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Patterned multiwall carbon nanotube films as materials of NO_2 gas sensors

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Abstract

Multiwall carbon nanotube (MWNT) films grown by thermal chemical vapor deposition on a micromachined substrate with a chrome heater and a diaphragm have been investigated as sensing materials of resistive gas sensors for nitrogen dioxide (NO_2). We fabricated the aligned MWNT films, which grew into mesh and serpentine shapes by photolithography. Photolithography patterned the cobalt catalyst layer. MWNT films showed a p-type electrical resistivity with decreasing electrical resistance upon exposure to NO_2. The sensor exhibited a reversible response at a thermal treatment temperature of 130 °C for a time constant of a few minutes. The resistance change to NO_2 of the mesh-shaped MWNT films was found to be larger than that of the serpentine-shaped MWNT films.
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Keywords: Diaphragm; Multiwall carbon nanotubes; Nitrogen dioxide (NO_2); Resistive gas sensor; Reversible response; Thermal chemical vapor deposition (CVD)

1. Introduction

The unique properties of carbon nanotubes (CNTs) have stimulated great interest owing to their tremendous technological promise ranging from nanoelectronics to hydrogen storage devices and to chemical sensors [1]. The relation between their geometry and electronic structure is of particular interest. Semiconducting or metallic behavior perhaps depends on the tube diameter and chirality. In particular, gas adsorption by the nanotubes has attracted a great deal of attention because it affects the electronic and transport properties of the CNT [2,3], such as fast response and high sensitivity towards environmental gases.

The latest experimental results [2,4] have reported that the electrical conductance of semiconducting single-wall tubes dramatically changes when the tubes are exposed to NO_2, O_2, and NH_3. Similar theoretical work has shown how the electronic properties of CNTs change when the CNTs are exposed to reducing or oxidizing gases. More recently, multiwall carbon nanotube films have been reported to show a p-type character with decreasing resistance upon exposures to sub-ppm concentrations of NO_2 [5].

Nevertheless, the microscopic chemical and physical interactions between adsorbed molecules and sensing tubes are not yet completely understood. In addition, CNTs have not been used often as materials of chemical gas sensors, because of the long recovery time and low sensitivity of the CNT rope and mat in an integrated device [2].

We fabricated a chemical sensor by using selectively grown MWNTs as the sensing element on a substrate of a stacked micro-heater structure [6,7] with a Cr heater and a diaphragm to improve the recovery time and sensitivity of the MWNT films. To offer more reaction area between MWNTs and NO_2 molecules, we designed the MWNT films so that they had mesh and serpentine shapes. The micromachined substrate and the MWNT deposition process are described, and the characteristics of the sensor when exposed to NO_2 are presented.

2. Experimental details

The CNT-based gas sensor was fabricated by a conventional silicon process. As shown in Fig. 1, the gas sensor is composed

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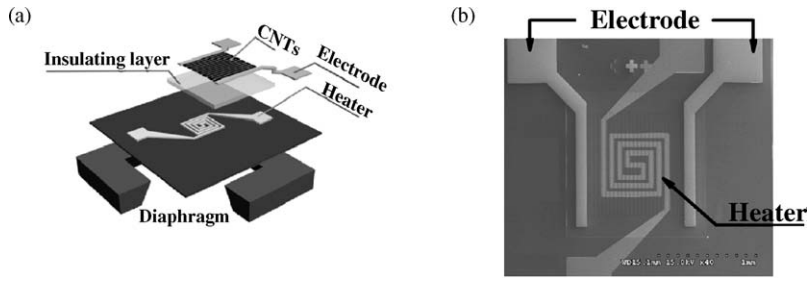

Fig. 1. (a) Photograph and (b) FE-SEM photomicrograph of an MWNT-based gas sensor.

of an MWNT film, a Cr heater resistor, a pair of electrodes, and a passivation layer (SiO_2) on a thermally insulated dielectric diaphragm that reduces the thermal gradient ($Si/SiO_2/Si_3N_4$ structure). The backside of a silicon substrate, 3 mm × 3 mm wide and 450 μm thick, was etched away to form a square diaphragm, 1.5 mm × 1.5 mm wide and 20 μm thick. On top of the substrate, a sensing area, 1.05 mm × 1 mm wide, was attached.

