Comparison of Gas Sensors Based on Oxygen Plasma-Treated Carbon Nanotube Network Films with Different Semiconducting Contents

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We report on the effect of oxygen plasma treatment on the performance of single-wall carbon nanotube (SWCNT) NH_3 gas sensors with different semiconducting contents (66% and 90% semiconducting SWCNTs). The performance of chemical sensors based on SWCNT networks depends on the concentration of semiconducting SWCNTs (s-SWCNTs), whose conductance can be significantly modulated by the absorbed molecules and the surface functionalization. After oxygen plasma treatment, the 66% s-SWCNT sample showed an increase in sensitivity from 0.0275%/ppm to 0.1525%/ppm (5.5 times), while the 90% s-SWCNT device demonstrated an increase in sensitivity from 0.1184%/ppm to 1.5707%/ppm (13 times). These results correspond to improvements in sensitivity of 57 times and 10 times compared with pristine and plasma-treated 66% s-SWCNT samples, respectively. In addition, the plasma-treated sensors exhibited much faster response and recovery times than the pristine one. The large improvement in performance was explained by the presence of oxygen-containing functional groups and the sp^2 – sp^3 structure change of SWCNTs, which changes the binding energy while increasing the uptake of polar molecules such as NH_3 .

Key words: Gas sensor, semiconductor SWCNT, oxygen plasma treatment, sensitivity

INTRODUCTION

Single-walled carbon nanotube (SWCNT) networks made of randomly distributed nanotubes are increasingly being used as a sensing element for chemical sensors such as carbon nanotube field-effect transistors (CNTFETs) and chemiresistors. These random networks or films have shown high sensitivity to O_2 , NH_3 , NO_2 , CH_4 , CO , and H_2 gases.^{1–6} One of the factors that make SWCNT networks complex is that they contain a mix of semiconducting and metallic nanotubes. In a normal SWCNT random network, approximately

one-third of the tubes have metallic properties, and two-thirds show semiconducting behavior, limiting their usefulness for gas sensors. For high sensitivity, it is extremely important to have a percolative network of semiconducting single-walled carbon nanotubes (s-SWCNTs), since only the conductance of s-SWCNTs can be significantly modulated by the absorbed molecules.^{7–14} The metallic single-walled carbon nanotubes (m-SWCNTs) can short the electrically conductive pathways of semiconducting SWCNTs.

Another approach to improve the sensitivity is to introduce oxygen-containing functional groups along the sidewall of the s-SWCNTs. These functional groups formed on the CNT surface are known to significantly increase the interaction of CNTs

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with gas molecules.^{15–18} CNT surfaces have been modified by changing their chemical composition using chemical and plasma treatments.^{19–21} Although both treatments introduce oxygenated functional groups ($-\text{COOH}$, $\text{C}=\text{O}$, $\text{C}-\text{O}$, etc.) into SWCNTs, they produce different effects on the CNT surfaces. Acid treatment converts the terminal carbons of SWCNTs into carboxylic acids, ethers, etc., while O_2 plasma treatment increases the amount of oxygen-containing defects on the entire surface of the CNT film.^{19,22}

Although many researchers^{17,23–25} have studied CNT gas sensors modified using plasma processes, there have been few reports on the effects of plasma treatments on the properties of the SWCNT network surface with different semiconducting contents. We fabricated NH_3 gas sensors based on single-walled carbon nanotube network films with different semiconducting/metallic nanotube ratios and evaluated the effect of the oxygen plasma treatment on the sensor performance regarding sensitivity and response time.

EXPERIMENTAL PROCEDURES

NH_3 gas sensors based on SWCNT networks were fabricated on a 4-inch glass wafer, as illustrated in Fig. 1. The sensor consists of an interdigitated Pd electrode on top of the SWCNT network. The device size is $3 \text{ mm} \times 8 \text{ mm}$ with an active area of 9 mm^2 .

