Nanotubes transistors based Selective Gas sensors : from laboratory to mass production

Louis Gorintin[*,**], Paolo Bondavalli[*], Gilles Feugnet[*],Florian Longnos[*] , Marc Chatelet[**], Fabrice Pardo[****], Charlie Koechlin [***,****]

[*]LMNP, Thales Research and Technology, Palaiseau, France, louis.gorintin@thalesgroup.com.
[**]LPICM, Ecole Polytechnique, Palaiseau, France, marc.chatelet@polytecnique.edu
[***]ONERA Palaiseau, Palaiseau, France, charlie.koechlin@onera.fr
[****] LPN-CNRS, Marcoussis, France, charlie.koechlin@lpn.cnrs.fr

ABSTRACT

Carbon NanoTube (CNT) transistors have been known for several years to be extremely sensitive to gases and so to be very good candidate to become very effective sensors. This is the reason why scientists are focused on the gas sensor design, even if their production is still a challenge. In this article, we will present our approach to achieve large-scale production of reproducible devices using CNT mats deposited by a dynamic airbrush technique. After optimizing the CNT based solutions, we will demonstrate that we can fabricate large array of Carbon Nanotubes Field Effect Transistors (CNTFETs) with reproductible characteristics. Wa can obtain Drain/Source current on/off ratio of 1 to 5/6 orders, by controlling precisely the density of CNTs deposed. Thanks to these good transfer characteristics, the detection limit of these devices can be lowered under the ppm, and this for a large range of gases.

The major issue for these sensors is their selectivity. To perform it, we have developed a new patented technology based on CNTFET arrays with different electrodes metals. In this contribution, we will demonstrate that each gas interacts specifically with each metal leading to a sort of electronic fingerprinting, thus allowing to discriminate each gas. We will also show the selective detection of NO2, NH3 and DMMP (sarin simulant).

Keywords: Carbon nanotubes , Transistors, Gas sensors, multi sensors, selectivity, Mass production

1 INTRODUCTION

Carbon NanoTubes (CNT) have been known to be one of the most promising material for several applications in electronics. But for the most part of them, if some experiments have shown a huge potential, few were able to reach industrialization and commercialization steps except for transparent electrodes, memories and electrical wires. In this contribution we will present our strategy and our last results on the large scale production of Carbon Nanotubes Field Effect Transistors (a.k.a. CNTFET) based sensors with extremely gas sensitive schottky contacts. In the first part we will deal with the sensing mechanism of these devices, then we will introduce our method for their industrial production and finally we will show the suitability of our concept to achieve selectivity after exposure to several gases.

2 CNTFET FOR GAS SENSING APPLICATION

The first measurements demonstrating the interaction between gas and CNTFET, using CNT as gate, were performed at Stanford University by Kong et al.[1] in 2000. Kong observed, after CNTFET exposure to Ammonia (NH3) and Nitrogen dioxide (NO2), respectively a reduction and an increase of the current (I_{DS}). If for several years, the interpretation of these phenomena was a debate, a certain agreement has recently been found. For single CNT devices, the main gas interaction with the device is at the contact between carbon nanotubes and the metallic electrodes.

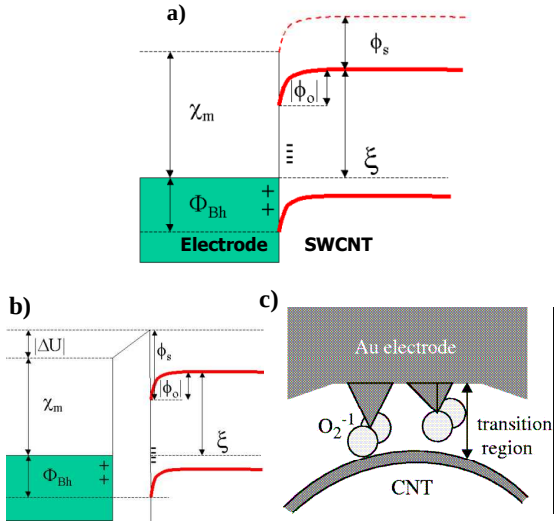

Figure 1 : a) Band diagram at metal/SWCNT (semiconducting) junctions in vacuum using the classical Schottky model, b) Band diagram at metal/SWCNT (semiconducting) junctions exposed to gas using the modified Schottky model, c) representation of the transition region between Au and SWCNT.