The details of our process are as follows: (1) a 1 μm thick SiO_2 layer was thermally grown on a p-type double-sided polished silicon wafer with a thickness of 450 μm. A 400 nm Si_3N_4 layer was deposited on the SiO_2 layer by low pressure chemical vapor deposition (LPCVD) (Fig. 2b); (2) for the flatness of the passivation layer, a 600 nm thin film of SiO_2 was deposited on a Si_3N_4 layer by plasma-enhanced chemical vapor deposition (PECVD), patterned by using Mask I, and then etched (Fig. 2c); (3) a 340 nm Cr thin film was deposited on the SiO_2 by RF-sputtering at room temperature. The Cr resistance heater was formed by the lift-off technique (Fig. 2d); (4) a 500 nm SiO_2 thin film as an electrical insulating layer was deposited on the Cr resistance heater by PECVD. The deposited SiO_2 layer was patterned and then etched by a reactive ion etching (RIE) method to make the contact space for the Cr resistance heater (Fig. 2e); (5) an 8 nm Co thin film was patterned to make the catalyst for the MWNT growth by lift-off technique (Fig. 2f); (6) a 340 nm Cr thin film was patterned to make the bonding pads and the pairs of electrodes for the sensing layer by lift-off technique (Fig. 2g); (7) a square window pattern was opened in the Si_3N_4 on the wafer backside by conventional photolithography and etched by CF_4 gas plasma (Fig. 2h). And then the silicon substrate was etched away by using an anisotropic etchant (KOH). Consequently the thermal isolation of the substrate was achieved, and the sensor structure was supported by a 20 μm thick square diaphragm produced; (8) finally, the MWNT-film was deposited by thermal chemical vapor deposition (thermal CVD) (Fig. 2i) [8].

The MWNTs were grown by the pyrolysis of cobalt (Co) and acetylene (C_2H_2) gas under the argon (Ar)/hydrogen (H_2) atmosphere in a reactor. The substrate was loaded into a quartz boat inside the thermal CVD quartz reactor. The temperature of the thermal CVD chamber was raised to the process temperature of 750 °C within 10–20 min by halogen lamps after evacuation down to 10^{-3} Torr. During this step, the substrates were firstly treated under a hydrogen (H_2) gas environment for nearly 10 min to activate the surface of the catalytic metal and to prevent the corrosion of Co and Cr metal due to residual gases. During the growth, the total pressure of the chamber was maintained at 20 Torr; the flow rate of the hydrocarbon source, C_2H_2, was 5 sccm, and the remaining 80 sccm was for the ammonia (NH_3) gas. After the MWNT was grown, the chamber was purged continuously by mixing H_2 and Ar until the chamber temperature reached the room temperature.

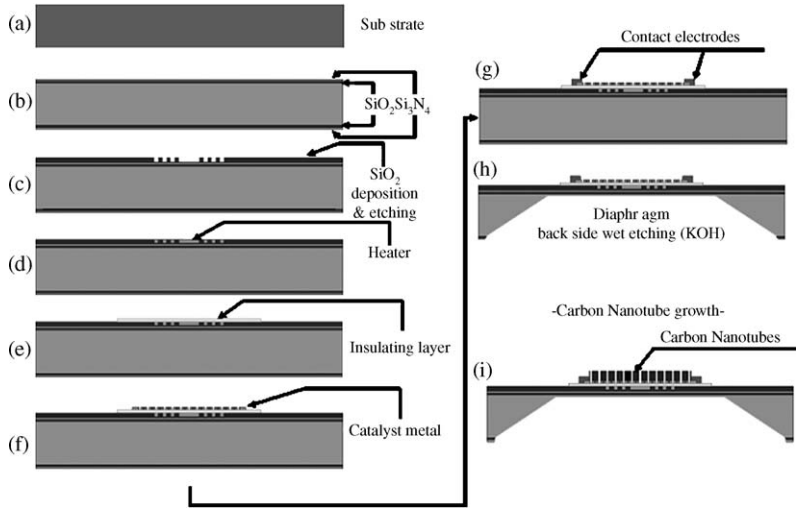

Fig. 2. Schematic drawing of the process flow for fabricating a selectively grown vertical MWNT gas sensor.

