to be −42.3 mV, which demonstrates that the carbon nanotubes are negatively charged in water \[45\]. So SWNTs will be absorbed and then deposited on the amino-terminated silicon substrate via electrostatic interaction. The optical image of interdigitated electrode arrays patterned onto the deposited SWNTs is shown in figure 3(a). The interdigitated arrays of electrodes possess a finger length of 600 μm and a gap size of 10 μm. The SEM image of deposited SWNTs between Au electrodes is given in figure 3(b). The nanotubes show a relatively uniform distribution in the whole region. For further enlargement of the dark box in figure 3(b) (shown in figure 3(c)), it is clearly observed that lots of SWNTs are highly connected each other between the interdigitated electrodes, which show that
the SWNT networks formed by the deposition technique is homogeneous at a large scale.

For quantitative analysis of uniformity, SEM images (3.5 μm × 3.5 μm) were taken at 90 different locations distributed randomly over a wafer, and the numbers of SWNTs were counted according to the SEM images. As shown in figure 4(a), the density of SWNTs is similar over the wafer scale. Figure 4(b) shows the distribution of the resistance of 90 SWNT sensors. The results show that the SWNT sensors obtained have a resistance of ∼667 Ω with a standard deviation of ∼35 Ω. It is shown that our method can produce an SWNT layer of uniformity over a wafer scale, based on the SEM observations.

Figure 5 shows the SEM images of deposited SWNTs with different densities. The density of SWNTs could be controlled by the concentration of the SWNT suspension and the deposition time. At the same time, it is also found that the deposited SWNTs can be strongly absorbed on the surface of the substrate so that they cannot be peeled off during the sensor fabrication process.

3.2. The response of SWNT-based sensors to DMMP vapor

After patterning the electrodes, the sensor responses to DMMP vapor were measured. Figure 6 shows the response of the deposited SWNT sensor to DMMP vapor in the concentration of 20–500 ppm. The sensor shows no saturation for a long exposure time of about 115 min, while the amount of resistance change of the sensor increases with the increase of DMMP vapor concentration at any exposure time. When the sensor
is exposed to DMMP vapor for about 16 min, the resistance change is about 65% of the total resistance change for about 115 min. We define the exposure time of about 16 min as the effective response time. The effective response time is an operational parameter for the sensor to differentiate different DMMP concentrations in a reasonable temporal span. In the following experiment, the sensor response ($R_r$) upon exposure to DMMP vapor under the effective response time is defined by equation (4):

$$R_r(\%) = \frac{(R_g - R_a)}{R_a} \times 100$$  \hspace{1cm} (4)$$

where $R_a$ is the resistance of SWNT networks in ambient air and $R_g$ is the resistance in the DMMP/N$_2$ mixed gas.

The effects of the density of deposited SWNTs on the sensor response were investigated. The resistance was measured by applying a low sampling voltage of 300 mV. The low power consumption of deposited SWNT sensors will ultimately lead to longer sensor battery lifetime and a greater potential for applications. The initial resistances ($R_a$) of SWNT sensors corresponding to those in figures 5(a)–(d) are 1873, 906, 646 and 485 $\Omega$, respectively. As shown in figure 7, the sensors based on deposited SWNTs show a large response to DMMP vapor. The resistance of the SWNTs dramatically increased when exposed to DMMP. The effect of deposited SWNT density on the sensor response is remarkable. At a low density of nanotubes (figure 7(a)), it is observed that the response transients are rather noisy. It may be that the SWNTs are separated from one another, so a continuous network of interconnected nanotubes is not formed yet. At slightly higher density (figure 7(b)), the resistance changed in a better manner than that of figure 7(a). The number of SWNTs between the electrodes is still not adequate so that the sensors actually lack stabilization of response. In figure 7(c), it is seen that the resistance response obviously increases. The density of deposited SWNTs is sufficiently high so that the nanotubes highly connect to one another and form continuous paths. However, the resistance response is decreased on further increasing SWNT density, as shown in figure 7(d). The networks of overlapping nanotubes begin to form at high concentrations, which makes the sensor unstable. Figure 8 presents the relationship between the density of deposited SWNTs and sensor response. The resistance response enhances with an increase of the density of deposited SWNTs and reaches a maximum value, 2.15% for 10 ppm DMMP and 3.25% for 20 ppm DMMP, at an appropriate density of deposited SWNTs (shown in figure 5(c)). In our
experiment, the optimal SWNT density for the sensor is 30–40 tubes $\mu m^{-2}$. This density is selected as representative in the following experiments.

