Gas fingerprinting using Carbon Nanotubes transistors arrays

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ABSTRACT

This paper deals with the realization of Carbon Nanotube Field Effect transistors (CNTFETs) for gas sensing applications. Such devices exploit the extremely sensitive change of the Schottky barrier heights between carbon nanotubes (CNTs) and drain/source metal electrodes: the gas adsorption creates an interfacial dipole that modifies the metal work function and so the bending and the height of the Schottky barrier at the contacts. Our aim is to realize the fingerprinting of a specific gas using a CNTFET based sensors array. This fingerprinting concept is based on the fact that the change of the metal electrode work function strictly depends on the metal/gas interaction and consequently the CNTFET transfer characteristics will change specifically as a function of this interaction. . To demonstrate this new concept, we have fabricated different CNTFETs using different metal contacts: Au, Pd, Pt. Using these transistors, we have shown that a specific gas, in our case DiMethyl-Methyl-Phosphonate (DMMP, a sarin simulant), interacts specifically with each metal: 2 ppm of DMMP reduced the transistor ON current by 20% for Pt based CNTFETs and by one order of magnitude for Pd based CNTFETs. We think that this new approach can be applied for highly selective sensing of various gases using ultra-compact, room temperature and very low power devices.

KEYWORDS : Gas detection, Carbon Nanotubes, Metal/CNT junction, Work Function

1. INTRODUCTION

The first paper showing the great potentiality of Carbon Nanotubes Field Effect transistors (CNTFETs) for gas sensing applications was published in 2000 [1]. Since then, many teams have focused their interest on this new kind of sensor. These devices exploit the extremely sensitive change of the Schottky junctions built up between carbon nanotubes (CNT) and drain/source metal electrodes : the gas adsorption induces an interfacial dipole that changes the metal work function and so the bending and the height of the Schottky barrier at the contacts [2, 3, 4]. It has been demonstrated that this kind of sensor can reach a sensitivity of 1ppb for DiMethyl-Methyl-Phosphonate (DMMP, a sarin simulant) [5]. This sensitivity is highly sufficient for an effective Sarin gas detection: 17ppb in 30 seconds is the Joint Service Operational Requirements (JSOR) for detectors [6] and 30ppb up to 30 minutes is the Immediate Danger to Health or Life (IDHL) [6]. The real issue is to improve the selectivity, thus reducing the risk of false alarm and various methods have been proposed so far. Among these methods, the deposition of polymers on the CNTFETs (functionnalization) is extensively studied and very promising results have been already obtained [see *e.g.*, ref. 7]. However, the use of polymers could present several drawbacks such as increasing the sensor response time and decreasing its lifetime as methods currently used to desorb gas molecules (thermal anneal and UV exposition) should degrade these polymers.Another issue is the lack of knowledge on the real physical effect of polymers: up to now the choice of polymer continues to be empirical and this also holds for biosensing applications [8]. Our approach for solving this selectivity problem, is to realize a sensor comprising an array of CNT-based transistors. Each transistor will be fabricated using different metals as source/drain electrodes. Actually using different metals implies that the work function of the contacts will be different. As a consequence the Fermi level alignment between metal and CNT, will change and therefore the characteristics of the Schottky barrier at the junction. We want to demonstrate that, after being exposed to a gas, each transistor will be influenced in a very peculiar way : this influence is strictly related to the interaction between a specific gas and a specific metal. Using this method, each gas will be "fingerprinted" and so unambiguously identified as schematically shown in Fig.1a and 1b.

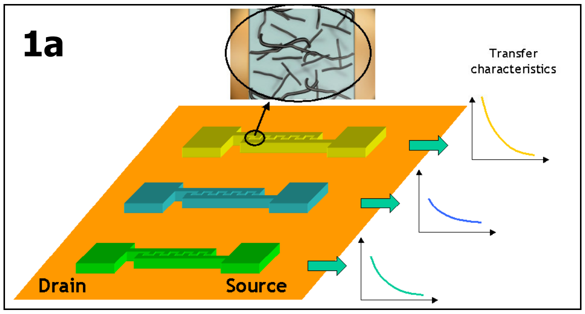

Fig. 1a: Three CNTFETs with three different metal interdigited electrodes (each color corresponds to a different metal) : in the inset, the carbon nanotubes chains connecting the two electrodes. On the right, the transfer characteristic (Source/Drain current as a function of the Gate Voltage) of each transistor.