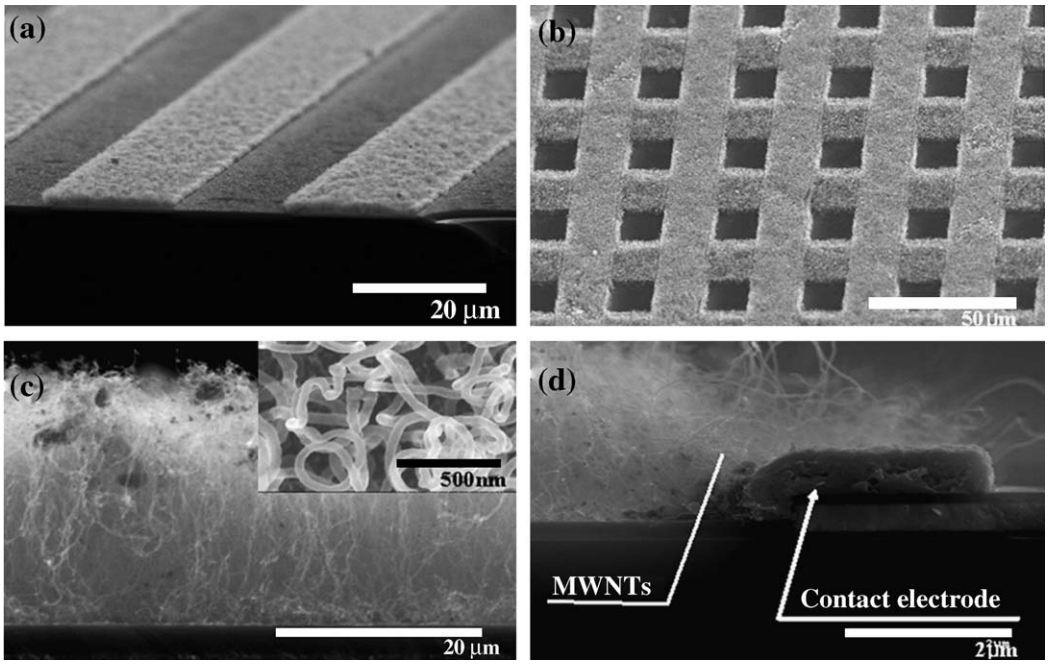

Fig. 3. FE-SEM photomicrograph of as-grown MWNTs: (a) top view of an as-grown serpentine-shaped MWNT film; (b) top view of an as-grown mesh-shaped MWNT film on the substrate of the stacked structure with a Cr heater and a diaphragm; (c) magnification of the as-grown structure of the MWNT film on the substrate of the stacked structure; (d) cross-sectional view of the electrode part.

3. Results and discussion

We experimentally present the grown vertical MWNTs on a thin cobalt catalyst layer patterned by conventional photolithography between two parallel patterned electrodes. Field emission scanning electron microscope (FE-SEM) images of the shape of the as-grown MWNT films are shown in Fig. 3. MWNT films grew into a mesh shape (shown in Fig. 3a) and a serpentine shape (shown in Fig. 3b). As shown in Fig. 3c, MWNTs were vertically aligned to the substrate in a uniform distribution. The diameter of MWNTs was about 30–40 nm with a height of 3–4 μm. MWNTs were grown on a Co catalyst with an 8 nm thickness at 750 °C for 5 min under $C_2H_2/NH_3/Ar$. The film contained some carbonaceous nanoparticles deposited on top of the tubes. The bright lines of the images are the aligned MWNTs. MWNTs appeared bright since the catalyst nanoparticles on top of the tubes were electrically conducting. As the size of the catalyst nanoparticles increased with the film thickness, the diameter of the CNTs increased linearly because the diameter of the catalyst tended to correspond to the inner diameter of MWNTs. It was necessary to remove CNTs from the substrates and disperse them onto pre-patterned electrodes for electronic applications.

To connect the patterned MWNT film and the electrode electrically, we form the overlapped part of the catalyst metal and the electrode metal. Then MWNTs are grown on the overlapped part. The grown MWNTs can establish good electrical connection with the electrode as shown in Fig. 3d.

An experiment was carried out with the same micromachined substrate [6,7]. To measure the dc electrical resistance R, the sensor was mounted in a test chamber with provision for injecting different environmental gases. The chamber was evacuated down for 30 min. After the valves of the reaction chamber were closed, a mixed gas of air and NO_2 was introduced at a pressure of 5×10^{-3} Torr into the test chamber for 40 s. When the chamber atmosphere changed from NO_2 to vacuum, the MWNT films were thermally treated by a heater. In thermal treatment, the "as-deposited" MWNT films were heated from 25 to 130 °C and then cooled back to 25 °C. The resistance was measured by using a Keithley 2400 series source meter, which recorded electrical resistance as a function of operating temperature. The initial resistance of the sensor is defined as R_0, which is the measured resistance after the thermal treatment in vacuum (10^{-3} Torr) at 130 °C for 3 min.