At this junction, we have a non intimate contact, leading to additional electrostatic phenomena for the charge carrier, due to gas adsorption. Indeed, the gas molecules create a dipole, and a potential drop ΔU at the interface. This model, first proposed by Yamada [2], allows us to obtain the following equation which describes the Schottky Barrier junction for a non-intimate model(1):

$$\Phi_{Bh} = E_G + \phi_s - \chi_m - |\Delta U| \quad (1)$$

Which is different from the more classical Schottky barrier equation :

$$\Phi_{Bh} = E_G + \phi_s - \chi_m \quad (2)$$

Where Φ_{Bh} is the Schottky barriers, ϕ_s the SWCNT electron affinities, E_G is the SWCNT band gap and χ_m, the metal work function.

This potential drop ΔU in eq. (1) depends on the gas affinity with the electrodes, the total number of occupied sites, and the competition with other gases in this air. (for more details on this theory please report to Bondavalli et al. explanation on the subject [3])

This is the reason why an array of CNTFET, achieved with different metal as electrodes could potentially lead to a selective sensor. Nevertheless the fabrication of large arrays of single CNT transistors is hard to achieve due to the complexity of positioning precisely an individual CNT.

3 CNT MATS FOR LARGE SCALE PRODUCTION OF SENSORS

To be able to achieve this kind of sensor at an industrial scale, there was a need to find an easier way to product them. As suggested by Snow [4], randomly organized CNTs with controlled behavior are good candidates for macro electronics devices. Thus we develop a technique which enables to make an homogeneous deposition of CNTs with a wafer scale compatibility using an automatic dynamic spray gun machine. Solution were obtained using commercial Single Wall CNTs (SWCNTs) from SouthWestNanoTechnologies, CoMoCat SG65 (90% of semiconducting SWCNTs). We were able to obtain, after sonication and centrifugation steps, stabilized solutions using N-Methyl-pyrrolidone (NMP) as solvent.

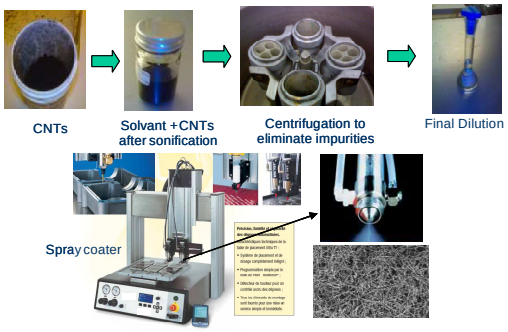

Figure 2 : Steps to obtain homogeneous CNTs mats

These solutions were then deposited on a substrate heated at more than 202°C (evaporation point for NMP) in order to evaporate instantaneously the solvent droplets hitting the substrate.

These mats were then used to implement our patented technology [5] : Arrays of 4 different metallic electrodes (Pt, Pd, Au and Ti) were obtained on a silicon doped and 100nm-oxydized wafer. Mats are then deposited on their top. The bulk doped silicon was used as a back gate.

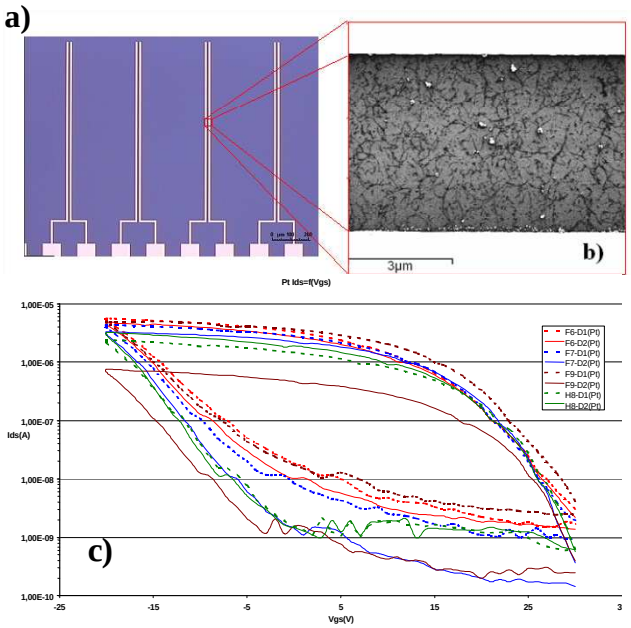

Figure 3 : a) Microscope image of CNTFET electrodes b) MEB image of the CNT deposition between two electrodes c) 8 different CNTFET Ids-Vgs characteristics for Pt electrodes under 1V

The CNTFETs obtained by this method have on-demand electrical characteristics and can be adapted to the targeted application and the electronic support constrain. In order to match the specifications for gas sensing application, the current range should be limited from 10-9 to 10-5. By measuring hundred of samples and thousands transistors using an automatic prober [6], we were able to evaluate the characteristics dispersion of these devices.

