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Carbon nanotubes as new materials for gas sensing applications

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Abstract

Carbon nanotubes (CNTs) deposited by plasma enhanced chemical vapor deposition on Si_3N_4/Si substrates provided with Pt electrodes have been investigated as resistive gas sensors towards NO_2. The electrical response has been measured exposing the films to sub-ppm NO_2 concentrations (10–100 ppb in dry air) at different operating temperatures ranging between 25 and 250 °C. The response to NO_2 has been found to be at maximum at around 165 °C. Upon exposure to NO_2 the electrical resistance of randomly oriented CNTs is found to decrease. The prepared films show reasonable dynamic of the electrical response and high reproducibility of the electrical properties. The resistance decrease of the CNTs when exposed to NO_2 gas and the sensor response to concentrations as low as 10 ppb NO_2, suggest the possibility to utilize CNTs as new sensors for air-quality monitoring.

Keywords: Carbon; Electrical conductivity; Films; Nanocomposites; Sensors

1. Introduction

Carbon nanotubes' (CNTs) special geometry and their amazing feature of being all surface reacting materials offer great potential applications as gas sensor devices with excellent sensitivity and fast response time. Reported studies on possible applications of carbon nanotubes as gas sensors have been focused either on isolated single wall carbon nanotubes (SWNTs) or on SWNT mats.[1–4] Experimental reports have shown that upon exposure to O_2, NO_2 or NH_3, the electrical conductance of the semiconducting SWNTs sensibly changes, while theoretical studies have predicted significant variation of the electronic properties of carbon nanotubes as effect of gas adsorption.[5,6] More recently, the application of MWNT–SiO_2 composited layer, deposited on a planar inductor–capacitor resonant circuit for the monitoring of NH_3, CO_2 and O_2 has been presented.[7] Those facts give new stimulus towards an effective application of carbon nanotubes as gas sensors considering that the sensor's scientific community is looking towards new materials to detect sub-ppm concentrations of various gases.

Regarding environmental applications, metal oxide chemoresistive sensors have demonstrated reliable performance[8] but still reduced detection limits. When oxidizing gases like O_3 and NO_2 have to measured in ambient air, concentrations as low as 80 and 100 ppb have to be detected with a high degree of accuracy and selectivity. Moreover the experimental evidence that most of the metal oxide sensors (MOS) are n-type semiconductors, which increases their resistance when in contact with oxidizing gases like O_3 and NO_2, strongly limits the possibility to improve sensor selectivity. Studies on the application of copper-phthalocyanine thin film sensors (CuPCs), which decrease their resistance in contact with NO_2 gas have been recently reported.[9] The possibility of arranging arrays of sensors based on metal oxide (MOS) organic CuPCs and eventually CNT sensors with an inverse response to oxidizing gases may represent a practical solution, which improves selectivity.

This paper outlines the results obtained for a series of CNT thin films sensors prepared by radiofrequency PECVD glow discharge. Specifically, we investigate the CNT electrical response to NO_2 gas in the concentration range 10–100 ppb. The aim of this work is to assess the possibility of whether carbon nanotubes films may be applied as innovative NO_2 sensor for environmental applications.

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2. Experimental

Nanotubes were grown using a radiofrequency plasma enhanced chemical vapor deposition (rf PECVD) system on a heated cathode capable of reaching a maximum temperature of 850 °C. Thin films (5 nm) of Ni metal layer were deposited by physical thermal evaporation technique onto planar Si/Si_3N_4 substrates provided with Pt sputtered interdigidital electrodes. After deposition the substrates were annealed in vacuum at 650 °C and held at this temperature for 45 min to enable the formation of Ni metal nanoparticles while maintaining the plasma off prior to initiating the deposition. The CNT depositions were carried out at 650 °C while flowing precursor CH_4 gas at a rate of 84 sccm and 1 torr pressure. The film deposition was performed with a rf bias voltage fixed at −150 V. The deposition time of 30 min gives a thickness of the nanoutube film of about 200 nm.