Fig. 4 shows the resistance response of the sensors to NO_2 gas of 100 ppm. Four sensors were fabricated and tested to examine the effect of the patterned serpentine- (Fig. 4a and b) and mesh-shaped (Fig. 4c and d) MWNT films. The resistance response of the sensor (R_r) is defined as R_G/R_0, where R_0 is the initial resistance of the sensor and R_G is the resistance of nanotube films when exposed to NO_2. The sensors were calibrated by using the resistance of the sensor exposed to NO_2 for 220 s. The specification and the R_r of four sensors are summarized in Tables 1 and 2, respectively. When the sensor was exposed

Table 1
Specification of the MWNT thin films

	Serpentine-shaped MWNT film		Mesh-shaped MWNT film	
Line-width (μm)	100	20	20	10
The number of corners	10	50	–	–
The number of grids	–	–	625	2450
Length (mm)	6.57	25.07	–	–
Area (mm^2)	0.486	0.52	0.77	0.775

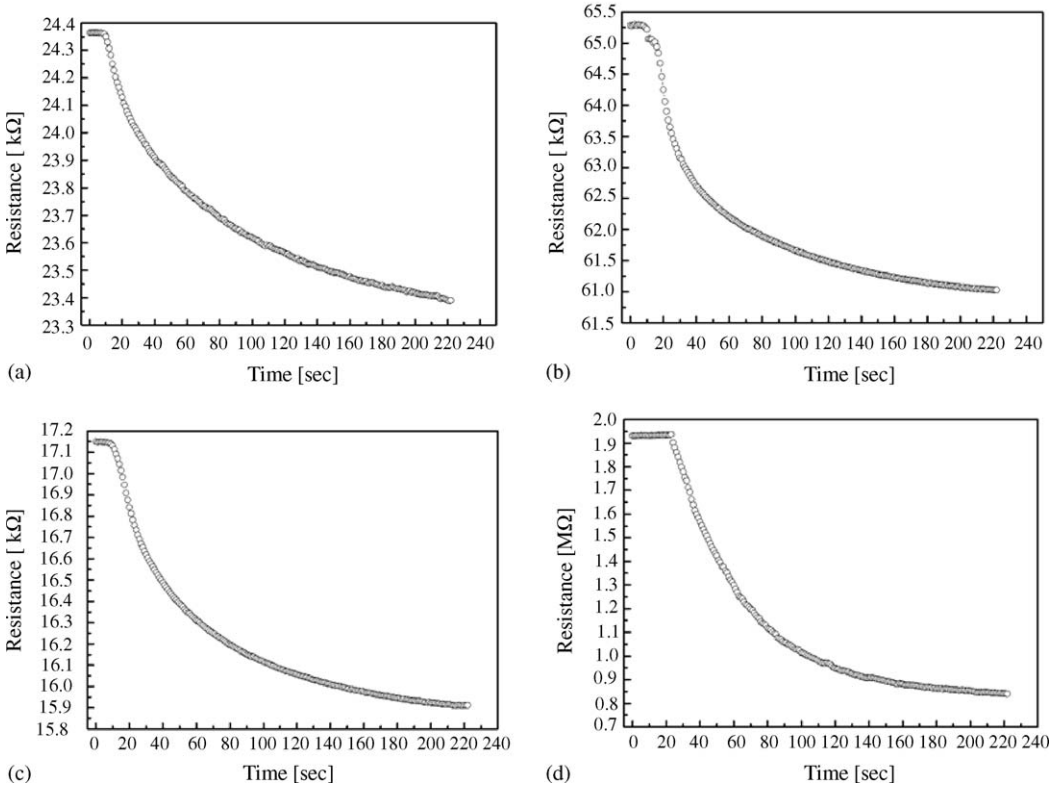

Fig. 4. Electrical resistance variation of serpentine-shaped MWNT films with the line-widths of (a) 100 μm and (b) 20 μm, and of mesh-shaped MWNT films with the line-widths of (c) 20 μm and (d) 10 μm for the NO_2 concentration of 100 ppm.