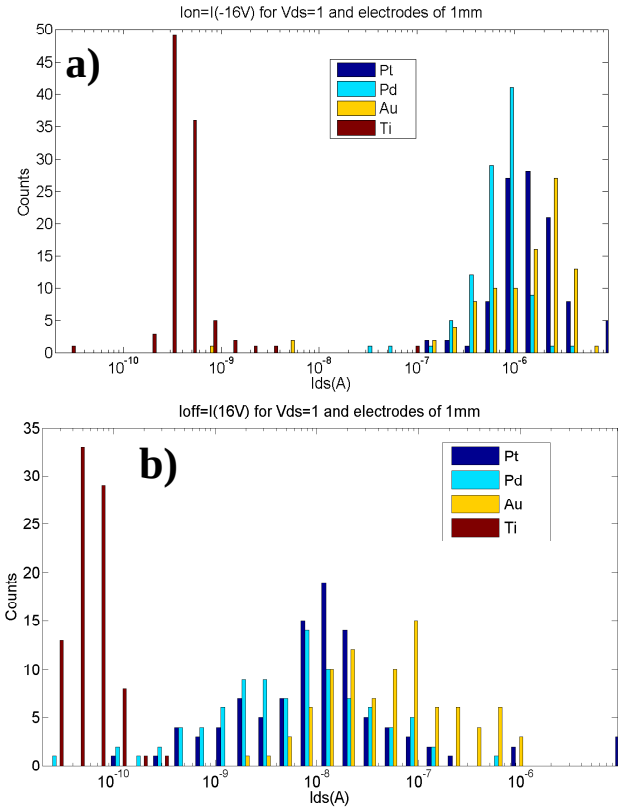

Figure 4 : a) histogram of Ion (Ids for Vds =1V and Vgs=16V) and b) Ioff (Ids for Vds =1V and Vgs=16V) values

Although they were realized on the same wafer, each metal presents a specific behavior: platinium and palladium transistors showed I_{on} (I_{ds} for V_{gs}=-16V) around 10^{-6} under 1V and an I_{on}/I_{off} ratio of 10^2, whereas gold transistor present a smaller I_{on}/I_{off} ratio and a larger dispersion. Titanium electrodes transistors exhibited very low current values compared with other metallic electrodes. This can be explained by Titanium oxidation under ambient condition, which lead to an high electrode resistance. Other metallic electrodes will be presented during the presentation to replace Titanium CNTFETs, which are out of specifications for electronics integration. In each case, we observed that the dispersion on I_{off} current is always larger than for I_{on} current. This is due to the aleatory percolation effect of metallic CNTs contained in the CNTs powder (10% according to the producer)

Then we tested these transistors under different environmental conditions.

4 CNTFET UNDER NEUTRAL ATHMOSPHERE

The samples were first bonded on a chip carrier and set up on a specific test bench. They were exposed, working continuously, during 64 hours under diazote N_2 ambient. The oxygen progressively desorbed from the electrodes, decreasing the potential drop on the electrode surface, and consequently the CNTFETs started to show an ambipolar characteristic after 36 hours of exposure. The same effect has been previously reported for single CNT transistors after 200°C annealling on vacuum [7] and under UV exposure[8].