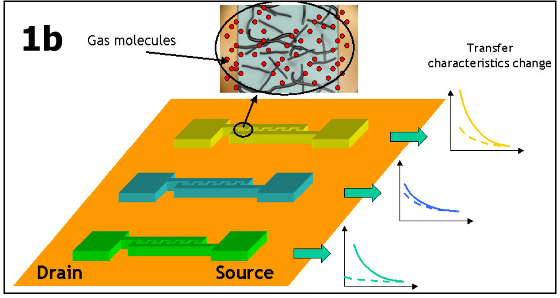

Fig. 1b: Change of the transfer characteristic of the three transistors as a consequence of the exposition to a particular gas (in the inset, the gas molecules that interact with the transistor) : the three transfer characteristics change in a different way as a consequence of the metal.

Another advantage of using this technique of gas fingerprinting, is that the desorption of the gas molecules can be easily achieved using either UV light [9] exposition or thermal heating [10] without risking to degrade the device performances. Finally, the sensing mechanism (change of metal work function) is well understood [11, 12 13] and this will ease the optimization of the device parameters.

2.THEORY

As quoted in the introduction, the first paper dealing with the use of CNTFETs for gas sensing applications was published in 2000 by the University of Stanford [1]. In this paper, the same CNT-based transistor was exposed to NO_2, NH_3 and ambient air. The transfer characteristic (I_{DS}-V_G) showed a shift of the "turn-on" voltage after being exposed to different gases. Initially this effect was attributed to doping of the carbon nanotube by charge transfer. In 2003, Avouris (IBM) observed that oxygen adsorption leads also to a shift of the turn-on voltage but demonstrated that this effect has to be attributed to a modification of the metal-nanotube junction rather than to a doping effect.

Actually, they demonstrated that the main effect of oxygen adsorption, and so of the other gases as well, is not to dope the bulk of the tube, but to modify the barrier and the metal-semiconductor contacts [12]. Therefore the change of the junction characteristics after exposition to a gas is related to the modulation of the contact resistance and not of the channel conductance [14]. Recently, these results have been confirmed by other teams [15] as well as by the University of Stanford in 2004 [8]. From a theoretical point of view, the effect of the gas on the metal/CNT junction can be explained using the model developed for organic compounds and metal junctions [13, 16]. Actually in this case the interface is characterized by the presence of interface dipoles which generate an electrostatic potential close to the electrodes. The presence of the interface dipoles created at the contact modifies the energy of the electronic levels in organic compounds and the work function of the metal surface. When the interface dipole points its negative pole towards the organic film and its positive pole towards the metal, the result is an increase of both the metal work function and the highest occupied molecular orbital (HOMO) energy of the organic film, by addition of an electrostatic energy. Therefore, the hole injection barrier is reduced. On the other hand, when the dipole direction is reversed, the metal work function is reduced and so is the electron injection barrier. In the case of a metal/CNT junction, similarly, the gas molecules introduce electric dipoles at the interfaces and modify the intensity of the dipole settled at the Metal/CNT junction. This change influences directly the metal work function and the Fermi level alignments. This consideration totally agrees with the simulations and experimental results in the case of oxygen exposition obtained by IBM [17] : changing the oxygen concentration changes the dipole strength and the metal work function is increased, thus reducing the hole injection barrier (the hole current raises). The same interpretation can be made when the metal/CNT Schottky barrier is modulated using polar chemical compounds [18]. From a sensor point of view, we can observe that a gas (or different gases) can change the transfer characteristics of the transistor [1]. We propose to use this mechanism to obtain the fingerprinting of a particular gas using different metals for the contacts : analyzing the change of transfer characteristics of each transistor after gas exposition could identify a gas unambiguously. Starting from these considerations, our approach is to realize an array composed by several CNT-based transistors. Each transistor will be fabricated using different metals as source/drain electrodes. In our case we have decided to use three different metals for the electrodes: Au, Pd, Pt. The work functions for these metals are respectively 5.1eV for the first two and 5.65eV for the last [19, 20, 21]. We decided to use these metals in order to verify if the gas interaction is related only to the work function difference between the different metals or if it depends on the specific origin of the gas and of the electrode. Actually if the interaction is only related to the work function difference so the change of the CNTFET based sensors response (transfer characteristic) will be nearly the same for Au and Pd when they are exposed to the same gas. Inversely, if the gas interacts differently with the two metals (chemical interaction?) and so with the junctions, the transfer characteristic change will be not the same.

