

Research Article

Role of the Material Electrodes on Resistive Behaviour of Carbon Nanotube-Based Gas Sensors for H₂S Detection

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Miniaturized gas-sensing devices that use single-walled carbon nanotubes as active material have been fabricated using two different electrode materials, namely, Au/Cr and NbN. The resistive sensors have been assembled aligning by dielectrophoresis the nanotube bundles between 40 μm spaced Au/Cr or NbN multifinger electrodes. The sensing devices have been tested for detection of the H₂S gas, in the concentration range 10–100 ppm, using N₂ as carrier gas. No resistance changes were detected using sensor fabricated with NbN electrodes, whereas the response of the sensor fabricated with Au/Cr electrodes was characterized by an increase of the resistance upon gas exposure. The main performances of this sensor are a detection limit for H₂S of 10 ppm and a recovery time of few minutes. The present study suggests that the mechanism involved in H₂S gas detection is not a direct charge transfer between molecules and nanotubes. The hypothesis is that detection occurs through passivation of the Au surfaces by H₂S molecules and modification of the contact resistance at the Au/nanotube interface.

1. Introduction

Among the many new technology opportunities and scientific challenges provided by carbon nanotubes (CNT), the sensing represents one of the most important topic. In particular, the design and fabrication of gas sensors assembled with CNT is a burgeoning research field still under development. The gas-sensing devices based on carbon nanomaterials can operate by a variety of different mechanism, such as resistivity change, capacitive effects, field-effect, and gas ionization [1, 2]. The resistive sensors, based on the property of some materials to modify their conductivity when in contact with chemical species, represent nowadays the most widespread class of gas sensors [3].

The intrinsic properties of CNTs meet indeed totally the requirements for a chemical sensor in terms of sensitivity, reproducibility, and durability [4, 5], whereas chemical/physical modifications of the nanotube walls can enhance the molecular specificity, making it possible to achieve a good selectivity [6].

Moreover the use of the carbon nanotubes as active sensing material for gas detection enables to minimize size/weight of the device, with reduction of power consumption and of manufacturing costs.

In our labs researches related to gas detection are carried out using resistive sensors assembled with single wall carbon nanotubes (SWCNTs) [7–9]. The experiments performed up to now demonstrated that such sensors are able to detect at room temperature sub-ppm levels of gas molecules (NO, NO₂, and NH₃) in some hundreds of μs . Moreover, after only few seconds, the devices are ready for a new operation. To reach such good performances, the main challenges to be managed are the relative orientation of the nanotubes and the application of a back-gate voltage [7–9].

The task of optimizing the organization of the SWCNT between the conductive stripes has been faced and successfully achieved by means of an dielectrophoresis process (DEP) that induces alignment of the SWCNT bundles between the electrodes [10]. A series of experiments confirmed that this kind of nanotube organization is indeed

strictly needed in order to increase the sensitivity of the device. The second task regards a proper tuning of the voltages applied to the back-gate contact during the various phases of the nanotube/gas interaction processes. The voltage tuning was found to strongly improve the response times and to allow sensor self-calibration.

In resistive devices the p-type semiconducting behaviour of SWCNT is exploited to discriminate species with different electronic properties; an electron-donor gas affects the conductivity in opposite way with respect to an electron-acceptor gas. In this contest the material of the electrode was assumed not to influence the sensor response.

However, it was noted [11] that the response of the SWCNT-based sensor was influenced by the nature of the electrode metallic material, and it was suggested that the interface between the nanotubes and the metal could play an important role in the response of the resistive sensors. This finding could open the way to a selective sensing, obtained by the use of different electrode materials.

In this context we felt it worthwhile to fabricate nanotube-based devices with electrodes made by different materials and to test their detecting performances for the H₂S gas. In the present study devices with electrodes made by Au/Cr and NbN were used.

The choice of NbN, a rather unconventional material for a gas sensor, was made because we asked for a second material with a work function (WF) value quite similar to that of Au (WF = 5,1 eV), but unable to chemically interact with S-containing species. Based on these requirements, the preference went to NbN (WF = 4.95 eV) [12], that is, chemically stable, also against oxidation, [13] and mechanically resistant.

H₂S is a flammable, dangerous, and reactive gas originated from soils and from human activities, such as coal combustions and petroleum refining. The levels of personal exposure that workers may receive range between 100 and 250 ppm [14].

Accurate and rapid detection of hydrogen sulphide is needed for safety reasons and environmental pollution control [15]. The sensing devices presently in use are rather bulky and expensive and moreover tend easily to saturate. There is therefore a pressing need of technological improvements for portable detectors with fast response for the identification of such a gas.

