Effects of oxygen annealing on gas sensing properties of carbon nanotube thin films

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Abstract

Carbon nanotubes (CNTs) thin films deposited by plasma enhanced chemical vapor deposition have been investigated as resistive gas sensors towards NO oxidizing gas. Effects of air oxidative treatment dramatically influence the nanotubes’ electrical resistance as determined by volt-amperometric measurements. In particular the electrical measurements show that electrical behavior of the CNT films can be converted from semiconducting to metallic through thermal treatments in oxygen. The electrical response was then measured exposing the films to sub-ppm NO concentrations (100 ppb in air) at 165 °C. Upon exposure to NO, the electrical resistance of CNTs was found to decrease. The obtained results demonstrate that nanotubes could find use as a sensitive chemical gas sensor for (a) the fast response accompanied by a high sensitivity to sub-ppm NO exposure, and (b) the precise recover of the base resistance value in absence of NO at a fixed operating temperature, likewise indicating that intrinsic properties measured on as prepared nanotubes may be severely changed by extrinsic oxidative treatment effects.

Keywords: Carbon nanotubes; Sensors; Oxygen annealing; Raman spectroscopy; XPS

1. Introduction

Carbon nanotubes (CNTs) have attracted their attention considerably in this last decade since their discovery in 1991 [1] due to their unique structure and properties. Carbon nanotubes have high mechanical and chemical stability, and thus can be used as modules in nanotechnology. There are two general categories of nanotubes. One is single-walled nanotubes (SWNT) that consist of a honeycomb network of carbon atoms, and can be imagined as a cylinder rolled from a graphitic sheet. The other is multi-walled nanotubes (MWNTs) that is a coaxial assembly of graphitic cylinders separated by approximately the plane space of graphite [2]. This makes nanotubes challenging materials to relate their atomic structure to their physical properties.

These unique properties make them the most promising candidate for the building blocks of molecular-scale machines and nanoelectronic devices [2–7]. The electronic structure of CNT can be either metallic or semiconducting, depending on their diameter and chirality [2]. These diverse electronic properties open a possibility of developing nanoelectronic devices as nanowires [8] or as metal/semiconductor heterojunctions [9] by combining metallic and semiconducting nanotubes. A possible approach is the modification of different parts of a single nanotube to have different electronic properties using controlled mechanical or chemical processes (e.g. nanotube bending or gas molecule adsorption) [10].

The study of gas adsorption on carbon nanotubes is currently at the center of an intense experimental and theoretical activity [11–13]. From a practical perspective the source of this interest lies in the potentially very large adsorptive capacity of the nanotubes, which makes them good candidates for use in gas storage applications [11]. Considering that the adsorption of gas on carbon nanotubes modifies sensibly their electronic properties, Kong et al. [14] proposed the use of CNTs as gas sensors. They showed that the electrical conductivity of an individual single-walled CNT changes dramatically upon exposure to gaseous molecules such as NO₂ and NH₃. Parallel theoretical work evidences how the electronic properties of CNTs change in the presence of...
adsorbed reducing and oxidizing gases [15]. Recently, a practical gas sensor for ammonia and water vapor, based on the measurement of the variation of electrical properties of ropes of MWCNT [16], has been proposed. Moreover, for the first time, we have proposed a gas sensor based on the measurement of the conductance variation of CNTs thin film directly grown by plasma enhanced chemical vapor deposition (PECVD) [17] onto a micro machined sensor support [18].

The aim of this paper is to present the results obtained with CNTs thin films prepared by radio frequency PECVD glow discharge before and after a thermal treatment in oxygen, investigating their electrical response to NO₂ molecules. We show here that the electrical properties of thin films of carbon nanotubes can be tuned by thermal treatments and a transition between semiconducting to metallic behavior can be induced through high temperature exposure to oxygen. Finally, the strong relation between the gas sensitivity upon exposure to NO₂ and the preparation conditions (i.e. oxidative treatment) will be also evidenced.

2. Experimental

Nanotubes were grown by using a radio frequency Plasma Enhanced Chemical Vapor Deposition (rf PECVD) system with a heated cathode capable of reaching a maximum temperature of 850 °C. A thin film (5nm) of Ni catalyst was deposited onto planar Si/Si₃N₄ substrates provided with Pt sputtered inter-digital electrodes. The substrates were heated to 650 °C and held at this temperature for 45 min to sinter the catalyst layer maintaining the plasma off prior to initiating deposition. The CNTs depositions were carried out with deposition pressure and temperature fixed at 1 Torr and 650 °C, respectively. The total precursor (CH₄) gas flow rate was kept constant at 84 sccm. 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 nanotubes film of approximately 200 nm. The CNTs film was oxidized in air by a thermal treatment consisting of heating in air the ‘as deposited’ carbon film from 25 to 650 °C.