3. SAMPLE PREPARATION

Our samples have been realized using n-doped Silicon substrates covered with 50nm of thermally grown SiO_2. The electrodes have been fabricated by UV photolithography : the metal deposition has been realized using evaporation technique and lift-off. The metal thickness were 35nm. For the Pt electrodes a 5nm thick layer has been added in order to improve the layer adhesion. The geometrical design of the metal electrodes has been optimised using interdigited metal fingers: in this way the possibility to obtain a connecting chain of carbon nanotubes (from random networks) is maximised. The distance between the different fingers varies between 2 and 15µm. The following step is to deposit the carbon nanotubes random network between the metal electrodes. This deposition starts by the fabrication of a suspension of carbon nanotubes in a liquid medium, in our case Dimethylformamide (DMF). One of the most important issues is that the carbon nanotubes are naturally grouped in bundles by Van der Wall forces. First, CNT bundles and residual impurities (*e.g.*, catalyst particles) have to be eliminated from the "mother" CNT suspension. This can be accomplished by sonication to "break" the bundles (1 hour) , followed by centrifugation (two phases of 10 minutes) and careful recuperation of the supernatant part of the suspension. Subsequently, the solution is deposed on the finger electrodes using a graduated micropipette and the samples are heated at 70°C in order to evaporate more quickly the solvent. Another important issue is that CNTs always come in mixtures of semiconductor and metallic specimens. No method, up to now, exists for separating semiconductor from metallic specimens. However, as far as random networks are concerned, it has been shown that, through a percolation effect, an overall semiconductor behaviour could be obtained, for carefully controlled areal densities [22]. Only two conditions must be fulfilled: the distance between the two electrodes must be larger than the carbon nanotubes length (otherwise metallic nanotubes could cause a short-circuit) [23,24] and the areal density of the deposited SWNTs has to be controlled carefully, because above the threshold for percolation, for high areal densities (5 to $10/\mu m^2$), the conduction is practically ohmic [22, 23, 24] with no gating effect. Recent studies show that the conductivity in the networks is controlled by the Schottky barriers at the contacts between metallic and semiconducting tubes [25].

The carbon nanotubes used for this work are super purified nanotubes. Their imurity contecnt is less than 5%, their diameter and length are respectively, before sonification, 1.0nm±0.2nm and 100-1000nm.

Then we have estimated the quality (impurity content, morphology) and the density of the carbon nanotube films, after evaporation of the solvents, using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Typical transistors realized using suspensions of CNTs in DMF are shown in Fig.2.

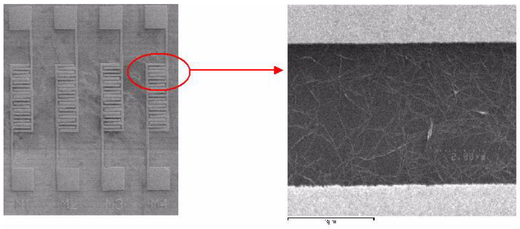

Fig.2: Left-hand side : SEM image of interdigited CNT transistors, Right-hand side : SEM image of carbon nanotubes random network between two electrodes

As we can see in Fig.2 on the right-hand side, the CNT distribution is quite uniform and CNT connect clearly the two electrodes.