Normal SWCNTs (with semiconducting content of 66%) and 90% s-SWCNTs were purchased from Hanwha Nanotec (Korea) and Nanointergris (USA), respectively. The 66% SWCNT films were spray-deposited all over the substrate using an SWCNT solution. To prepare the solutions for the spray-coated films, 3 mg SWCNT diluted with 150 ml dichlorobenzene was tip-sonicated for 20 min to obtain a homogeneous solution. The film thickness was controlled by holding the spray conditions constant and varying the spray application rate. After depositing 66% s-SWCNT solution onto the substrate, the wafers were annealed on a hot plate at 190°C for 2 h in air. The 90% s-SWCNT network was deposited using a solution method.²⁶ Prior to the deposition of SWCNTs, the glass wafer was oxygen plasma-treated (50 W, 10 sccm oxygen flow

rate, 10 min) and functionalized by an amine acid using poly-L-lysine solution. The 90% s-SWCNT solution was subsequently dispensed onto the self-assembled monolayer-modified surface and dried for 2 h, followed by negative photoresist spin-coating onto the preprocessed wafer. To form the interdigitated electrode and contact pads, Pd was evaporated using a thermal evaporation system and a lift-off process. The unnecessary SWCNT film was removed by oxygen plasma etching (50 W, 20 sccm oxygen flow rate, 5 min) using the photoresist as a sacrificial layer. Then, the wafers were thoroughly washed with acetone, followed by ethanol and deionized water. Finally, the wafers were dried by blowing N_2 gas.

Then, the SWCNT networks were eventually plasma-treated in oxygen gas under much milder conditions than those applied in etching. The typical parameters, optimized through several experiments, were $10 \text{ cm}^3/\text{min}$ O_2 flow rate, 25°C substrate temperature, and 10 W radiofrequency (RF) power for 10 s. An atomic force microscopy (AFM) system was used to record the topography and measure the SWCNT film thickness. In Fig. 2, the 66% s-SWCNT thickness derived from AFM line profiles obtained for a spray application rate of $1 \text{ ml}/\text{cm}^2$ was about 71 nm.

Scanning electron microscopy (SEM) images of the fabricated sensor device are shown in Fig. 3a and b. A submonolayer film was obtained for the 90% s-SWCNT, as shown in Fig. 3b. The sensors are labeled as “66” and “90,” corresponding to the 66% and 90% semiconducting SWCNT networks, respectively, whereas the plasma-treated sensors are labeled as “p-66” and “p-90,” respectively. X-ray photoelectron spectroscopy (XPS) was used to

Fig. 1. Schematic illustration of the NH_3 gas sensor with an interdigitated electrode.

Fig. 2. (a) AFM 3D image and (b) line profile of 66% s-SWCNT network film. A–A' is a line perpendicular to the patterned SWCNT film.

estimate the generation of oxygen-containing groups on the surface of the SWCNT network before and after plasma treatment.

An LCR meter (20 kHz, 1 V_{rms} test signal) was used to measure the NH₃ gas sensing properties of different SWCNT films as a function of NH₃ gas concentration levels in an environmental chamber. The gas concentration was varied from 3.6 ppm to 64.2 ppm.

RESULTS AND DISCUSSION

Figures 4 and 5 show the measured dynamic responses of the 66% s-SWCNT and 90% s-SWCNT network sensors for an abrupt change in NH₃ concentration. The responses are normalized by the initial resistance R_0 . As can be seen from the waveforms, the sensors show a reversible but very asymmetrical change in resistance when cycled between NH₃ and N₂.

