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Sensors for sub-ppm NO_2 gas detection based on carbon nanotube thin films

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Carbon nanotubes (CNTs) deposited by plasma-enhanced chemical vapor deposition on Si_3N_4/Si substrates have been investigated as resistive gas sensors for NO_2. Upon exposure to NO_2, the electrical resistance of the CNTs was found to decrease. The maximum variation of resistance to NO_2 was found at an operating temperature of around 165 °C. The sensor exhibited high sensitivity to NO_2 gas at concentrations as low as 10 ppb, fast response time, and good selectivity. A thermal treatment method, based on repeated heating and cooling of the films, adjusted the resistance of the sensor film and optimized the sensor response to NO_2. *© 2003 American Institute of Physics.* [DOI: 10.1063/1.1545166]

In recent years, carbon nanotubes have been studied intensively due to their importance as building blocks in nanotechnology. Their special geometry and unique properties offer great potential applications, including nanoelectronic devices, energy storage, chemical probes and biosensors, field emission displays, etc.[1–4] To date, reported studies on possible applications of carbon nanotubes as gas sensors have focused either on isolated single wall carbon nanotubes (SWNTs) or on SWNT mats.[5–8] In particular, it has been found that, upon exposure to O_2, NO_2, or NH_3, the electrical conductance of the semiconducting SWNTs changes.[5–8] Theoretical studies have also predicted significant changes in the electronic properties of carbon nanotubes because of gas adsorption.[9,10] These results provide motivation toward application of carbon nanotubes as gas sensors to detect sub-ppm concentrations of oxidizing gases like NO_2, O_3, and Cl_2.

The present work focuses on carbon nanotube (CNT) thin films prepared by a radio-frequency plasma-enhanced chemical vapor deposition (PECVD) glow discharge system for the detection of NO_2. The main goal of this work was to determine if thin carbon nanotube films could be used as an innovative NO_2 sensor having sub-ppm sensitivity, stability, and selectivity at reasonably low operating temperatures.

Carbon nanotube thin films were grown using a radio-frequency (rf) PECVD system. A thin film (5 nm) of a Ni catalyst was deposited onto Si_3N_4/Si substrates provided with platinum interdigital electrodes and a back-deposited thin-film platinum heater commonly used in gas sensor applications.[11] The substrates were heated to 650 °C and held in a vacuum at this temperature for 45 min to induce a cluster formation of the catalyst layer before activating the CNT plasma deposition.[12] The CNTs film deposition was performed with fixed rf bias voltage, pressure, and temperature of -150 V, 1 Torr, and 650 °C, respectively. The total precursor (CH_4) gas flow rate was kept constant at 84 sccm. A deposition time of 30 min produced a nanotube film that was about 200 nm thick.

High-resolution field emission scanning electron microscopy (SEM) images of CNTs deposited by pure methane plasma on annealed Ni layers are presented in Fig. 1. A scanning electron microscopic investigation was performed with a LEO 1530 field emission scanning electron microscope, operated at 5 kV. Figure 1(a) shows a top view of the film, where nanotubes with almost uniform diameters (35–40 nm) are present. A side view image shows entangled and aligned carbon nanotubes with a metal cap predominantly located at the top of the nanotubes.

The resistance of the films was measured using a voltamperometric technique (Keithley 2001 multimeter), recording electrical resistance as a function of the operating temperature, using three different thermal treatments. Figure 2 shows the change of electrical resistance with temperature in flowing, dry air (500 sccm/min). The first thermal treatment consisted of heating the ''as-deposited'' carbon film from 25 to 250 °C and then cooling it back to 25 °C. The second and third thermal treatments consist of heating from 25 to 322 °C followed by cooling to room temperature. During the first thermal treatment (line AA′), the resistance slightly decreases. The response was reversible when cooling to room temperature (line A′A). The measured resistance versus temperature reported in Fig. 2 (line AA′A), may imply that the band gap of the CNTs is either absent or very small. Raman spectroscopic measurements (data not shown) suggest the presence of disorder in the structure of these nanotubes.[13] According to previous work,[14] this disorder could induce a residual density of the states within the band gap, giving a metallic character to the deposited nanotubes.