2. Experimental

The sensor consists in a field emission transistor (FET)-like 3-pin multifinger element having an infinite electrical resistance, that starts to drop when the nanotubes are deposited between the interdigitated electrode stripes. The resistance is measured between drain-source pins, and the gate is used to improve the desorption rate.

Two kinds of materials, namely, Au/Cr and NbN, were employed to fabricate the microelectrodes. Au/Cr (Cr is the adhesive layer) or NbN films were deposited on the SiO₂-insulating layers grown on a p-doped Si substrate. The Au and Cr deposits (thickness: 80 nm and 20 nm, resp.) were

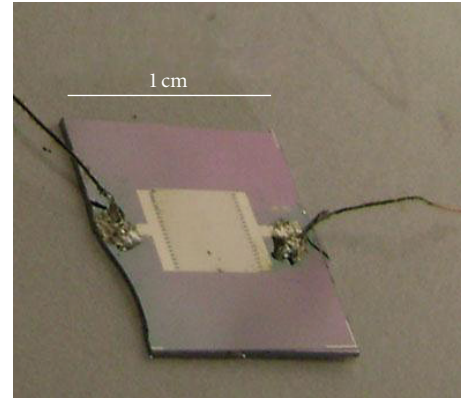


FIGURE 1: Optical image of the tested sensor.

produced by thermal evaporation of solid targets, the NbN deposits by DC-reactive sputtering, following an already established procedure [16].

The interdigitated microelectrodes, 40 μm spaced, were patterned by a lift-off technique. The dimensions of the sensor are about 1 × 1 cm (Figure 1).

The sensing element is realized using controlled amounts of commercial SWCNT (Nanocyl: purity > 90% wt, diameter: 0.8–1.6 nm, length 5–30 μm), purified following previously settled procedures [17] and dispersed in CHCl₃. The dispersions are sonicated in order to assure a good dispersion of the nanotubes and deposited by casting on the electrode platform within the interdigitated Au/Cr or NbN electrodes.

The alignment of the nanotubes between the electrodes is carried out by means of a dielectrophoretic method. An AC field having a frequency of 1 MHz and 12 V_{pp} is applied up to the complete evaporation of the solvent (CHCl₃). Details have been reported in [9].

The experiments have been performed using a H₂S/N₂ gas mixture purchased by Rivoira S.p.A. in a tank with a certificated concentration of 100 ppm of H₂S in N₂. Further dilutions have been obtained by means of a flow meter system. The final H₂S concentrations used for the experiments were 10, 20, 40, 60, 80, and 100 ppm. The flowing of the gaseous mixtures occurred at 200 sccm for 300 sec under standard conditions (25°C, 1 atm). The desorption processes were carried out applying a back bias of 6 V for 20 sec, coupled with a thermal shock at the temperature of 90°C for 15 sec.

3. Results and Discussion

As shown in Figures 2(a) and 2(b), the DEP process provides a useful way to align SWCNTs between electrodes establishing a good electrical connection to the external measurement circuit.

The alignment of the SWCNTs amplifies the conductance changes of the material when exposed to the gas [7, 9]. We have firstly tested a multifinger device fabricated with Au/Cr stripes.

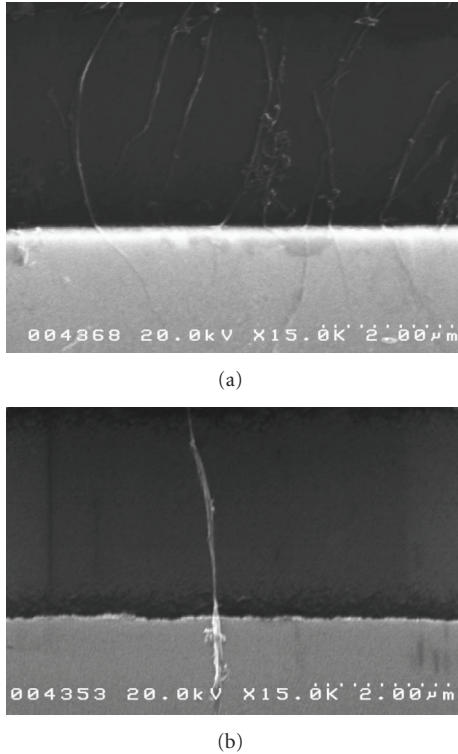


FIGURE 2: (a) and (b) FE-SEM images of SWCNT bundles aligned between the electrodes of the multifinger device.