The morphology of the as deposited and air oxidized CNTs films was observed by Scanning Electron Microscopy (SEM). A field emission scanning electron microscope LEO 1530 operated at 5 kV has been used. The composition of the films was studied in a ‘home-brewed’ UHV high resolution X-ray Photoelectron Spectroscopy (XPS) apparatus described elsewhere [19].

The samples were studied with Raman spectroscopy by using 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 100X objective lens, the illuminated spot on the sample surface was focused to approximately 2 μm in diameter. The resolution of the Raman spectra was better than 1cm⁻¹ with the typical acquisition time of 30 s.

The electrical resistance of the films was measured as a function of temperature in flowing dry air (500 sccm) by a volt-amperometric technique with a Keithley 2001 multimeter. NO₂ mixtures were prepared by continuous mixing of the original gas (5 ppm in air) with dry air in a MKS147 multi gas mass controller in order to have gas concentrations at the outlet of 100 ppb NO₂. Electrical measurements were carried out selecting the temperature of the films in the range 25–250 °C.

3. Results

High-resolution field emission SEM images of CNTs deposited by pure methane plasma on annealed Ni layers are reported in Fig. 1. Fig. 1a shows a side view of the as deposited film with nanotubes with almost uniform diameters (35–40 nm). From Fig. 1a it is evident that a metallic cap is predominantly positioned at the top of the nanotubes. SEM image of the air oxidized CNTs
(Fig. 2) shows a similar structure as in Fig. 1a, but with larger outer diameters of the nanotubes and with aggregated carbonaceous particles. In both cases (Fig. 1a and Fig. 1b) the nanotubes have grown in a random and curly fashion.

The XPS spectrum of carbon 1s component detected on the as deposited (continuous line) and oxidized (dashed line) samples is reported in Fig. 2. For both samples it seems that the CNTs are composed of graphite layers of good crystallinity and do not contain any other bonding states such as C–O or carboxylic groups, which introduce a peak at 286–289 eV \( \text{eV} \). The only remarkable difference of the shape between the two spectra is that the oxidized film presents a greater asymmetry on the high binding energies side of the carbon peak. This effect can be ascribed to an increased metallic behavior of the CNTs film \( \text{metallic behavior} \). Moreover, the analysis of all XPS spectra (not reported here) indicates that for the sample annealed at 650 \( ^\circ \text{C} \) in air, a reduction of approximately 10% of the carbon content, the increase of oxygen linked to nickel and no appreciable variation of oxygen physi-sorbed on the carbon nanotubes, which, as already pointed out, does not give any contribution on the C 1s spectra.

Fig. 3 displays the Raman spectra in the 1270–1670 cm\(^{-1}\) region for CNTs thin films with 632 nm laser wavelength excitation. The two main features in the Raman spectra are the D and G peaks at approximately 1330 cm\(^{-1}\) and 1600 cm\(^{-1}\), respectively. The G band corresponds to the symmetric \( E_{2g} \) vibrational mode in graphite-like materials, while the appearance of the strong D line can be interpreted as being due to \( \text{strong D line} \): (a) the turbostratic structure of carbon sheets in tubes, namely the finite size nanometer order of the crystalline domains; and (b) the high density of the twisty tubes. Thus, the enhancement of the D lines at 1330 cm\(^{-1}\) accounts for the large amount of crystalline domains on the nanometer scale. Moreover, we found that the tangential mode Raman scattering depends sensitively on the processing conditions. In particular Fig. 3 shows that for air oxidized CNTs the Raman component at 1590 cm\(^{-1}\) is down shifted \( \approx 10 \text{ cm}^{-1} \) with respect to that observed for the as deposited sample.