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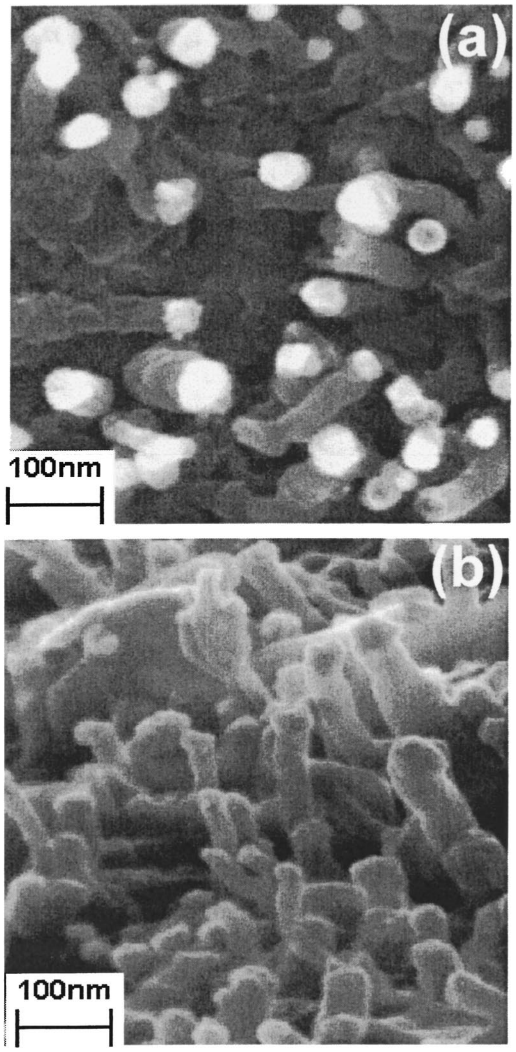

FIG. 1. High-resolution SEM photograph of CNTs grown on a 5 nm Ni catalyst layer thickness; (a) top view and (b) side view.

When heating the CNT's film during the second thermal treatment, sensor resistance followed line AA′B and cooling it to room temperature, the response followed curve BC′C. In fact, at temperatures higher than 250 °C, sensor resistance sharply increased from 150 Ω to approximately 600 Ω (line A′B). When cooling from 322 °C to room temperature, sensor resistance surprisingly increased, reaching approximately 1270 Ω at 25 °C (point C). When heating the film during the third thermal treatment, sensor resistance followed line CC′D, while it followed line DE when cooling to room temperature.

It turns out that if the heating and cooling thermal cycle is maintained within the temperature range of 25–250 °C, sensor response is always reversible (lines AA′ and CC′). At temperatures higher than 250 °C, microstructural irreversible rearrangements of the structure take place. It is presumed that a transition from a metallic to semiconductor response of the material takes place. This assumption is based on the experimental evidence that shows that the electrical resistance sharply increases when heating to temperatures higher than 250 °C (lines A′B and C′D) and that the resistance increases again when cooling from 322 to 25 °C (lines BC and DE).

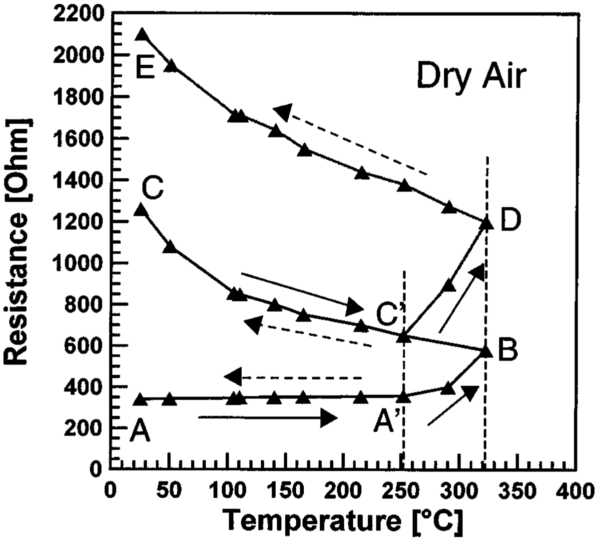

FIG. 2. Change of the CNTs' film resistance as a function of temperature in dry air. First thermal treatment (line AA′A); second thermal treatment (line AA′BC′C); and third thermal treatment (line CC′DE).

The possibility of fixing the value of the resistance in air by selecting the number of thermal treatments, without complicated doping procedures, makes carbon nanotube films unique compared to metal oxide sensors. Moreover, circumstances to maintain film resistance within the range of 0.1–2 kΩ, which is significantly lower than that reported for metal oxide sensors (500 kΩ–50 MΩ), makes CNTs film integration in electronic circuitry easier and cheaper, since lower dc voltages are required to drive the sensor response.

The electrical properties of CNTs to NO_2 gas were measured by an automated system. Dry air was mixed with diluted NO_2 mixtures (5 ppm in air) using a MKS147 multigas mass controller, in order to have gas concentrations at the outlet in the range of 10–100 ppb. Electrical measurements were carried out by selecting the operating temperature of the film in the temperature range of 25–250 °C using both the first and second thermal treatments. It turns out that at a 165 °C operating temperature, the change of sensor resistance in dry air in relation to the one measured at 100 ppb NO_2 gas reached its maximum. This temperature is probably an intrinsic property of the material, since it is not affected either by the preparation of the material or by the experimental conditions.

