

# Sensitivity to NO<sub>2</sub> and cross-sensitivity analysis to NH<sub>3</sub>, ethanol and humidity of carbon nanotubes thin film prepared by PECVD

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## Abstract

The NH<sub>3</sub>, H<sub>2</sub>O, and C<sub>2</sub>H<sub>5</sub>OH cross-sensitivities to the NO<sub>2</sub> electrical response of carbon nanotubes (CNTs) thin films for gas sensing applications is reported. CNTs have been deposited by plasma enhanced chemical vapor deposition (PECVD) on Si<sub>3</sub>N<sub>4</sub>/Si substrates provided with Pt electrodes. Microstructural features as determined by SEM, TEM (electronic scanning and transmission microscopy) and Raman spectroscopy have highlighted the growth of well developed tubular carbon structures of 30–40 nm diameter and 100–200 nm length. CNTs have shown a p-type response with decrease in resistance upon exposure to NO<sub>2</sub> gas (10–100 ppb) and the highest sensitivity at 165 °C working temperature. The NO<sub>2</sub> gas sensitivity has resulted to be improved by annealing the as-grown films at temperatures higher than 330 °C. No response has been found by exposing the films to CO and CH<sub>4</sub> in the working temperature range 25–250 °C. An amount of 500 ppm of NH<sub>3</sub> and ethanol, as well as 80% relative humidity (RH), have resulted to increase the electrical resistance of the films. Cross-sensitivity test have highlighted strong interference of ethanol and ammonia gases to the NO<sub>2</sub> response, while negligible cross-sensitivity effects have been found with humidity at 80 RH. The reproducibility of the electrical response to NO<sub>2</sub> is also reported. © 2003 Elsevier B.V. All rights reserved.

**Keywords:** Carbon nanotubes; Cross-sensitivity; Ammonia; Ethanol; Humidity

## 1. Introduction

The high surface area, size, hollow geometry and chemical inertness of carbon nanotubes (CNTs) makes them attractive for demanding applications in the field of gas sensing. To date studies on possible applications of CNTs have been focused either on individual single-walled carbon nanotubes (SWNTs) as sensitive materials towards O<sub>2</sub>, NO<sub>2</sub> and NH<sub>3</sub> [1–3] or on multi-walled carbon nanotubes (MWNT) mats as NH<sub>3</sub>, CO, CO<sub>2</sub> humidity and O<sub>2</sub> gas sensors [4–6]. More recently, we have reported on the preparation of thin films CNTs by radio frequency plasma enhanced chemical vapor deposition (rf-PECVD) on Si/Si<sub>3</sub>N<sub>4</sub> substrates, provided with interdigital Pt electrodes, for NO<sub>2</sub> monitoring at low concentrations (10–100 ppb in air) [7].

Although considerable theoretical efforts have been devoted to the study of the possible interaction of a variety of gas molecules including NO<sub>2</sub>, O<sub>2</sub>, NH<sub>3</sub>, N<sub>2</sub>, H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, and Ar with CNTs materials [8–11], few experimental data are available elucidating the effects of gas adsorption

on the electrical properties of CNTs [1–7,12–14] for gas sensing applications. By first principles calculations on individual SWCNTs, it has been estimated that NO<sub>2</sub> and O<sub>2</sub> molecules would yield considerable larger adsorption energies than H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, and Ar [8–11]. NO<sub>2</sub> and O<sub>2</sub>, chemisorbed on the CNTs surface, behave as electrons acceptors, while physisorbed molecules like H<sub>2</sub>O, NH<sub>3</sub>, CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, and Ar act as electron donor, respectively. These theoretical predictions have been partially confirmed in practice as highlighted by previous experimental research. It was indeed demonstrated how NO<sub>2</sub> and O<sub>2</sub>, oxidizing gases decrease the electrical resistance of p-type CNTs [1,2,7], while the opposite effects is demonstrated by ammonia and humidity [1,4,14]. Nevertheless, to date, both theoretical and experimental approaches have not yet fully investigated the effects of simultaneous interactions between competitive oxidizing and reducing gaseous species on the electrical response of CNTs gas sensors.

In this paper we report preliminary investigations on: (i) the effects of a thermal treatment process which enables to improve the sensor sensitivity to sub-ppm concentrations of NO<sub>2</sub> gas, (ii) the sensitivity response to oxidizing/reducing gases and vapors like NH<sub>3</sub>, humidity, C<sub>6</sub>H<sub>6</sub> and ethanol, and (iii) the cross-sensitivity analysis by comparing how

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the NO<sub>2</sub> electrical response is affected by the presence of interfering gases like NH<sub>3</sub>, humidity and ethanol vapor. The aim of this work is to assess the possibility, if CNTs films may be applied as innovative NO<sub>2</sub> sensor for environmental applications.