to NO_2 at room temperature, R_r of all sensors decreased. This decrease can be explained by the conventional p-type semiconductor theory. Upon exposure to electron-accepting molecules, the electron charge transfer was found to be from the electron-acceptor to the p-type semiconductor. Therefore, exposure to the electron-accepting gases such as CO_2 and NO_2 resulted in the Fermi level shift of the nanotube closer to the valence band. This shift enriched the hole carriers in the nanotube and decreased the resistance of the nanotube. In general, MWNTs tend to conduct (metallic) at room temperature, while SWNTs behave as semiconducting materials. However, MWNTs can contain some semiconducting tubes among predominant metallic ones. The semi conducting MWNTs actually can be utilized as materials of gas sensors [9].

In MWNT films, the molecular interaction effects are averaged over metallic and semi conducting tubes. In addition, the inner tubes in MWNT films are blocked from interacting with NO_2 because the molecules are not expected to diffuse into MWNT films. This explains the small resistance change of the MWNT films by gas exposure unlike the large change of an individual semiconducting SWNT.

Table 2
The resistance response (R_r) of the sensors according to the shape and line-width of the patterned MWNT films for NO_2 gas concentration of 100 ppm

Shape	Line-width (μm)	R_r
Serpentine-shaped MWNT film	100	1.041
	20	1.069
Mesh-shaped MWNT film	20	1.077
	10	2.42

According to the shape of patterned MWNT thin films, we find that the R_r is changed. The resistance of the mesh-shaped MWNT film with the line-width of 10 μm decreased by about 2.5-fold of the magnitude after NO_2 of 100 ppm was introduced. For comparison, three sensors were operated at room temperature to detect NO_2 of 100 ppm with an R_r of ∼1.06. SWNT ropes and mats at room temperature detected NO_2 of 200 ppm with an R_r of ∼1.5 [2]. The R_r of the mesh-shaped MWNT film was higher than that of the serpentine-shaped MWNT film probably because the number of reaction spaces between MWNTs and NO_2 molecules was increased as shown in Table 2.

Fig. 5 shows the resistance response of the sensors to NO_2 gas of 10, 50, and 100 ppm. The line-widths of a serpentine shape (Fig. 5a) and a mesh shape (Fig. 5b) were 20 and 10 μm, respectively. Two sensors were tested to examine the effect of the patterned serpentine- and mesh-shaped MWNT films in the various NO_2 concentrations. The test sensors of the serpentine-shaped and mesh-shaped MWNT films are designated as sample 1 and sample 2, respectively.

The resistance of the sensor continuously decreased even for 5 min and was not saturated, as shown in Fig. 5a and b. However, the R_r of sample 2 was saturated in 100 ppm NO_2, as shown in Fig. 5b. These phenomena explained that the density of MWNTs was suited to 100 ppm. As the result, the R_r to NO_2 concentrations of 50 and 100 ppm showed a slight difference. After NO_2

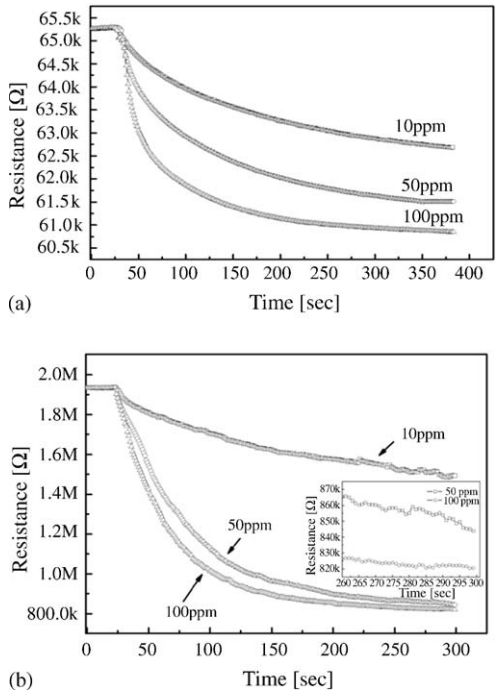

Fig. 5. Electrical resistance variation of MWNT films at an operating temperature of 25 °C and NO_2 concentrations between 10 and 100 ppm: (a) a serpentine-shaped MWNT film; (b) a mesh-shaped MWNT film.