The untreated sensors demonstrated a very long response time during absorption and incomplete recovery of their initial resistance during desorption. They recovered only 70% to 80% after shutting off the NH₃ flow. This may be caused by the difference in the NH₃-SWCNT bonding mechanisms or energy. It is well known that NH₃ molecules may be absorbed onto SWCNTs through both physisorption and chemisorption.^{27–29} Upon switching from NH₃ to N₂ atmospheres, the weakly physisorbed NH₃ molecules are released by the kinetic energy of the flowing N₂ molecules, which causes a reversible change in the resistance. On the other hand, the chemisorbed molecules cannot be removed by simply passing N₂ gas, causing a buildup of chemisorbed NH₃ on the SWCNT surface and hence an irreversible change in the resistance.²⁸

After plasma treatment, both p-66 and p-90 samples showed much quicker response and recovery times than the equivalent untreated sensors. It is also apparent that the treated SWCNT sensors (p-66 and p-90) still responded more slowly during desorption than during absorption. The response and recovery times (to the 90% point of the final steady-state resistance value) corresponding to a

22.6 ppm NH₃ concentration were determined from Fig. 6 and are presented in Table I. The measured response time before treatment was found to be almost the same for the 66 and 90 sensors. However, the 66 sample showed a 90% step change in just 94 s after plasma treatment, which corresponds to an improvement in response time of 468%, while the p-90 samples showed a 3.34 times faster adsorption time compared with the untreated 90 samples.

Fig. 4. Responses (a) before and (b) after plasma treatment of 66% s-SWCNT network sensors to different NH₃ concentrations at room temperature. R_0 is the initial resistance.

Fig. 3. SEM images of (a) 66% s-SWCNT and (b) 90% s-SWCNT networks.

Fig. 5. Responses (a) before and (b) after plasma treatment of 90% s-SWCNT network sensors to different NH_3 concentrations at room temperature. R_0 is the initial resistance.

Figures 7 and 8 show the calibration curves at room temperature for the same devices as in Figs. 4 and 5, respectively. It can be seen from these figures that the sensors show much better responsiveness ($\Delta R/R_0$) with the plasma-treated 90% network than with the 66% film, indicating that the resistance of the semiconducting-enriched SWCNT network is more significantly affected by the oxygen plasma.

The normalized sensitivity S (in %/ppm NH_3) was calculated from the calibration slope in Figs. 7 and 8 and is listed in Table II. It can be seen from Table II that the semiconducting CNT content and plasma activation significantly affected the sensitivity of the SWCNT gas sensors. The p-66 samples showed an increase in sensitivity from 0.0275%/ppm to 0.1525%/ppm (5.5 times) after plasma treatment, while the p-90 devices demonstrated a sensitivity of 1.5707%/ppm, which is equivalent to an improvement in sensitivity of 13 times compared with pristine 90 samples and 10 times compared with p-66 samples. This enhanced performance may be due to factors associated with the oxygen plasma treatment, such as functional groups and defects on the treated SWCNT network surface.

Fig. 6. Response and recovery times of pristine and plasma-treated SWCNT sensors with different semiconducting contents: (a) 66% and (b) 90% s-SWCNT devices. The response time is the 0% to 90% rise time, and the recovery time is the 100% to 10% fall time. The NH_3 concentration was 22.6 ppm.

Table I. Response and recovery times before and after plasma treatment of 66% and 90% SWCNT sensors

Sample	66	p-66	90	p-90
Response time (s)	440	94	442	132
Desorption time (s)	X	934	X	1052

NH_3 concentration 22.6 ppm.

The role of oxygen-containing functional groups and defect sites in molecular adsorption has been reported previously.^{30–32} XPS analysis is often performed to determine the chemical modification of plasma-treated SWCNT networks. Figure 9 shows examples of XPS C 1s spectra of 66% and 90% s-SWCNTs before and after plasma treatment for 10 s with an O_2 gas flow rate of 10 cm^3/min and plasma power of 10 W. The typical C 1s peak is shown at approximately 285 eV. The additional O 1s peak at 533.4 ± 0.5 eV increased while the C 1s signal

decreased after plasma treatment. To identify the groups attached to the surface of the SWCNT networks, the C 1s peak can be decomposed into five components. Chemical assignments for deconvoluted peaks were based on binding energies quoted in the literature: The main peak at 285.0 ± 0.1 eV corresponds to sp^2 -hybridized graphite-like carbon atoms (C=C); Peak 2 centered at 285.8 ± 0.2 eV is attributed to sp^3 -hybridized carbon atoms (C-C); Peaks at 287.2 ± 0.1 eV, 288.6 ± 0.1 eV, and 298 ± 0.1 eV are attributed to C-O (alcohol/ether), C=O (ketone/aldehyde), and O-C=O (carboxyl/ester) species, respectively.