4. RESULTS

We started the test phase performing measurement of the electrical behavior of the different junctions. In our case the most important characteristics is the evolution of the current between drain and source as a function of the gate voltage. Around 50% of the transistors are effective. Most of them are characterized by a distance between the interdigited electrodes of more than 10µm. Actually, the other ones, with a distance between the electrodes less than 10µm, show a metallic behaviour: the distance is too low and some chains connecting the two electrodes are composed by metallic CNTs only. For this reason we decided to compare the electrical behavior of the transistors characterized by a finger distance of 15µm. However our interest is focused on the sensing behaviour of the CNTFETs, so we want to analyze the change of the transfer characteristics after exposition to DMMP gas. First we have contacted one transistor for each type of junctions and mounted it on a TO39 support. The TO39 has subsequently been inserted inside a chamber for testing transistor on DMMP flow. We have exposed the transistors to a DMMP gas concentration of 2ppm and we have measured the change of the transfer characteristics at the same voltage between the two electrodes (V_{DS} = 1V).

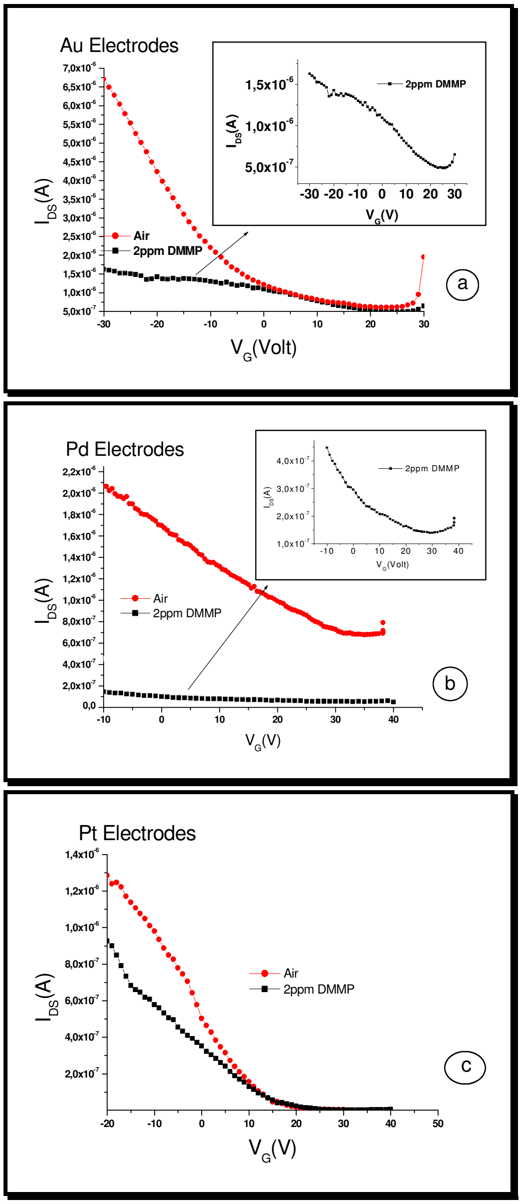

Fig.3: Transfer characteristics change for the different metal electrodes after DMMP exposure (V_{DS} = 1V). The insets in fig. 5a and 5b show the detail of the transistor response after being exposed to 2ppm of DMMP.

As we can see in Fig.3, the change of the transfer characteristics is very different for the CNTFETs fabricated using different metals : for the Pd, Au and Pt, the I_{DS} is reduced respectively to 1/10, 1/5 and 4/5 of their initial values measured in air. These reductions are reached for a value of the gate voltage of around 30 Volts after the turn-on voltage threshold of each transistor. After this value, the transistors reach the saturation threshold.

From these measures, we can deduce that different metals interact in a different way with the DMMP. Particularly interesting is the fact that the Pd and Au transfer characteristic change is very different even if the work functions of the two metals are nearly the same. This shows that the change in the CNTFETs characteristics is not simply related to the metal work function difference but very probably to a specific chemical interaction between the metal and the gas : the DMMP influences the change of each metal work function in a very specific way and so the change of the response of the transistor.

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