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Original Article

Effect of structure and morphology of carbon nanotubes on NO_2 gas sensing

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Abstract

In this research, we investigated the effect of structure and morphology of carbon nanotubes (CNTs) on nitrogen dioxide (NO_2) gas sensing. CNTs were synthesized by thermal chemical vapor deposition (TCVD) at different synthesis temperatures. The structure and morphology of CNTs were investigated by various characterization tools such as scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman spectroscopy. The resistance changes of CNTs were obtained upon NO_2 gas exposure with concentrations of 600, 1,800 and 3,000 ppm at room temperature. Our results show that the CNTs prepared at 950°C showed the highest response. We suggest that the response of CNTs to NO_2 gas depends more strongly on the interstitial area and electronic structure than on the defects of CNTs. These results are in good agreement with the theoretical calculations on adsorption sites (surface, pore, groove and interstitial) and electronic structure (metallic or semiconducting) reported by previous studies.

Keywords: carbon nanotubes, thermal chemical vapor deposition, gas sensor, catalytic particles

1. Introduction

Since their discovery in 1991 (Iijima, 1991) carbon nanotubes, CNTs, have received widespread attention due to their interesting electronic structure, and thermal and mechanical properties, for example (Dresselhaus *et al*., 2004). From these properties, CNTs were considered for applications in various fields such as field emitter, nano-electronic devices and gas sensors. Especially, the CNTs are very promising as gas sensors due to small device size, high specific surface area, fast response and high sensitivity at room temperature and at high temperature. The results of previous studies showed that the application of the CNTs can monitor various gases, such as O_2 (Huang *et al*., 2009), CO_2 (Faizah, 2009), NH_3 (Wang *et al*., 2004; Faizah, 2009) and NO_2 (Ueda *et al*., 2008). The NO_2 is more toxic than the other gases as it is dangerous to the body, where it can cause irritation, sore throat, and other symptoms. A careful protection makes it necessary to have a device that can measure the amount of NO_2 gas in the risk range. However, previous studies until now have introduced only very poor information on structure and morphology of the CNTs used as gas sensors (Valentini *et al*., 2004; Wongwiriyapan *et al*., 2006). Detection of molecules of NO_2 gas with various concentrations was studied for only one synthesis temperature of CNTs and therefore for only one condition of their structure and morphology. There are investigations on the electrical properties of CNTs such as conductivity and resistance change; how-

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ever there are only very few studies of the effect of structure and morphology of CNTs on NO_2 gas sensing performance until now.

In this research, the CNTs were synthesized by thermal vapor deposition (TCVD) at temperatures of 850°C, 900°C and 950°C using C_2H_2 gas with a flow rate of 20 sccm (standard cubic centimeters per minute, sccm). The CNTs synthesized at different conditions were used to detect NO_2 gas with concentrations of 600, 1800, and 3000 ppm in argon (Ar) gas at room temperature, in order to analyze the effect of structure and morphology of CNTs on NO_2 gas sensing performance. To investigate the relationship between the effect of synthesis temperature of CNTs and their qualities on NO_2 gas sensing performance, we used scanning electron microscopy/transmission electron microscopy (SEM/TEM) images, D/G band ratio in the Raman spectra and electrical resistance to obtain information about the morphology, structure and NO_2 sensitivity, respectively.

2. Experimental

Silicon (Si) substrates (20 mm × 20 mm) with silicon dioxide layer were cleaned by ultrasonic in acetone for 10 min. A 20 nm-thin film of Ni was deposited on the Si substrates by DC sputtering method. The Ni-covered Si substrates were then loaded into the TCVD system (Figure 1a). Ar gas with flow rate of 500 sccm was supplied into the TCVD system to prevent oxidation of the catalytic metal when raising the temperature. In order to form the catalytic metal particles in nanometer size, the Ni-deposited Si substrates were etched by ammonia (NH_3) gas with a flow rate of 50 sccm for 20 min at temperatures of 850°C, 900°C and 950°C. The CNTs were grown on the Ni-deposited Si substrates using C_2H_2 gas with a flow rate of 20 sccm for 15 min at the same temperatures as used for NH_3 pretreatment at atmospheric pressure. The surface morphology and length of CNTs were examined by SEM. The measurement of diameter of CNTs was investigated by TEM. The graphitic structure and crystallinity of CNTs were identified with a Raman spectrometer.