was evacuated from the chamber, the resistance of the sensor returned to the initial value very slowly (it took about 6 h; data are not shown). These phenomena reflect that NO and NO_2 bind weakly with low diffusion barriers; this weak bond allows the formation of NO_3 with a strong binding energy and a long life on a SWCNT surface [10]. The sensors were calibrated by using the resistance of the sensor exposed to NO_2 for 5 min. The calibration time (5 min) for the detected gas was determined so that the resistance decrease could be high enough to be measured even for lower values of NO_2 concentration and the R_0. The R_r values for the calibration time are summarized in Table 3. The R_r of the sample 2 was ~1.3–2.5 forNO_2 concentration at room temperature. For comparison, sample 1 at room temperature detected NO_2 concentration with an R_r of ~1.04–1.073. Thus, the sensors based on a mesh-shaped film can be operated at room temperature with a two times magnitude of the R_r for the other shape.

Table 3
The resistance response (R_r) of the sensors according to the shape of the patterned MWNT films for NO_2 gas concentrations of 10, 50, and 100 ppm

Sample	10 ppm	50 ppm	100 ppm
Serpentine-shaped MWNT film	1.04	1.06	1.073
Mesh-shaped MWNT film	1.3	2.28	2.42

Fig. 6 shows the resistance of the MWNT film as a function of time when exposed to cycles of a sequence of NO_2 exposure (sensing) and evacuation (recovery) at NO_2 concentrations ranging from 10 to 100 ppm. Curve (i) represents the NO_2 response of the film at the operating temperature of 25 °C. Curve (ii) represents the response of the film to NO_2 as the gas was evacuated from a chamber during cooling of the film from 130 to 25 °C.

Fig. 6c indicates the variation of the sensor temperature as a function of the power dissipated by the Cr resistance heater. The micro-heaters of the same pattern and thickness were used. At the

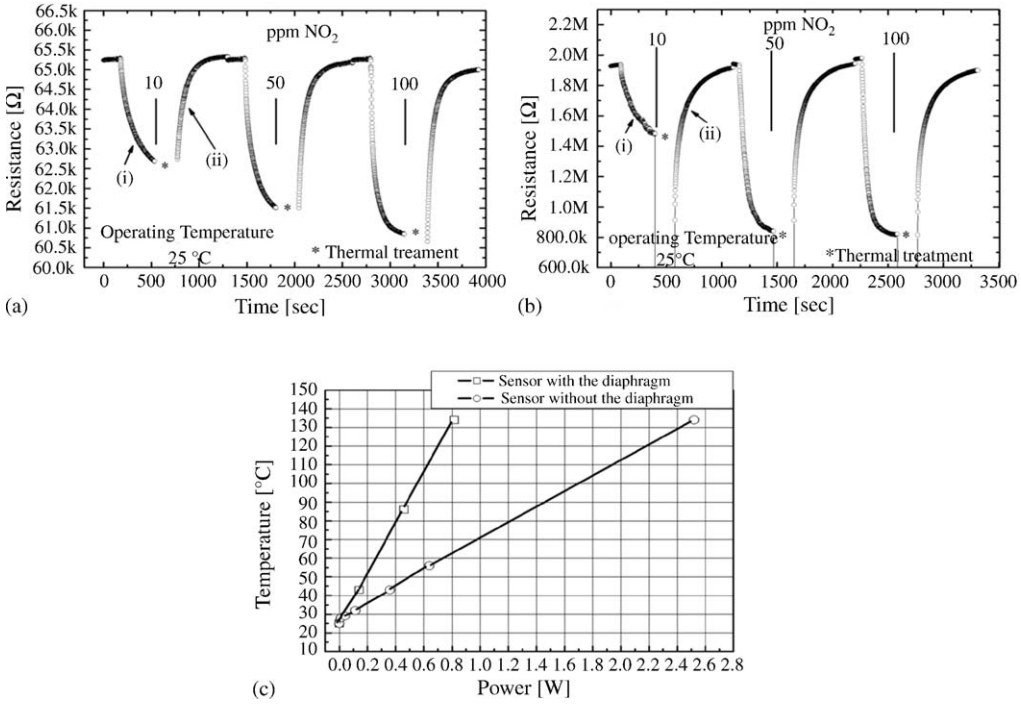

Fig. 6. Resistance changes of the sensor as a function of time for three cycles of a sequence of NO_2 concentrations ranging from 10 to 100 ppm: (a) a serpentine-shaped MWNT film; (b) a mesh-shaped MWNT film; (c) plot of ambient temperature as a function of input power to a Cr heater. (i) Resistance change of an MWNT film after exposure to NO_2 at room temperature and (ii) resistance change of an MWNT film after heating and out-gassing.