The resistance of the films in dry air was measured by a volt-amperometric technique recording the electrical resistance as a function of the operating temperature, during two different thermal treatments. The first thermal treatment consists in heating of the deposited carbon film from 25 to 250 \( ^\circ \text{C} \) and cooling back to 25 \( ^\circ \text{C} \). The second thermal treatment consists in heating from 25 \( ^\circ \text{C} \) up to 290 \( ^\circ \text{C} \) followed by cooling to room temperature. Fig. 4 shows the variation of electrical resistance with temperature in flowing dry air (500 sccm) for the different thermal treatments and for the two different CNTs film: as deposited and after air oxidation. In particular, Fig. 4 (upper panel) shows that for the as deposited CNTs during the first thermal treatment (line AA’), the resistance decreases from 345 to 182 \( \Omega \). The response is reversible when cooling to room temperature (line A’A). The measured resistance vs. temperature reported in the upper panel of Fig. 4 (line AA’A), suggests that the semiconductor response of the material prevails. During the second thermal treatment the sensor resistance follows the line BB’. Then, when cooling from 290 \( ^\circ \text{C} \) to room temperature, the sensor resistance surprisingly increases, reaching approximately 480 \( \Omega \) at 25 \( ^\circ \text{C} \) (point C). This effect can be ascribed to the purification of the film from graphitic nanoparticles burned during the heating. In particular, the effect of
Fig. 4. The variation of resistance as a function of temperature in dry air of the as deposited film during the first (line AA’) and the second (line BB’C) thermal treatment; the change of the resistance as a function of temperature in dry air of the air oxidized CNTs film at 650 °C.

thermaltreatment on the electrical properties of nanotubes suggests that some kind of defects is initially present in nanotubes and is then removed by the thermal treatment.

From Fig. 4 (lower panel) it is clear that during the first thermal treatment, contrary to as deposited CNTs, air oxidized nanotubes show a reversible resistance increase with increasing temperature (line AA’A). When heating and cooling during the second thermal treatment, the air oxidized CNTs shows that the electrical response also in this case is reversible with an overall slight increase of the resistance with respect to the first thermal cycle. The measured resistance vs. temperature reported in the lower panel of Fig. 4 may imply a metallic-like behavior of the oxidized CNTs film.

The analysis of the electrical properties of CNTs interacting with NO₂ gas (100 ppb) was carried out by selecting the operating temperature of the film in the temperature range of 25–250 °C. It turns out that the relative change of the sensor resistance in dry air with respect to the one measured with 100 ppb NO₂ reaches its maximum at 165 °C together with a very good reproducible base resistance (i.e. the resistance in dry air) [17].

Fig. 5 shows the electrical response of the CNTs exposed to NO₂ gas in dry air. The test has been carried out by exposing the films to dynamic adsorption-desorption cycles (100 ppb NO₂ in dry air-dry air) at the operating temperature of 165 °C. The curves represent, respectively: (a) the response to 100 ppb of NO₂ of the film submitted to the first thermal cycle (AA’A Fig. 4a); (b) the response of the same film to NO₂ after the second thermal treatment (BB’C Fig. 4a) and (c) represents the response of the air oxidized film to NO₂.

Both as deposited and air oxidized films show a decrease in electrical resistance when exposed to NO₂ gas. From the results of Fig. 5 we have calculated the sensitivity of the three different films to 100 ppb of NO₂ as 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 the presence of 100 ppb of NO₂. The results are summarized in Table 1 where noteworthy are: the strong increase of the sensitivity for the sample submitted to the second thermal cycle (Fig. 5b) with respect to that

![Fig. 4. The variation of resistance as a function of temperature in dry air of the as deposited film during the first (line AA’) and the second (line BB’C) thermal treatment; the change of the resistance as a function of temperature in dry air of the air oxidized CNTs film at 650 °C.](image1)

![Fig. 5. Resistance changes at an operating temperature of 165 °C in the presence of 100 ppb NO₂ of: (a) as deposited CNTs film after the first thermal treatment; (b) as deposited CNTs film after the second thermal treatment and (c) CNTs film annealed in air at 650 °C.](image2)

**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>After first thermal treatment</th>
<th>After second thermal treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited CNTs</td>
<td>13.8</td>
<td>17</td>
</tr>
<tr>
<td>Air oxidized CNTs</td>
<td>3.1</td>
<td>3.7</td>
</tr>
</tbody>
</table>
after the first thermal treatment (Fig. 5a), and the strong decrease of the sensitivity for the sample annealed up to 650 °C (Fig. 5c).

4. Discussion

The two main experimental results obtained from the studies on the electrical behavior of our CNTs thin films can be summarized in the following two items:

a. the transition from a semiconducting to a metallic behavior of the CNTs film occurs after thermal annealing in oxygen at high temperature (650 °C);

b. the response to NO₂ of the as deposited CNTs is higher than that obtained for the oxidized ones.

Moreover, by selecting the adequate thermal treatment at low temperature (approx. 300 °C) both the base resistances of the as deposited film as well as the sensitivity to NO₂ increase.