Figure 3 shows the dynamic gas response of CNT films at an operating temperature of 165 °C and NO_2 concentrations ranging from 10 to 100 ppb. Curve (a) represents the NO_2 response of the film after the first thermal treatment (AA′, Fig. 2). Curve (b) represents the response of the same film to NO_2 after the second thermal treatment (CC′, Fig. 2). The amazing result reported here is that the CNT film is sensitive to NO_2 at concentrations as low as 10 ppb. When the NO_2 concentration is increased and decreased stepwise in this range, the sensor response is reproducible and stable. It is interesting to note that recovery time τ is a few minutes, while sensors based on resistance changesof single walled nanotuberopes exhibit a recovery time of 8–12 h after exposure to higher NO_2 concentrations[5] (200 ppm of NO_2).

In Fig. 3 we can see that, if we define sensor sensitivity (S) as the ratio $S=[(R_A-R_G)/R_A]\times 100$, where R_A repre-

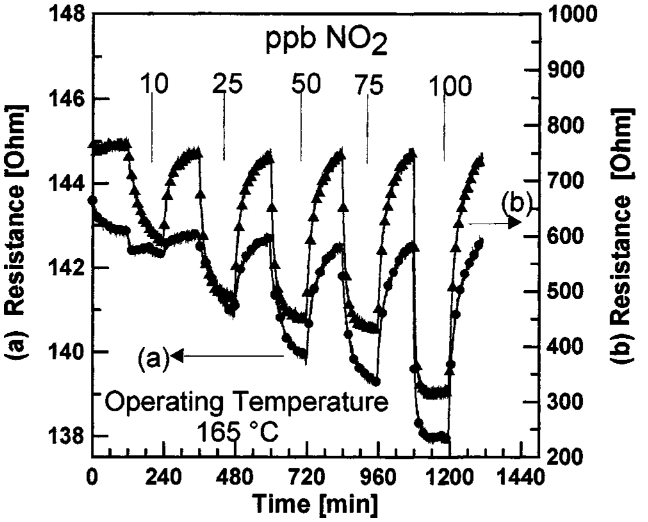

FIG. 3. Resistance changes at an operating temperature of 165 °C and NO_2 concentrations ranging from 10 to 100 ppb. (a) resistance change of the film after the first thermal treatment; (b) resistance change of the film after the second thermal treatment.

sents resistance in dry air and R_G resistance in gas, at 100 ppb NO_2, gas sensitivity increases from $S=3.3\%$ after the first thermal treatment to $S=56\%$ after the second one, respectively. It turns out that by selecting a proper thermal treatment, both the base-line resistance of the sensor film (i.e., the resistance in dry air), as well as sensor sensitivity to NO_2, may eventually be tailored and improved.

In order to explain the results, the chemical nature of the NO_2 molecule is considered. Recent experimental results[5,6] show that the electrical conductance of an individual semiconducting single walled tube strongly increases upon NO_2 gas exposure and that the NO_2 is identified as an electron acceptor. In light of the present work, it is reasonable to propose that this behavior in the nanotube film is also due to adsorbed NO_2 in the tube wall. According to recent theoretical calculations,[9] a possible interpretation of the electrical response of CNT films to NO_2 gas could be explained in terms of the physical absorption of this molecule. NO_2 has an unpaired electron and is known as a strong oxidizer. Upon NO_2 adsorption, a charge transfer is likely to occur from the CNTs to the NO_2 due to the electron–acceptor character of NO_2 molecules. The electrical response of the CNTs indicates that there is a charge transfer between the test gas and sensing element, and hence, that the physisorption of gases in the nanotubes is the dominant sensing mechanism.

The sensor response to CO (100 ppm in dry air) interfering gas was also evaluated at operating temperatures of 25–250 °C. No significant change in resistance was observed. Metal oxide semiconductor gas sensors reported to date are known to increase their resistance when interacting with oxidizing gases like NO_2, Cl_2, and O_3,[15] and decrease their resistance with reducing ones, like CO and H_2. The decrease of CNT sensor resistance with NO_2 is an interesting feature of this material. In fact, by integrating CNTs with *n*-type metal oxide sensors, results in inverse responses to oxidizing gases, induced by the presence of *n*- and *p*-type materials, and may represent a strategy to improve selectivity.

Finally, if one considers the long-term stability of the electrical response and that drift phenomena often reported in the case of many metal oxide sensors are due to the grain growth and chemical instability of the surface metal ions,[15] one may presume that CNT sensors are more stable since they are not affected by mass transfer phenomena or by the change of the chemical nature of the surface carbon.

In conclusion, CNT thin films prepared by plasma-enhanced chemical vapor deposition demonstrate their potential as a class of materials for NO_2 detection for environmental application, with detection limits as low as 10 ppb. Moreover, it has been proposed that the sensitivity of CNT thin films can be improved only by the proper selection of thermal treatment protocols.

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