Before treatment, the 90% s-SWCNT samples showed a greater percentage of oxygen (34.09 at.%)

Fig. 7. Calibration plots of resistance variation versus NH_3 concentration for 66% s-SWCNT sensors. $\Delta R = R - R_0$.

Fig. 8. Calibration plots of resistance variation versus NH_3 concentration for 90% s-SWCNT sensors. $\Delta R = R - R_0$.

Table II. Comparison of sensitivity before and after plasma treatment for 66% and 90% SWCNT sensors

Sensor	66	p-66	90	p-90
Sensitivity (%/ppm)	0.0275	0.1525	0.1184	1.5707

compared with the 66% s-SWCNT samples (16.37 at.%). Apparently, the polar NH_3 molecule forms strong hydrogen bonds with oxygen atoms in the oxidized tubes. So, the resistance change of the semiconducting SWCNTs by charge transfer induced by adsorption of NH_3 molecules determines the sensor response. On the other hand, the interaction of the NH_3 molecules with untreated metallic SWCNTs is very weak,^{18,33} and the electrical properties of m-SWCNTs are relatively insensitive to the interaction with NH_3 , exhibiting a small change in their electrical resistance.

The p-66 devices showed a large increase in O/C ratio after treatment. Therefore, it can be assumed that, by plasma treatment, oxygen species were effectively grafted onto the m-SWCNTs to react directly with gas molecules. Furthermore, the sp^2 C=C fraction of the p-66 networks decreased after plasma treatment, whereas the C-O, C=O, and O-C=O fractions increased. These changes suggest that C=C bonds are oxidized and new C-O_x groups are generated on the surface of m-SWCNTs by plasma treatment.

Unlike p-66 samples, the oxygen functionality in the p-90 samples remained almost unchanged after a short period of oxygen plasma treatment, due to the saturated oxygen-containing functional groups, while the sp^3/sp^2 ratio increased greatly from 0.256 to 0.611, indicating the more semiconducting nature of plasma-treated SWCNTs³⁴ and the presence of carbon atoms not bound to oxygen atoms.³³ The existence of sp^3 defects provides anchoring sites for ammonia molecules to adsorb onto the surface of SWCNTs. These results suggest that the sensitivity of SWCNT network (particularly highly enriched semiconducting SWCNT) gas sensors may be largely enhanced through the conversion from m-SWCNTs (sp^2 sites) to s-SWCNTs (sp^3 sites) and/or defect generation as well as oxygen-containing functional groups.

CONCLUSIONS

We explored the effect of oxygen plasma treatment on the characteristics of SWCNT network NH_3 sensors with different semiconducting/metallic ratios. After plasma treatment, the oxygen plasma-treated 90% s-SWCNT network exhibited much higher sensitivity to NH_3 gas than the 66% sample, and a large improvement in the response and recovery times compared with the untreated 90% sample. These results indicate that the oxygen plasma more strongly influences semiconducting-enriched SWCNT networks than normal SWCNT film, possibly indicating that more functionalities and defects are generated on the s-SWCNT network than on m-SWCNTs. Our results provide new insights into the role of the plasma process towards strong improvement in the performance of SWCNT network (particularly highly enriched semiconducting SWCNT) gas sensors.

Fig. 9. XPS spectra of untreated and plasma-treated s-SWCNT network films: (a) 66% s-SWCNT and (b) 90% s-SWCNT. Insets show deconvoluted curves of untreated 66% and 90% s-SWCNT films.

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