The obtained results can be explained by considering the gasification of the nanotubes and nanoparticles due to the annealing in oxygen. Previous experiments performed by thermo-balance and transmission electron microscopy in situ [23] showed that at temperatures of approximately 550 °C, the gasification rate of the residual carbon nanoparticles remained after the nanotube’s growth was higher than that of nanotubes with a consequent swelling of thinner tubes. At higher temperatures, starting from 850 °C, nanotubes were easily gasified at the cracks, defects and strains in the tubes and at these temperatures there is no obvious difference in the gasification rate between nanotubes and nanoparticles. A similar effect may happen in our sample after the thermal annealing in air at 650 °C. In fact, together with a reduction of the carbon content as evidenced by XPS results, from the SEM images we observe in the film the presence of nanotubes with larger diameter and the formation of agglomerates, which give rise to the film nanoporous-like structure.

Moreover, in Raman measurement, this nanotube-adsorbates interaction is expected to affect mostly the Raman scattering from metallic nanotubes, because only metallic tubes have isoenergetic electronic states at the vibrational energy of 1590 cm⁻¹ [24]. The large downshift of the G band in Raman scattering from the carbon nanotubes film upon oxygen annealing up to 650 °C confirms the observation of the metallic behavior of this film. The excitation of the 1590 cm⁻¹ phonon by isoenergetic fast electrons was evidenced in a recent high field electrical transport measurement on metallic SWNTs [25]. The metallic behavior of MWNTs after annealing in air at high temperatures, also observed by ESR measurements [26], is also justified from the C 1s shape of our XPS measurements. Furthermore, as evidenced by XPS results where we do not observe any bond between oxygen and carbon nanotubes in the annealed film, one can exclude that the metallic behavior of the annealed films could be attributed to the presence of substitutional oxygen in the carbon matrix.

To discuss the sensitivity results we have to remind recent experimental results [24,25,27] that the electrical conductance of an individual semiconducting single walled tube strongly increases upon NO₂ gas exposure and that the NO₂ is identified as an electron acceptor. In light of the present work, it is reasonable to propose that this behavior in our nanotube films is also due to adsorbed NO₂ on the tube wall. According to recent theoretical calculations [28], a possible interpretation of the electrical response of the as deposited CNTs’ films to NO₂ gas could be explained in terms of physical absorption of this molecule. NO₂ has an unpaired electron and is known as a strong oxidizer. Upon NO₂ adsorption, a charge transfer is likely to occur from CNTs to NO₂ due to the electron-acceptor character of NO₂ molecules inducing the formation of electronic levels in the semiconducting nanotube gap, very near to the Fermi level, which increase its conductivity. Finally, to explain the variation in the sensitivity of the different films reported in Fig. 5 and in Table 1, we have to take into account that the adsorption and the uptake of the oxidizing gas have the maximum of efficiency in the case of defective nanotubes [29]. Our results can induce us to give the following picture of the film morphology and of its transformation after the various annealing procedures. In the as deposited film a high percentage of semiconducting nanotubes, i.e. the smaller ones, is present. They are covered and embedded in carbon impurities. The annealing in air up to 250 °C does not induce any structural modification in these films. The resistance variation upon NO₂ is evident (curve (a) of Fig. 5). Around the annealing temperature of 300 °C the film starts to be purified from nanoparticles, but the nanotubes do not change their morphology and electrical properties and the film maintains its semiconducting behavior but its resistance at room temperature increases. A large number of NO₂ molecules can interact with the defective sites free from impurities located on the wall of the nanotubes producing the strong electrical modification observed (curve (b) of Fig. 5). On the contrary, the explanation for the change of the resistance observed for the oxidized CNTs film when exposed to NO₂ is that, for metallic or very narrow gap nanotubes, the electronic levels introduced by the NO₂ presence do not result in a substantial change in the density of states at the Fermi level and, thus, in the charge carriers in the nanotube [16].

5. Conclusions

In this paper the electrical response to NO₂ molecule of carbon nanotubes thin films prepared by plasma enhanced chemical vapor deposition has been investi-
gated. The change of the resistance as a function of temperature suggests that CNTs thin films after oxygen treatment are metallic, while in the case of as deposited tubes the occurrence of a band gap is observed. CNTs sensors sensitivity to NO is found largely influenced by oxidative treatment. Structural modifications induced by the annealing in air are proposed to be responsible for strong changes on the sensitivity of the film when used as resistive gas sensors. Possible strategies focused for improving sensitivity were proposed by the proper selection of thermal treatment protocols.

References