As shown in Figure 1b, CNT gas sensors were fabricated with two electrodes of copper wire on the top of CNTs surface. Silver glue was used to create contacts on both surfaces of the CNTs with electrode spacing of 16 mm for sensing area 16×20mm (Figure 1b). The recovery was done in air atmosphere at 100°C. CNTs synthesized at 850°C, 900°C, and 950°C were used to detect NO_2 gas with concentrations of 600, 1,800 and 3,000 ppm for 30 min at room temperature. The response of the CNT gas sensors was measured using a Keithly 2400 source meter. The CNT gas sensors response was defined as $\frac{(R_{NO_2} - R_{Ar})}{R_{Ar}} \times 100$, where R_{Ar} is the resistance in pure Ar gas and R_{NO_2} is the resistance in NO_2 gas.

3. Results and Discussion

In order to study the effect of their structures and morphologies, CNTs were grown at different temperatures. Figure 2 shows SEM images of CNTs synthesized at 850°C, 900°C and 950°C. The CNTs have a high density and are not

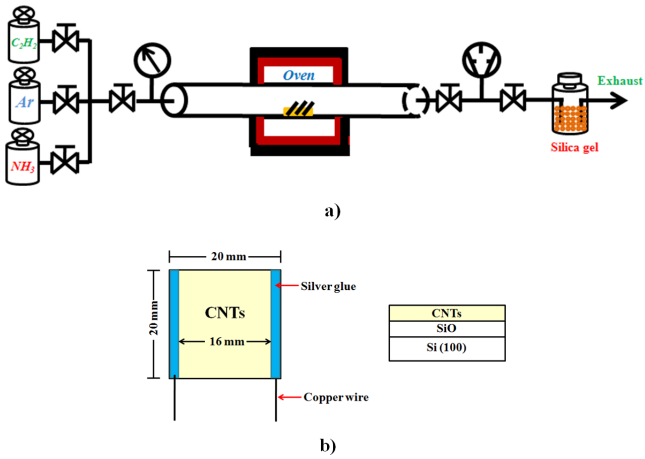

Figure 1. a) Thermal chemical vapor deposition set up for the synthesis of CNTs. b) Sensor device structure.

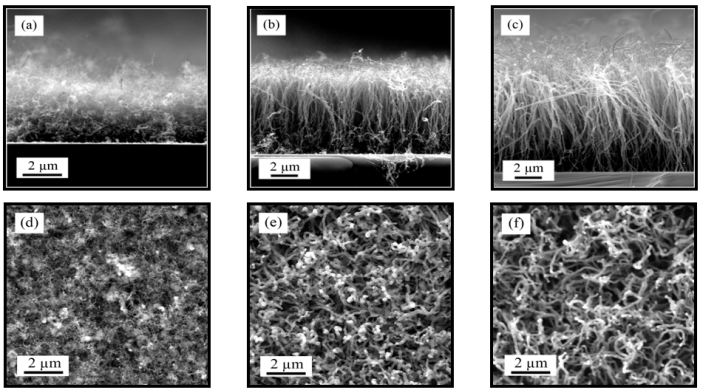

Figure 2. SEM images of CNTs growth at different temperatures. Cross-sectional view of CNTs synthesized at (a) 850°C, (b) 900°C, and (c) 950°C, and top view of CNTs synthesized at (d) 850°C, (e) 900°C, and (f) 950°C.