The scanning electron microscopy investigation was performed on a field emission scanning electron microscope LEO 1530 operated at 1 and 5 kV. Raman scattering spectra were recorded by a Jobin Yvon micro-Raman LabRam system in a backscattering geometry. A 632.8 nm He–Ne laser was used as the light source and the power of the laser was adjusted by optical filters. By using a 100× objective lens, the illuminated spot on the sample surface was focused to about 2 μm in diameter. The resolution of the Raman spectra was better than 1 cm^{-1} with the typical acquisition time of 30 s.

The electrical properties of CNTs to NO_2 gas were measured by an automated system. Dry air was mixed by an MKS147 multi gas mass controller with diluted NO_2 mixtures (5 ppm in air) in order to have gas concentrations at the outlet in the range 10–100 ppb. Electrical measurements were carried out selecting the operating temperature of the films in the temperature range 25–215 °C. The resistance of the films was measured by a volt–amperometric technique by a Keitley 2001 multimeter.

3. Results and discussion

3.1. Structural characterization

Scanning electron microscopy images of CNTs deposited by pure methane plasma on annealed Ni layers are reported in Fig. 1. Fig. 1a shows the SEM picture of the CNTs grown on 5 nm thick Ni layer. Fig. 1b shows the same CNTs deposited but at higher magnification. From Fig. 1a and b a Ni metal cap, predominantly at the top of the nanotubes, is visible. Cross sectional SEM image shows that the tubes are well packed and aligned. TEM observations highlighted

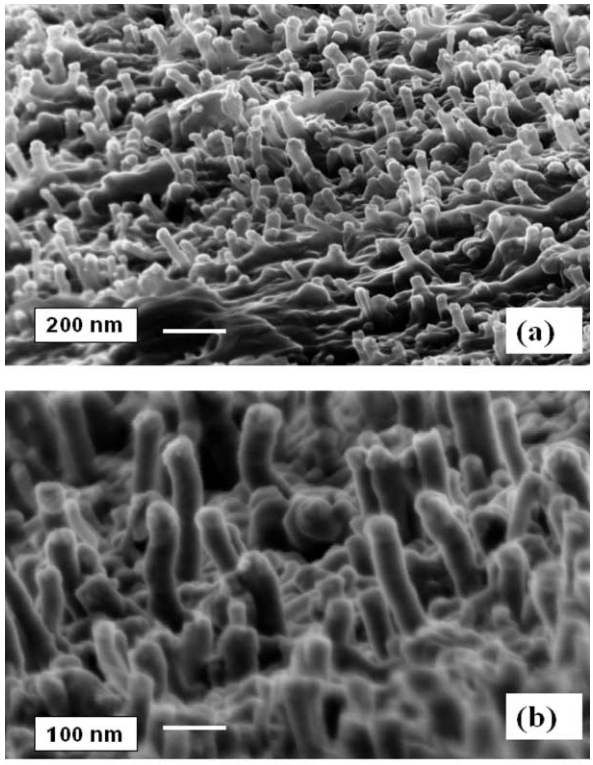

Fig. 1. (a) SEM photograph of CNTs grown on 5 nm thick Ni metal layer; (b) higher magnification of CNTs.

also that CNTs' dimensions were comprised between 20–30 nm diameter and 150–200 length. According to previous research,[10,11] the above results seems to confirm that carbon nanotubes final structure and diameter, depend on the diameter of the Ni nanoparticles, formed during the annealing of the metal layer at 650 °C, which acts as templates, during the subsequent rf-PECVD process, in the formation of the cylindrical body of the CNTs.

The Raman spectra of CNTs is plotted in Fig. 2. The two main features in the Raman spectra are the D and G peaks at about 1350 and 1600 cm^{-1}, respectively. The G band corresponds to the symmetric E_{2g} vibrational mode in graphite-like materials, while the D band is