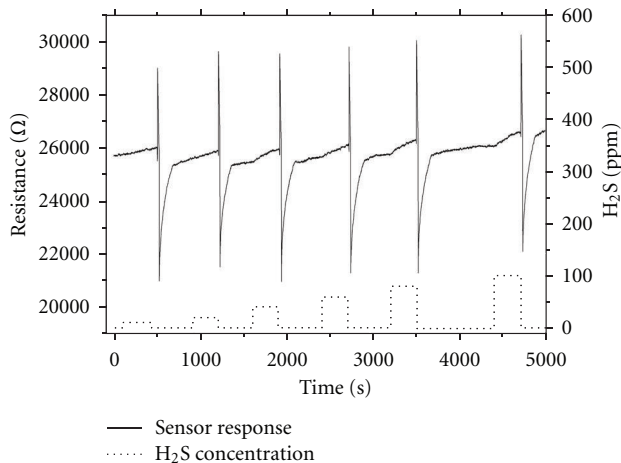


FIGURE 3: Resistance curves as a function of time for H₂S concentrations of 10, 20, 40, 60, 80, and 100 ppm (in N₂), under standard conditions. The narrow peaks are due to the effect of the applied gate voltage coupled with a thermal shock (90°C), required for the complete desorption of the gas.

Figure 3 reports the resistance values as a function of time and shows the behaviour of the sensor for H₂S concentrations of 10, 20, 40, 60, 80, and 100 ppm (in N₂), measured under standard conditions. The narrow peaks are due to the effect of the applied gate voltage coupled with a thermal shock (90°C), required for the complete desorption

of the gas. Using this approach the recovery time of the sensor was at the longest 5 min for the higher H₂S concentrations.

In order to better visualize the sensor response, we report in Figure 4 for each concentration the relative curve of resistance variation ($\Delta R = R_f - R_0$), where R_0 is the resistance of the sensor exposed to pure N₂, and R_f is the maximum value of the resistance. The resistance of the device increases upon exposure to the H₂S, and the curve is Langmuir type. As seen from the graphs of Figure 4, very short response times are obtained, the longest being about 5 min for the H₂S concentration of 100 ppm.

The $\Delta R/R_0$ data, reported in Figure 5 as a function of the different H₂S concentrations, demonstrate a very high precision of the sensor response (see error bars) with a linear trend for concentrations of H₂S ranging from 10 to about 60 ppm.

For each concentration 3 measurements have been carried out. The electrical resistance's data and the error bars are obtained by averaging over the 3 measurements. The sensitivity of the sensor is reported in terms of relative resistance change, $\Delta R/R_0$.

A different situation occurs using the same sensing material and the same procedures for the assembling of multifinger devices fabricated with NbN stripes. In this case, independently from the H₂S concentration, no signals related to gas adsorption could be detected (Figure 6). The resistance (R_{NbN}) of about 13.6 kΩ shown in Figure 6 is referred to the entire sensor device, that is, the multifingers NbN electrodes interconnected by means of SWCNTs. This R_{NbN} value obtained enables us to exclude the presence of Nb₂O₅ on the metal contacts because, in the case of Nb oxide formation, a higher value of resistance would be detected. The absence of signals in the presence of H₂S deserves some comments.

In general, the resistive response of SWCNT to gaseous species has been interpreted in terms of charge transfer between the p-type semiconducting SWCNT and electron-donors or electron acceptors species [18–21]. In their study, however, Suehiro et al. [11] noted that different electrode materials could modify the response of resistive SWCNT-based sensor and ascribed such behaviour to the occurrence of effects different from the conventional direct gas/nanotube interaction. In the present case too, the absence of resistance variation when using the NbN-based electrodes suggests that no H₂S uptake by the nanotubes occurs under our experimental conditions. The fact that the exposure to H₂S does not result in a resistance variation when using NbN electrodes means that the detection of H₂S is driven by a mechanism intrinsically different from a electron transfer between nanotubes and adsorbed molecules.

On the basis of the results obtained using different materials for electrode fabrication, it can be argued that the H₂S is not directly detected by the Au/Cr-based electrodes through a mechanism of charge transfer between nanotube and gas molecules, as in the case of other species, such as NOx or NH₃, but rather through the modification of the Au-SWCNT contact resistance.