thermal treatment temperature of 130 °C, the micro-heater with a thermally insulated dielectric diaphragm consumed a power of 817 mW, which was smaller than that of the micro-heater without a dielectric diaphragm (2.52 W), because the dielectric diaphragm of low thermal conductivity provided good thermal isolation between the substrate and the heated active area on the diaphragm [6]. A silicon micro machining process such as electrochemical etching, which gives a better control on the dimensions of the silicon diaphragm, may be used as well. A thinner and narrower silicon membrane may reduce the heat loss due to the conduction and convection, which are related to the area of the silicon diaphragm and the distance between the silicon diaphragm and chip frame, respectively.

Here, we define the recovery time as the time of 90% total resistance change. The thermal treatment temperature of 130 °C activates the desorptive process that results in fast recovery of the sensor from the MWNT films. During the cooling of the film from 130 to 25 °C in vacuum (10^{-3} Torr), the resistance slightly increases. The sensor does not have much sensitivity decay during the sensing cycles; this shows the repeatable sensing characteristics. If the thermal cycle of heating and cooling of the sensor is maintained within the temperature range of 25–130 °C, the sensor response is always reversible. It was also found that the resistance responses of all sensors with and without the recovery process did not change. We confirmed that the sensitivity of the MWNT film-based sensors is dependent on the patterned shape.

4. Conclusion

An MWNT-based NO_2 sensor was successfully fabricated by a selective growth method on a micromachined substrate. The MWNT sensor could detect NO_2 of ppm-level at room temperature. The MWNT thin films can be better recovered only by properly selecting the thermal treatment protocols. The normalized resistance sensitivity of the mesh-shaped MWNT film was higher than that of the serpentine-shaped MWNT film probably because the number of reaction areas between MWNTs and NO_2 molecules was increased. The sensor response and recovery time can be controlled by how the MWNT films are selectively grown and how the MWNT films are patterned on a micromachined substrate.

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References

[1] R. Saito, G. Dresselhaus, M.S. Dresselhaus, Physical Properties of Carbon Nanotubes, Imperial College Press, London, 1998.
[2] J. Kong, N.R. Franklin, C. Zhou, M.G. Chapline, S. Peng, K. Cho, H. Dai, Nanotube molecular wires as chemical sensors, Science 287 (2000) 622–625.
[3] P.G. Collins, K. Bradley, M. Ishigami, A. Zettl, Extreme oxygen sensitivity of electronic properties of carbon nanotubes, Science 287 (2000) 1801–1804.
[4] K.G. Ong, K. Zeng, C.A. Grimes, A wireless passive carbon nanotube-based gas sensor, IEEE Sens. J. 2 (2002) 82–88.
[5] L. Valentini, I. Armentano, J.M. Kenny, C. Cantalini, L. Lozzi, S. Santucci, Sensors for sub-ppm NO_2 gas detection based on carbon nanotube thin films, Appl. Phys. Lett. 82 (2003) 961–963.
[6] M. Baroncini, P. Placidi, G.C. Cardinali, A. Scorzoni, Thermal characterization of a micro-heater for micromachined gas sensors, Sens. Actuators A 115 (2004) 8–14.
[7] I. Simon, N. Bârsan, M. Bauer, U. Weimar, Micromachined metal oxide gas sensors: opportunities to improve sensor performance, Sens. Actuators B 73 (2001) 1–26.
[8] C.J. Lee, D.W. Kim, T.J. Lee, Y.C. Choi, Y.S. Park, Y.H. Lee, W.B. Choi, N.S. Lee, G.-S. Park, J.M. Kim, Synthesis of aligned carbon nanotubes using thermal chemical vapor deposition, Chem. Phys. Lett. 312 (1999) 461–468.
[9] K. Kaneto, M. Tsuruta, G. Sakai, W.Y. Cho, Y. Ando, Electrical conductivities of multi-wall carbon nanotubes, Synth. Met. 103 (1999) 2543–2546.
[10] S. Peng, K. Cho, P. Qi, H. Dai, Ab initio study of CNT NO_2 gas sensor, Chem. Phys. Lett. 387 (2004) 271–276.

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