well aligned in Figure 2(a). Figures 2(b) and 2(c) show vertically aligned CNTs indicating appropriate density of Ni particles on the substrate and implying some van der Waals interactions between neighboring CNTs along the direction normal to the substrate. The length of CNTs was 8.1±1.0 and 10.0±1.2 μm at 900°C and 950 °C, respectively. The result demonstrates that the length of CNTs can be controlled by adjusting the growth temperature. The images from TEM (Figure 3) give evidence that the CNTs were multi-walled carbon nanotubes (MWNTs). The diameter of CNTs synthesized at 850°C, 900°C, and 950°C were 85.2±30.8, 99.8±32.0. and 104.6±10.2 nm, respectively, showing that the diameter of CNTs increases with increasing synthesis temperature. Obviously, the size of Ni particles is increased when prepared at higher temperature. At higher temperature the migration rate of Ni particles on Si surface increases and facilitates the agglomeration of Ni particles leading to the greater diameter of CNTs (Choi *et al.*, 2000).

Figures 3a and b show TEM images of the bamboo-like structure of CNTs obtained at the growth temperature of 900°C. In Figure 3b, the high magnification image is obtained at the junction part in bamboo shaped structure. The bamboo-like structure of CNTs is formed at the growth temperature of 900°C and 950°C. The promotion of bamboo-like structure suggests that the carbon atoms diffuse via surface and bulk of catalytic metal particles to form the graphitic sheets. Then, the carbons accumulated at the inside surface of catalytic metal particles, probably mainly via bulk diffusion, can form the compartment graphitic sheets. While the tube grows upward, the next compartment layer is produced on the catalytic particles (Lee and Park, 2001).

The Raman spectra of the CNTs at different synthesis temperature are shown in Figure 4. All spectra show mainly two Raman bands, G-band, originating from graphite structure, and D-band, originating from disordered carbon. The CNTs synthesized at 850°C, 900°C and 950°C show the G-band at 1,583, 1,578 and 1,568 cm^{-1}, respectively, and the D-band at 1,347, 1,353 and 1,340 cm^{-1}. The intensity ratio between G band and D band I(D)/I(G) is an indication of the crystalline perfection of CNTs. The I(D)/I(G) ratio of CNTs synthesized at 850°C, 900°C and 950°C were 1.00, 0.43 and 0.38, respectively. The C_2H_2 gas can be dissociated better at higher than at lower temperature values. Therefore, the crystalline perfection of CNTs was improved with an increase of the synthesis temperature.

Figures 5a to c show the resistance changes of CNTs versus time after heating abruptly from room temperature to 150°C under Ar gas for 30 min. The resistance of CNTs prepared at 850°C decreased with increasing time at 150°C due to the transfer of some electrons from the valence band

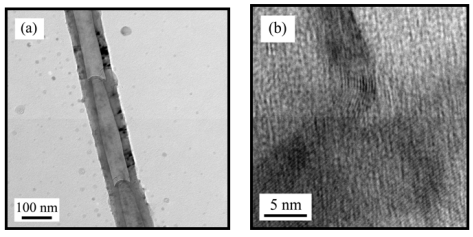

Figure 3. TEM images of CNTs synthesized at 900°C. (a) Multi-walled bamboo-like structure, (b) junction part of graphite in bamboo-shaped multi-walled carbon nanotubes.

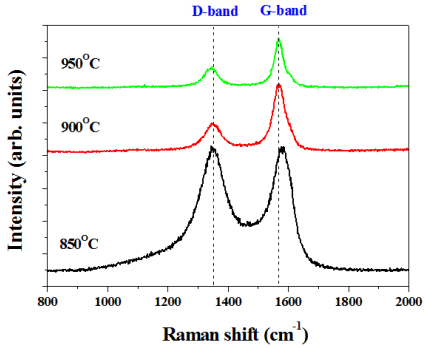

Figure 4. Raman spectra of CNTs at different synthesis temperature.