The sensor responses to different concentrations of DMMP vapor were investigated. Figure 9 shows the response of the deposited SWNT sensor to DMMP vapor at a concentration of 5–80 ppm. The initial resistance ($R_a$) of the sensor is 630 $\Omega$. The experiment was conducted at room temperature. When the sensor was exposed to DMMP vapor, the resistance increased immediately. It is obvious that the sensor responses increase with the increasing DMMP concentration. It takes less than 5 min to completely recover.

**Figure 7.** Response of the deposited SWNT sensors to 10 and 20 ppm of DMMP at various nanotube densities. The densities of the deposited SWNTs correspond to that in figure 5.

**Figure 8.** Effects of the density of deposited SWNTs on the sensor response.

**Figure 9.** Response of the deposited SWNT sensors in varying concentrations ranging from 5 to 80 ppm.
The same results are also observed in figure 7. The fast recovery observed in the deposited SWNT sensor is due to the good interconnection between the SWNTs and Au electrodes. On account of the limiting capability of the gas mixing system used in our experiment, the sensor can only make a response to DMMP vapor at a concentration of 5 ppm. In addition, figure 9 shows that the resistance of the deposited SWNT sensor can completely return to the original value by illuminating it with an IR lamp and evacuating the testing chamber. The results show that the SWNT-based sensor exhibits a good and fast response, non-baseline drift and excellent reversibility.

To investigate the reproducibility of the sensor, the deposited SWNT sensor was repeatedly exposed to 10 ppm DMMP vapor, as shown in figure 10. Resistance response levels of the sensor are maintained and the recovery abilities are not reduced after several sensing cycles. Such behavior indicates that the SWNT-based sensor has a good repeatable characteristic.

A control experiment was carried out, where SWNTs were deposited on Au electrodes by dielectrophoresis (AC electric field: 20 V peak-to-peak voltage and 10 MHz frequency). The initial resistances \( R_0 \) of the deposited SWNT sensor and dielectrophoresis SWNT sensor are 618 and 635 \( \Omega \), respectively. The resistance responses of the two sensors to different DMMP concentrations under the effective response time were measured and tabulated in table 2. It is obvious that the deposited SWNT sensor has a higher resistance response than that of a dielectrophoresis SWNT sensor for each DMMP concentration. When the DMMP concentration is lower than 50 ppm, the dielectrophoresis SWNT sensor has a very weak resistance response.

Two sensing mechanisms are proposed for the interaction between SWNTs and DMMP. One is the direct charge transfer between the deposited SWNTs and DMMP, which makes a reduction of the hole density in SWNTs and causes an increase in their electrical resistance [36]. The other is physisorption of DMMP vapor on SWNT networks. A variety of active sites available for DMMP sorption exist on the tube’s surface. Adsorbed DMMP molecules affect electron transport through the SWNT networks, resulting in resistance change. In particular, the intercross sites of the SWNT networks may have a significant effect on the sensor behavior [32].

4. Conclusions

Uniform SWNT networks were prepared by a deposition technique at a wafer scale. The density of deposited SWNT networks can be controlled by changing the concentration of the SWNT suspension and the deposition time. Combined with a conditional microfabrication process, a novel SWNT-based sensor was made. The deposited SWNT sensors exhibit an excellent response to DMMP vapor at room temperature and low power consumption at a sampling voltage of 300 mV. Optimized results for the sensing of DMMP were obtained when the SWNT density was 30–40 tubes \( \mu m^{-2} \). It is demonstrated that the sensor can yield a rapid, reversible and reproducible response to DMMP vapor. Energy-efficient miniaturized gas sensors can be manufactured at wafer scale by combining the deposition technique with a ‘bottom-up’ process. This deposited SWNT sensor is promising for the detection of other gases at room temperature.

Acknowledgments

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References


Table 2. Comparison of resistance response between the deposited SWNT sensor and the dielectrophoresis SWNT sensor to different DMMP concentrations.

<table>
<thead>
<tr>
<th>DMMP concentration (ppm)</th>
<th>50</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposited SWNT sensor</td>
<td>4.513</td>
<td>6.235</td>
<td>9.657</td>
</tr>
<tr>
<td>Dielectrophoresis SWNT sensor</td>
<td>0.226</td>
<td>0.258</td>
<td>0.316</td>
</tr>
</tbody>
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[38] Hersee S and Ballingal J M 1990 J. Vac. Sci. Technol. A **8** 800–4