A modulation of the Schottky barrier is thought to take place between the gold electrode and SWCNTs when exposed

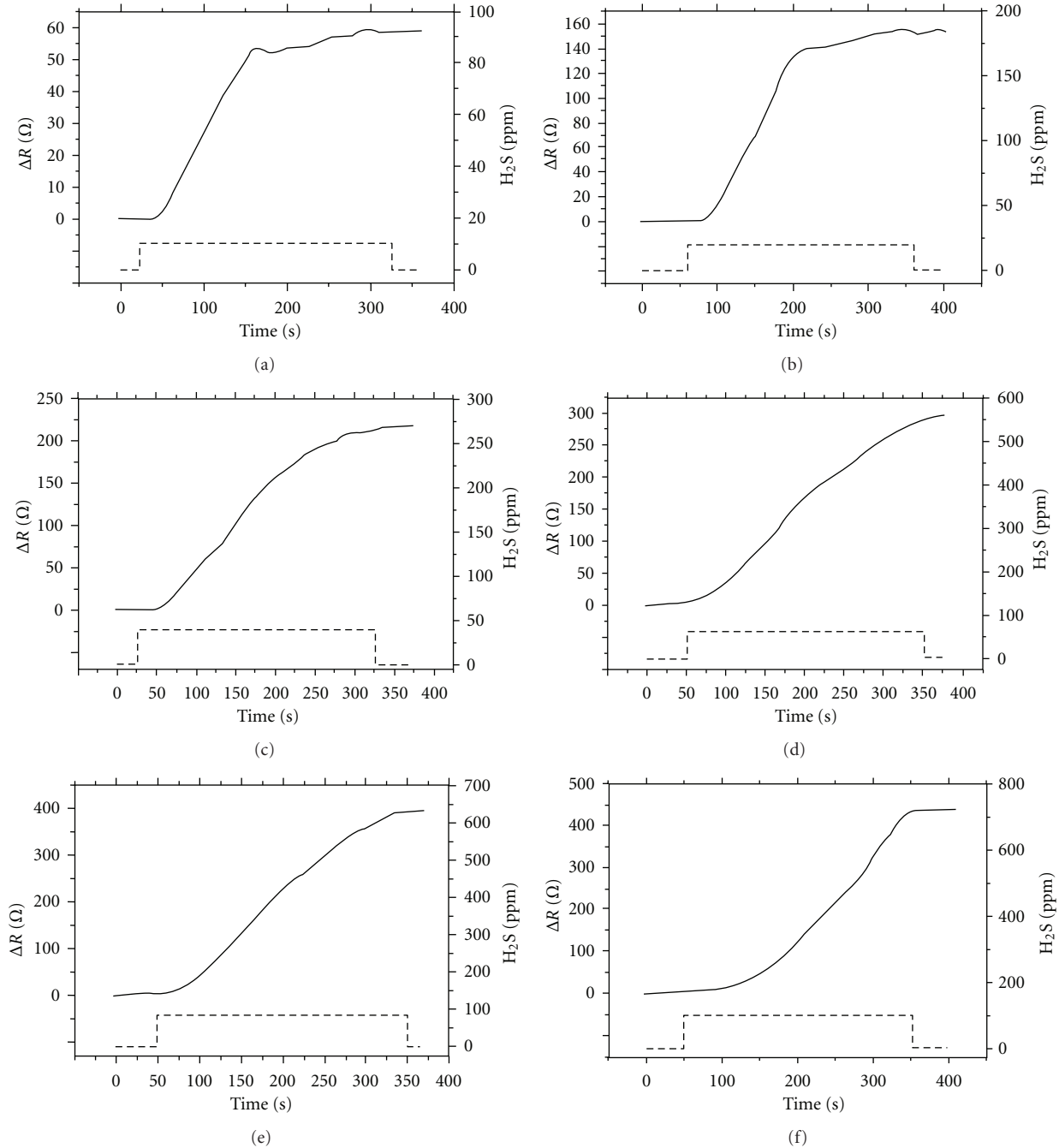


FIGURE 4: Curve of the resistance variation ($\Delta R = R_f - R_0$) versus time where R_0 is the resistance of the sensor exposed to pure N_2 , and R_f is the maximum value of resistance. The H_2S concentrations (in N_2) are: (a) 10, (b) 20, (c) 40, (d) 60, (e) 80, and (f) 100 ppm, respectively.

to H_2S . The adsorbed gas molecules modify the Au/SWCNT Schottky contact areas and induce instantaneous modulations of the metal contact work function, which changes the device's resistance.

In other words, selective chemisorption of the molecules on Au and passivation of the Au/SWCNT interface are responsible for the measured increase of the contact resistance between Au and nanotubes.