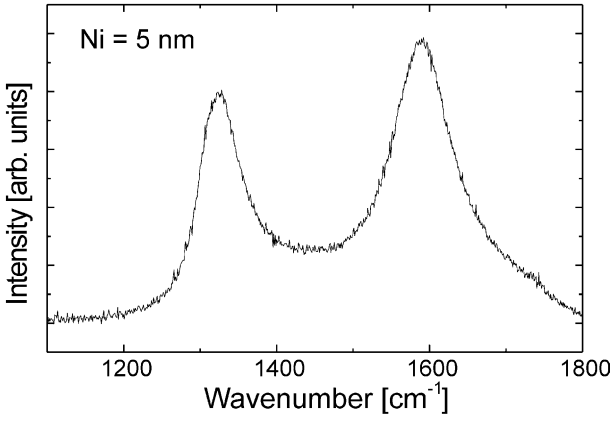

Fig. 2. Raman spectra of CNTs grown on 5 nm thick Ni metal layer.

activated in the first-order scattering process of sp^2 carbons, by the presence of substitutional hetero-atoms, vacancies, grain boundary or other defects and by finite size effects, all of which lower the crystalline symmetry of the quasi-infinite lattice.[10] From the results here reported, two different carbon structures can be identified: randomly oriented CNTs which form in pure methane plasma and CNTs with more uniform orientation and larger diameter. The broad shape of the peaks indicates also that CNTs' structure is highly disordered, characterized by a large amount of pure amorphous carbon films, exhibiting a graphitelike microstructure.

3.2. Gas sensing characterisation

Electrical characterization has been carried out by recording the electrical resistance in flowing dry air (1000 sccm/min) during a thermal treatment protocol which comprises heating from room temperature (each steps last 60 min) to 50, 75, 115, 165, 215 °C and cooling from 215 back to 25 °C.

Sensor conductivity easily fit to an activation law of the form $G_0 \approx \exp(-\Delta E/2kT)$ with $\Delta E = 100$ meV. This small activation energy may imply that the band gap is either absent or very small. As previously discussed, Raman spectroscopy indicates the presence of disorder in the structure of these nanotubes. This disorder, according to previous works[12] could induce residual density of the states within the band gap giving a predominant metallic character to the nanotubes.

Fig. 3 shows the electrical response of the CNTs to NO_2 gas in dry air. The test has been carried out by exposing the films to dynamic adsorption–desorption cycles (dry air–100 ppb NO_2–dry air) and changing the operating temperature from 25 to 215 °C.

The CNT's film is sensitive to NO_2 even at room temperature, as highlighted by the resistance decrease at 25 °C. The operating temperature of the oxide has been identified to be 165 °C as a trade off between high sensitivity and fast and reproducible base line recovery (i.e. the resistance in air). This temperature is confirmed to be an intrinsic property of the material, since it was not affected by the preparation conditions. From Fig. 3 it turns out that sensor resistance decreases when CNTs are exposed to NO_2 gas. NO_2 has an unpaired electron and is known as a strong oxidizer. Upon NO_2 adsorption, electron charge transfer is likely to occur from CNTs to NO_2 because of the electron-withdrawing power of the NO_2 molecules. The NO_2 molecules' adsorption deplete electrons from the CNTs, increase the concentration of conducting holes in the p-type CNTs, thus causing the resistance to decrease. These results are in accordance with recent research[11] which reports that the electrical resistance of an individual semiconducting tube decreases dramatically upon NO_2 gas exposure and that the NO_2 is identified as charge acceptor. In light of the present work, it is reasonable to propose that this p-type response of our films is due to a direct adsorption mechanism of NO2 molecules on CNT tube walls.

Fig. 4 show the dynamic response of the CNT sensors to NO_2 concentrations ranging from 10 to 100 ppb and dry air, at 165 °C operating temperature. The film shows a resistance decrease when exposed to NO_2 gas. The amazing result here reported is that the CNTs' film is sensitive to NO_2 at concentrations as low as 10 ppb.