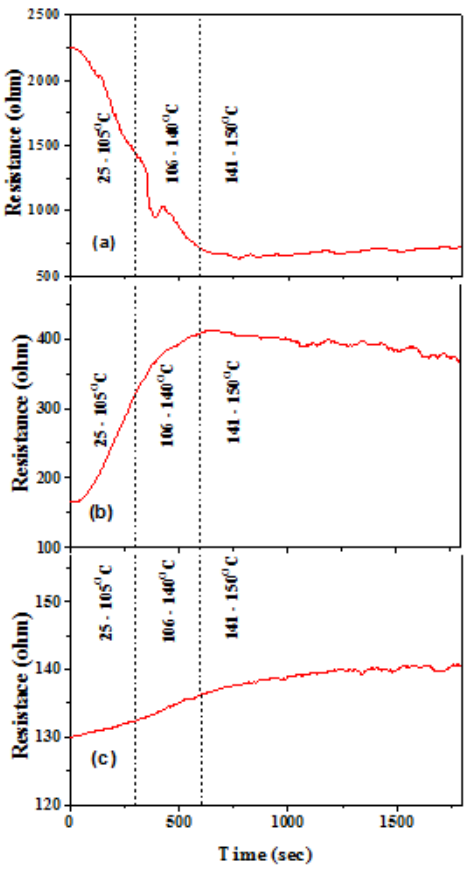

Figure 5. Resistance versus time of CNTs synthesized at (a) 850°C, (b) 900°C and (c) 950°C after heating abruptly from RT to 150°C. The corresponding temperature increase is indicated.

to the conduction band; these CNTs behave like semiconductors. In contrast, the resistance of CNTs prepared at 900°C and 950°C increased after increasing the temperature, because of increased electrons processes; this is a behavior like that of metals. The initial resistances of CNTs synthesized at 850°C, 900°C and 950°C were 2,251.70, 165.55 and 130.9 Ω, respectively. The higher initial resistance of CNTs synthesized at 850°C than that of CNTs synthesized at 900°C and 950°C is due to their disorder and defects of the tube walls.

The experimental results for response of CNTs to NO_2 gas with a concentration of 600, 1,800 and 3,000 ppm as a function of time was studied at room temperature as shown in Figures 6a to c. The resistance of the CNT gas sensors was decreased by NO_2 gas because electrons were transferred from CNTs to NO_2 gas molecule and the hole density in the CNTs increased. The response of CNTs synthesized at 850°C to NO_2 gas of 600 ppm was small and unstable, while the response to NO_2 gas of 1,800 and 3,000 ppm was 0.97 and 1.76%, respectively. In addition, the response of CNTs synthesized at 900°C and 950°C to NO_2 gas of 600, 1,800, 3,000 ppm was 1.17%, 2.92%, 3.66% and 2.46%, 3.51%, 6.35%, respectively (see Table 1). The response time of the CNTs sensor varies approximately between 32 to 128 seconds.

The results showed that the response of CNTs synthesized at 900°C and 950°C was considerably higher than of CNTs synthesized at 850°C. The reason may arise from three factors, the absorption area and the electronic structures of CNTs. First, we consider the area where NO_2 gas is absorbed. From Figure 2a and 2d it can be seen that CNTs synthesized at 850°C are overlapping and tangling tubes on the substrate. Most of NO_2 gas molecules probably move to the top surface of CNTs when the gas is released into the gas sensor system. The absorption in this area and therefore the transmission of electrons into gas molecules is low; consequently the response signal is low (Zhao *et al*., 2002). Furthermore, it was found that the response of CNTs synthesized at 950°C due to their longer tubes and thereby lager surface area is higher than that of synthesized at 900°C. When NO_2 gas moves to the interior of CNTs group, NO_2 gas molecules can be absorbed at interstitial sites. Calculation showed that the interstitial sites are best for charge transfer compared to other sites such as surface, groove and pore (Zhao *et al*., 2002).

