Carbon Nanotubes as new materials for gas sensing applications

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The high surface area, size, hollow geometry and chemical inertness remarkable properties 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 on multi walled carbon nanotubes (MWNT) mats as NH_3 , CO, CO₂ humidity and O₂ gas sensors. More recently we have reported on the preparation of thin films CNTs by radio frequency plasma enhanced chemical vapor deposition (rf-PECVD) on Si/Si₃N₄ substrates, provided with interdigital Pt electrodes, for NO₂ monitoring at low concentrations (10-100 ppb in air) [1-2].

In this paper we report preliminary investigations on: the sensitivity response to oxidizing/reducing gases and vapors like NH₃, Humidity, C_6H_6 , Ethanol, as well as the cross sensitivity analysis by comparing how the NO₂ electrical response is affected by the presence of interfering gases like NH₃, Humidity and ethanol vapor. Aim of this work is to assess the possibility if carbon nanotubes films may be applied as innovative NO₂ sensor for environmental applications.

High-resolution field emission SEM image of CNTs deposited by rf-PECVQ technique is reported in Figure 1. The figure depicts well alligned CNTs, with diameters of 30 nm and typical Ni metal caps positioned at the top of the nanotubes.

The electrical response of the films was measured by a volt-amperometric technique recording the electrical resistance as function of the gas concentration. The operating temperature was set at 165° C, as a trade off between high sensitivity and fast and reproducible base line recovery.

Figure 2 shows the CNTs film gas response at 165 °C to NO₂ (100ppb), NH₃ (500ppm), C₆H₆ (100ppm), H₂O (80 % Relative Humidity) and Ethanol (500 ppm). The sensitivities to CO (100 ppm) and CH₄ (1000ppm), negligible as compared to that of other gases, are not reported in the figure. The resistance of the CNTs film decreases in the presence of NO₂, while it increases with NH₃, C₆H₆, 80% RH and ethanol. This behavior is in agreement with density functional calculations studies which have predicted for the NO₂ molecule electron charge transfer from the CNTs to the NO₂ molecule, whereas for the NH₃ molecule electrons to the CNTs.

Cross sensitivity or selectivity tests have been utilized to ascertain the CNTs ability to discriminate a target gas (i.e. NO_2) in the presence of interfering ones. Figure 3 shows the NH_3 (500 ppm) cross sensitivity to the measure of NO_2 (100 ppb) at 165 °C operating temperature and dry air carrier gas. The cross sensitivity test here proposed, comprises a first exposure (a-region) to 100 ppb NO_2 in dry air, followed by a second one (b-

region) where the CNTs film is exposed to fixed concentrations of interfering gases (NH₃ or Ethanol or Humidity) and 100 ppb NO₂, and a third one (c-region) carried out under the same conditions as (a) region. Cross response analysis highlighted interference effects to the NO₂ response in the order Ethanol > NH₃> humidity.

In conclusions CNTs thin films prepared by PECVD have demonstrated their potentiality as a new class of materials for NO_2 detection, for environmental applications, with detection limits as low as 10 ppb.



Fig. 1 High resolution SEM photograph of CNTs grown on a 5 nm Ni catalyst layer thickness



Fig. 2 The time-dependence change of the resistance of annealed CNTs films to 100 ppb NO₂, 500 ppm NH₃, 100 ppm C_6H_6 , 80% relative humidity, and 500 ppm ethanol



Fig.3 The time-dependence change of the resistance of annealed CNT films to (a-region) 100 ppb NO₂, (b-region) 500 ppm NH₃ and 100 ppb NO₂, (c-region)100 ppb NO₂

- L. Valentini, C. Cantalini, L. Lozzi, I. Armentano, J. M. Kenny, S. Santucci "New Sensors for sub-ppm NO₂ Gas Detection Based on Carbon Nanotube Thin Films", **Appl. Physics Lett.**, in publication
- [2] C. Cantalini, L. Valentini, L. Lozzi, I. Armentano, J.M. Kenny, S. Santucci, "NO₂ gas sensitivity of Carbon Nanotubes Obtained by Plasma Enhanced Chemical Vapor Deposition", Sens. & Act. B, in Publication