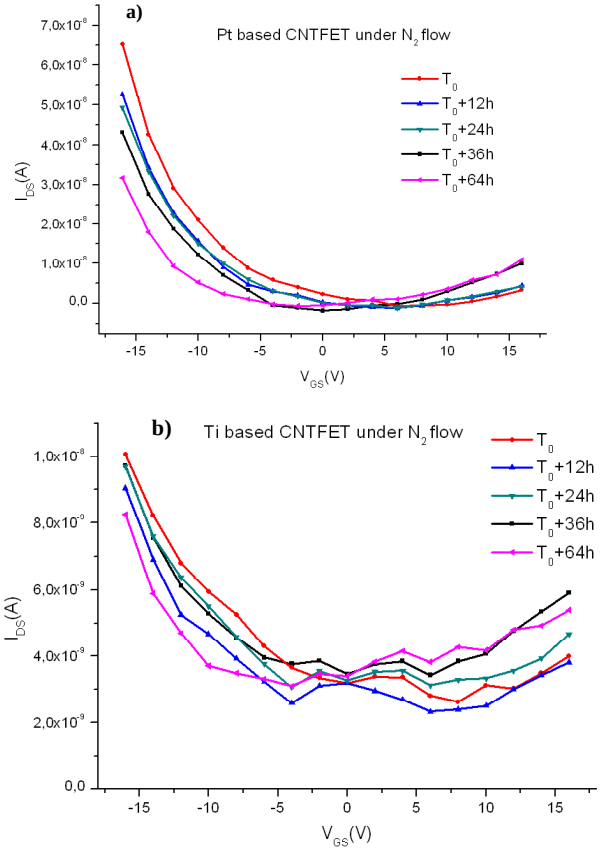

Figure 5: Pt(a) and Ti(b) CNFET Ids-Vgs characteristics change under N_2 atmosphere

These changes were strictly related to the metal used to fabricate the electrodes and were larger for Pt-CNTFET and Au-CNTFET than for the other two metals. This underlined that our CNTFET matrix could recognize O_2 adsorption and desorption due to the oxygen affinity.

5 CNTFET EXPOSED TO NH3 AND DMMP

This 4 different metal matrix of CNTFET was then exposed to 10ppm of NH3 and different concentrations of DMMP (simili sarin), from 16ppm to 300ppm exposure.

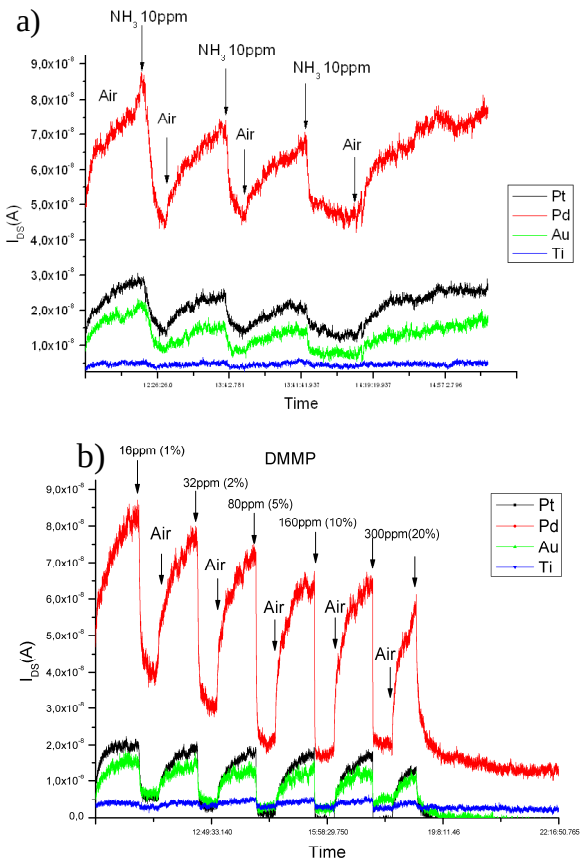

Figure 6: exposure of 4 CNTFET with Pt, Pd Au and Ti as electrodes to 10ppm of NH3 (a) and concentration ranging from 16ppm to 320ppm DMMP (b) for Vgs=-4V and Vds=1V

For both gases we observed a reduction of the current (I_{DS}) for all the of the CNFET, but the ratio before and after exposure (Table 1) was not the same.

	DMMP(16ppm)	NH3 (10ppm)
Pt	3,8	1,7
Pd	1,9	1,6
Au	2,3	2,1
Ti	1,4	1

Table 1: Ids before and after 10 mn exposure ratio under 16ppm of DMMP and 10ppm of NH3 for Vgs=-4V

This table shows that our devices achieve a clear selectivity between these two gases. Besides more performing mathematical methods like Principal Component Analysis (PCA) or neuronal network treatment could enhanced the selectivity capabilities of these devices.

The next steps of our work is to build a large data base for various gases and other available metals for electrodes in order to enlarge the field of applications of our CNTFET based sensors.

6 ACKNOLEDGEMENT

This study has been performed in the frame of the NANOSENSOFIN (Carbon NANOtubes based SENSOrs for gas electronic FINgerprinting) and CAPTEX project funded by French National Research Agency (ANR).

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