Second, we considered the electronic structures of CNTs synthesized at different temperatures. It was found that

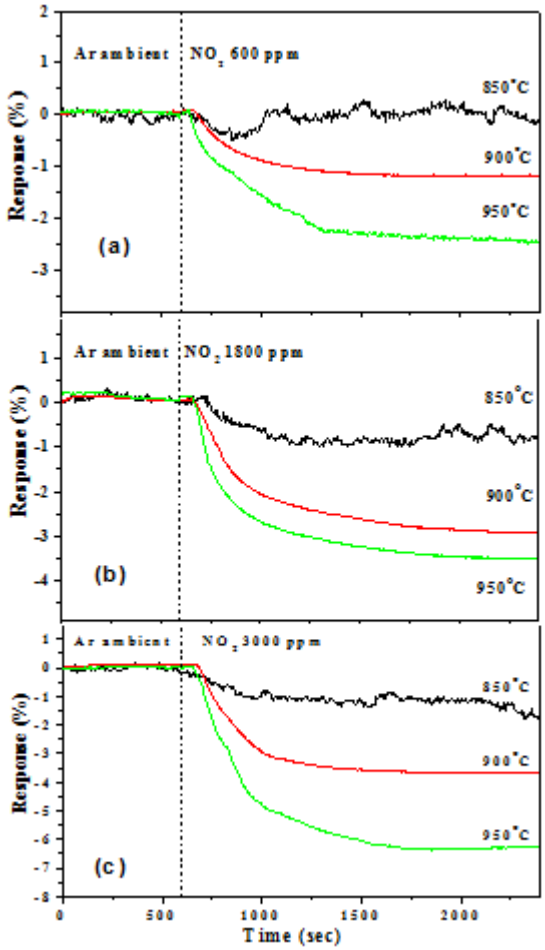

Figure 6. Response of CNTs synthesized at different temperatures to NO_2 gas of (a) 600 ppm, (b) 1,800 ppm, and (c) 3,000 ppm.

CNTs synthesized at 850 °C show semiconductor resistance behavior while CNTs synthesized at 900°C and 950°C show a metallic one. Previous studies reported that the NO_2 absorption on metallic CNTs due to charge transfer and electron affinity is energetically more favorable than that on semiconductor CNTs (Seo *et al*., 2005). Therefore, CNTs synthesized at 900°C and 950°C showed a higher response. Third, when considering the defects of CNTs on NO_2 gas sensing performance, it was found that the perfect CNTs gave the highest response. This is in disagreement with previous studies both

Table 1. Initial resistance and response of CNTs synthesized at different temperatures.

Growth temperature (°C)	Initial resistance (Ω)	Response (%) of CNTs to NO_2 concentrations (ppm)		
		600	1800	3000
850	2,251.70	N/A	0.97	1.76
900	165.55	1.17	2.92	3.66
950	130.09	2.46	3.51	6.35

theoretical and experimental reporting that the defected CNTs showed high response (Valentini *et al*., 2004). We find in contrast that the effect of defect of CNTs is not the main factor governing the NO_2 gas sensing performance. However, the aspect of sensitivity of CNTs sensor will improve by making new interdigitate electrodes. In addition, to use conductive polymer/CNTs composite with high electron conductivity is another idea for improvement of sensitivity.

4. Conclusions

CNTs were synthesized on Ni-deposited SiO/Si substrates by TCVD at temperatures of 850°C, 900°C and 950°C using C_2H_2 gas with a flow rate of 20 sccm. The results showed that the diameter, length and crystallinity of CNTs can be controlled by the synthesis temperature. This way, CNT gas sensors with different structures and morphologies were used to detect NO_2 gas with concentrations of 600, 1,800 and 3,000 ppm at room temperature. It turned out that the CNTs, prepared at 950°C, due to their greater absorption area and favorable electronic structure exhibited the highest response to NO_2 gas. It is concluded that not the defects of CNTs, but the absorbing interstitial area and the electronic structure of CNTs play the key role for their performance as NO_2 gas sensors.

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