## 2. Experimental

Nanotubes were grown using a radio frequency plasma enhanced chemical vapor deposition (rf PECVD) system on a heated cathode capable of reaching a maximum temperature of 850 °C. A thin film (5 nm) of a Ni catalyst was deposited onto a planar Si/Si<sub>3</sub>N<sub>4</sub> substrate provided with Pt sputtered interdigital electrodes. The substrate was heated to 650 °C and held at this temperature for 45 min to sinter the catalyst layer maintaining the plasma off prior to initiating the deposition. CNTs depositions were carried out with deposition pressure and temperature fixed at 1 Torr and 650 °C, respectively. The total precursor (CH<sub>4</sub>) gas flow rate was kept constant at 84 sccm. The film deposition was performed with a rf bias voltage fixed at –150 V. A deposition time of 30 min gives nanotubes film thickness of about 200 nm.

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. The resolution of the Raman spectra was better than 1 cm<sup>–1</sup> with the typical acquisition time of 30 s. The scanning electron microscopy (SEM) investigation was performed on a field emission SEM LEO 1530 operated at 1 and 5 kV.

The electrical properties of CNTs to NO<sub>2</sub> gas were measured by an automated system. Dry air was mixed by a MKS147 multi-gas mass controller with diluted NO<sub>2</sub> 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 at the operating temperature of the films in the temperature range of 25–215 °C. The resistance of the films was measured by a volt-ampometric technique by Keitley 2001 multimeter.

## 3. Results and discussion

### 3.1. Structural characterization

High-resolution field emission SEM images of CNTs deposited by pure methane plasma on annealed Ni layers are reported in Fig. 1. Fig. 1(a) shows the separation zone between the Pt electrode and the sensitive CNTs film. Fig. 1(b) shows a high magnification of the as-grown nanotubes region. From Fig. 1(b) it turns out that a metal cap can be observed predominantly at the top of the nanotubes which were seen to grow in a random and curly fashion.

The presence of the metal cap at the top of the nanotube seems to indicate a growth mechanism of CNTs similar to

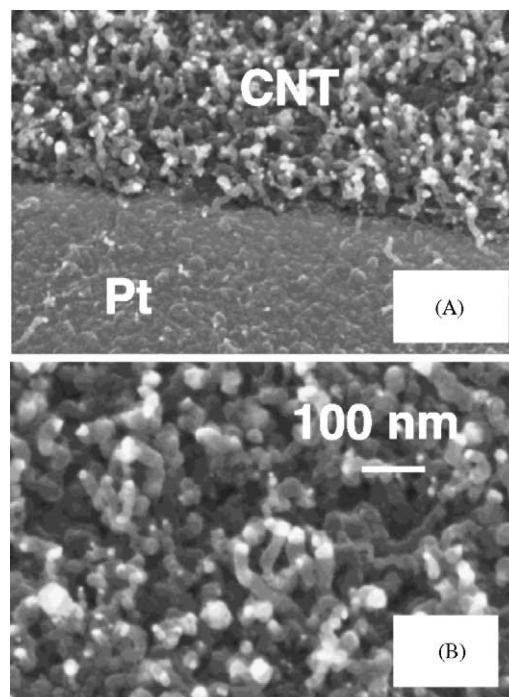


Fig. 1. SEM photomicrograph of as-grown CNTs: (A) top view with highlighted the Pt electrode region and the as-grown structure of CNTs on Si/Si<sub>3</sub>N<sub>4</sub> substrate; (B) magnification of the as-grown structure of CNTs on Si/Si<sub>3</sub>N<sub>4</sub>.

that reported in Refs. [15,16] which comprises the following steps: (a) deposition by physical methods on Si/Si<sub>3</sub>N<sub>4</sub> substrates, of a metal catalyst layer (1–10 nm thick of Ni, Fe or Co), (b) fragmentation of catalyst into nanoparticles by sintering or annealing, (c) decomposition of CH<sub>4</sub> on the top of the surface of the Ni particle, and (d) growth of nanotubes below Ni catalyst by carbon diffusion through the Ni particle. Moreover, as carbon atoms are further supplied, a carbon–metal eutectic alloy is formed. As soon as carbon concentration reaches its saturation limit, carbon atoms initiate to diffuse on the Ni metal surface and to precipitate on the outer edge of the Ni metal particle. The Ni metal particle, which acts as a template, is eventually lifted up from the substrate by the growing carbon nanotube cylindrical body.

The reason why CNTs are not growing on Pt, as shown in Fig. 1(a), is due to the lack of fragmentation of the Ni film on platinum electrode, reasonably due to diffusion of Ni atoms into platinum during the annealing process at 650 °C, leading eventually to the formation of a binary Ni–Pt alloy.

The tubular structure of the nanotubes was verified using TEM microscopy as shown in Fig. 2. The nanotubes generally consist of 20–30 nm graphitic shells, 150–200 nm long with a defective “bamboo-like” structure. The Ni catalyst particle is always found at the top of the nanotubes. According to previous research [15,16], the above results seem to confirm that CNTs final structure and diameter, depends on the diameter of the Ni nanoparticles, formed during the annealing of the metal layer at 650 °C.

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