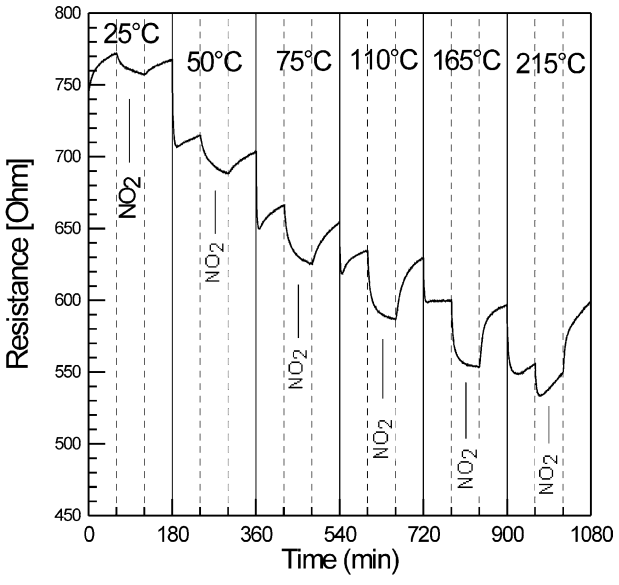

Fig. 3. Dynamic gas responses at different operating temperatures in dry air and 100 ppb NO_2 gas of the CNTs.

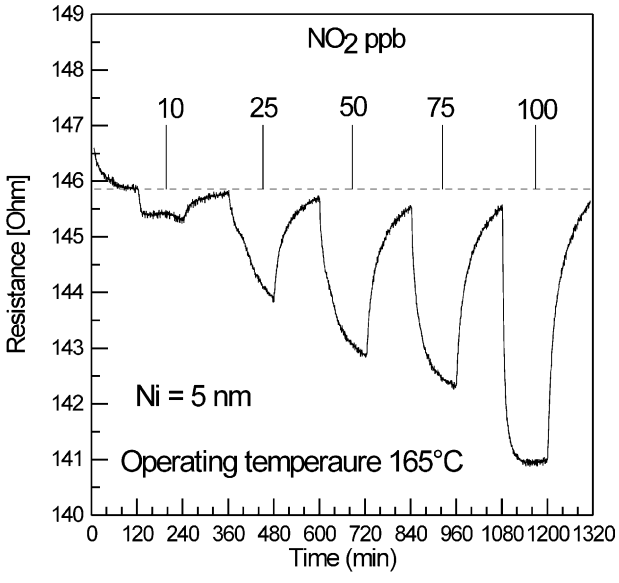

Fig. 4. Dynamic sensor response at 165 °C operating temperature and NO_2 concentrations ranging from 10 to 100 ppb in dry air carrier gas.

When the NO_2 concentration is increased and decreased stepwise in this range, the base line resistance (i.e. the resistance in air) is repeatable and stable. It is interesting to note that the recovery time $\tau_{90\%}$ is 5 min while sensors based on resistance changes of single walled nanotube ropes exhibit a recovery time of 8–12 h after exposure to higher NO_2 concentrations[12] (200 ppm of NO_2). Moreover if we define sensor sensitivity (S) as the relative response given by the ratio $S=[(R_A-R_G)/R_A]\times 100$, where R_A represents the resistance in dry air and R_G the resistance in gas, at 100 ppb NO_2, gas sensitivity yields $S=3.4\%$. This value of sensitivity although not so high, can be improved by a proper selection of the Ni metal layer thickness. It turns out that by decreasing the Ni layer thickness, smaller Ni nanoparticles are formed during annealing, enabling the formation of CNTs with smaller diameters, which eventually determines improved gas sensitivities.[13]

4. Conclusions

Multi-walled carbon nanotube thin films have been prepared by plasma enhanced chemical vapor deposition on 5 nm thick Ni metal layers, previously evaporated on Si/Si_3N_4 substrates for gas sensing applications. Raman spectroscopy has revealed that CNTs' structure is highly disordered, characterized by a large amount of pure amorphous carbon films, exhibiting a graphite-like microstructure (sp^2), while SEM observations confirmed the formation of well developed CNT cylindrical structures with 20–30 nm diameter and 150–200 nm length. Upon exposure to NO_2, at 165 °C operating temperature, the CNTs' response is at its sensitivity maximum. The electrical resistance of nanotubes to oxidizing gases is found to decrease suggesting the occurrence of a p-type response. Sensors response to NO_2 gas at concentrations as low as 10 ppb suggest the possibility to utilize CNTs as new sensors for air-quality monitoring.

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