Considering the strong bonding forces acting between Au and H_2S [22], this interpretation is also able to explain the need of a simultaneous thermal and electrostatic shock (voltage gate) to obtain complete desorption of the gas and recovery of the sensor.

It is to be noted that some papers [22–27] reported about gas sensors assembled with nanotubes decorated by metal nanoparticles. In these systems the metallic species act as

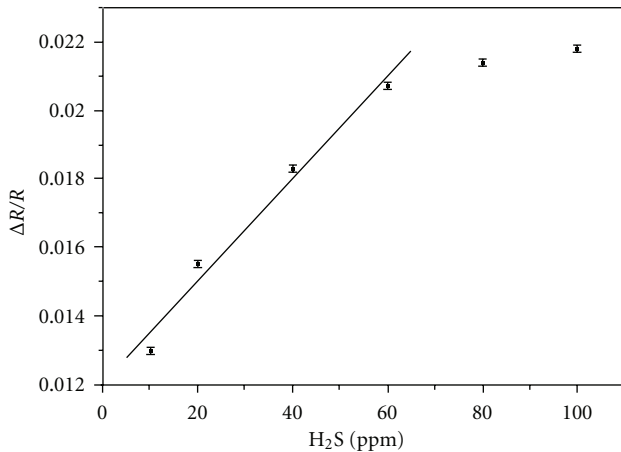


FIGURE 5: Relative resistance change ($\Delta R/R_0$) for the different H₂S concentrations.

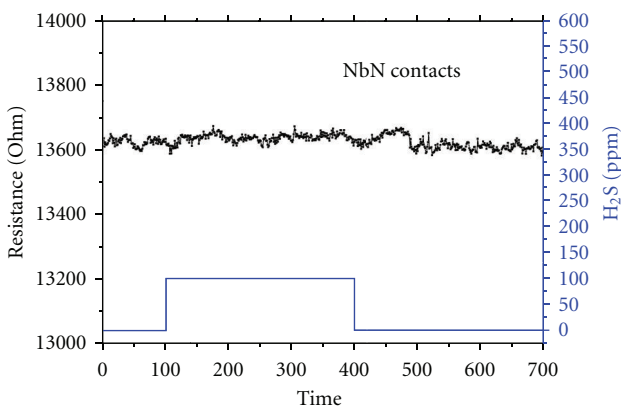


FIGURE 6: Sensing device fabricated using NbN electrodes: resistance changes upon exposure to 100 ppm of H₂S.

the sensing materials, and a charge transfer occurs between metal clusters and nanotubes. As regards H₂S, due to the large amount of metal nanoparticles, very low concentration of the gas could be detected [24–26]. On the other hand, such sensors saturate for gas concentration around 10 ppm, a value clearly below the threshold limit that poses serious health risks in workplaces or through accidental exposures.

4. Conclusions

We have fabricated two types of gas detectors using the same SWCNT as active material and either Au/Cr or NbN for the electrodes of the multifinger device. The task of ordering the nanotube bundles perpendicularly to the electrodes of the sensors has been pursued by using DEP. The other focal point, that is, the reduction of the recovery time and the optimization of the response time, has been overcome by the combined use of a back gate potential and of a thermal shock.

In the investigated concentrations range (10–100 ppm), the response of the sensor fabricated using Au/Cr electrodes

is characterized by high level performance in terms of reproducibility and response times.

The accurate detection, at room temperature, of H₂S concentrations near to the threshold of health risk makes our devices really useful for in-door and out-door safety applications, including use in coal and natural gas processing, petroleum industries, security monitoring, and biogas production.

The fact that the NbN-based electrodes does not enable to register the presence of the gas suggests the lack of a specific interaction between nanotubes and H₂S, that is, a poor electron-donor specie. The experiments performed using electrodes fabricated with different materials allowed us to highlight that a mechanism different from a charge transfer between gas molecules and nanotube is responsible for H₂S detection. The conductivity changes detected by our circuit are instead likely caused by the Schottky barrier modulation at the metal/SWCNT interface induced by chemisorption of H₂S on the Au electrode [28].

It is to be underlined that the operating mechanism of this kind of sensors could represent an attractive approach towards a selectivity based not only on the conventional nanotube functionalization but also on the combination of different electrode materials for manufacturing a multi gas sensor platform. The perturbations of the conductivity induced in the nanotube-based circuit by the chemical interaction of a gaseous species with a selected electrode material give indeed easy to read out direct information. These sensors can be essential components to interface with conventional electronic architectures in a lab-on-chip hybrid system.

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