

# Highly Selective Sensing of DMMP and NH<sub>3</sub> Using CNTFET Based Gas Sensors Obtained using Spray-gun Technique and Fabricated with Different Metals As Electrodes

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## ABSTRACT

This paper deals with the fabrication of CNTFET obtained using carbon nanotube networks and with the utilization of these last as gas sensors. The method for depositing uniform and highly controlled density CNT mats is spray-gun technique. Using this technique we have demonstrated that we can achieve CNTFET with  $I_{on}/I_{off}$  reproducible ratios of around  $10^5/10^6$ . These transistors have been subsequently exposed to Acetic Anhydride which is a heroin precursor, showing a very short response time and a recovery time, without heating, of around 30 minutes. In this paper are also shown preliminary results after exposure of CNTFET to subppm concentrations of DMMP and NH<sub>3</sub> using two different metals as electrodes. In this case devices were obtained using drop-casting technique.

**Keywords:** CNTFET, Gas Sensors, Deposition technique, CNT networks

## 1 INTRODUCTION

This paper deals with the prove of concept of an highly selective gas sensors based on Carbon Nanotube Field Effect transistors (CNTFETs). Such devices exploit the extremely sensitive change of the Schottky barrier heights between Single Wall Carbon NanoTubes (SWCNTs) 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 [1, 2, 3, 4].

## 2 SAMPLE FABRICATION

Considering that no cheap and rapid method, up to now, exists for separating semiconductor from metallic specimens, we decided to use SWCNT mats as transistor channel. The principal advantages are two. Firstly the use of SWCNT mats instead of individual SWNTs (facilitating methodology) results in percolation networks with a better overall electrical control of the system. Secondly, using

Spray-gun technique we can achieve uniform and highly controlled SWCNT densities which allows us to obtain CNTFET with highly reproducible electrical characteristics reducing, at the same time, dramatically the final device cost. Systematical test results on our devices will be shown during the conference ( $I_{DS}$  as a function of SWCNT mat densities or electrodes distance).

Spray-gun technique allowed us to improve dramatically results obtained using drop-casting technique. Actually, the principal issue for this technique was the so-called “coffee-ring” effect of the drops containing carbon nanotubes: CNTs had the tendency to be fixed on the border of the drop and so to produce a non-uniform mat. The number of operating transistors was consequently very low.

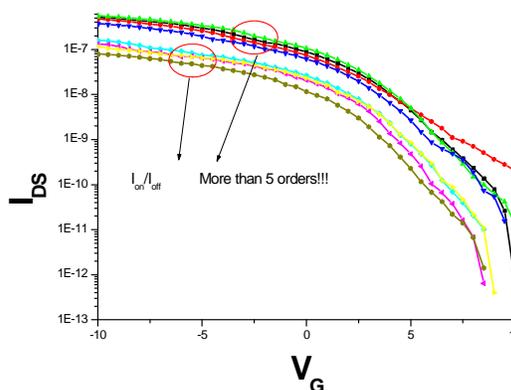


Figure 1:  $I_{DS}$  as a function of  $V_{GS}$  for CNTFET obtained using Spray-gin technique.

After achieving CNTFETs using Spray-gun technique, we have studied the effect of the CNTFET electrodes (fingers) distance on  $I_{on}/I_{off}$  ratio. We have obtained a law linking this two parameters, confirming the reproducibility of our results. The theoretical explanation of this phenomenon (not in the aim of this contribution) will be shown in a paper that has to be published soon.

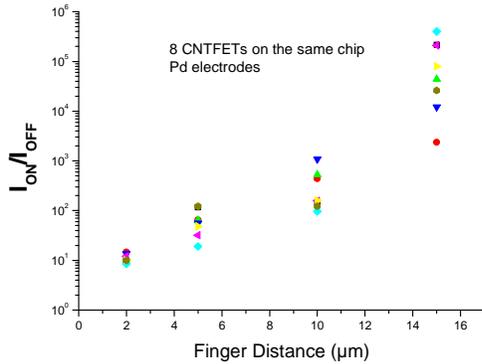


Figure 2:  $I_{ON}/I_{OFF}$  ratio as a function of the finger distance for CNTFETs on the same chip.

### 3 TESTS USING GASES (DROP CASTING TECHNIQUE)

Spray-gun technique has been optimized only recently. Previously we performed tests using sample obtained using drop-casting deposition technique. The gas electronic 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 (approach patented [5]). In a previous paper [6], we demonstrated that using Au, Pd, Pt metals we achieve a change of the transfer characteristics which is different for each transistor after exposure to 2ppm DMMP gas (DiMethyl-Methyl-Phosphonate, nerve agent-simulant) : we observed a current reduction of 90% for Pd, 80% for Au and 20% for Pt. To demonstrate sensitivity for subppm concentration, then we have exposed transistors obtained using Au,Pt and Mo to 0.5 ppm of DMMP.

In this case, we have observed that the  $I_{DS}$  for Au, Mo and Pt, is reduced respectively of 60% (see Fig.3), 25% (see Fig.4) and 10% (see Fig.5) of their initial values measured in air for  $V_{DS}=1$  Volt. These results were obtained for  $V_{GS}$  value of around -25 Volts. The three figures give an example of the trend followed by the CNTFETs with different metal electrodes : the same behavior is observed for all the tested transistors (20 for each metal) with an error of around  $\pm 5\%$  on the current reduction percentage (see Table1).

To preliminary demonstrate selectivity of our sensor and thus the concept of “electronic fingerprinting” we have exposed CNTFET achieved using Pd and Au, to two gases, DMMP and  $NH_3$ , which have the same “electron-withdrawing” behavior. We exposed our array to a sub ppm concentration of 0.5ppm of DMMP and  $NH_3$  and identified

two electronic fingerprinting which seems to definitively demonstrated the high selectivity of our concept also for gas with similar electronic behavior (results will be shown during the conference).

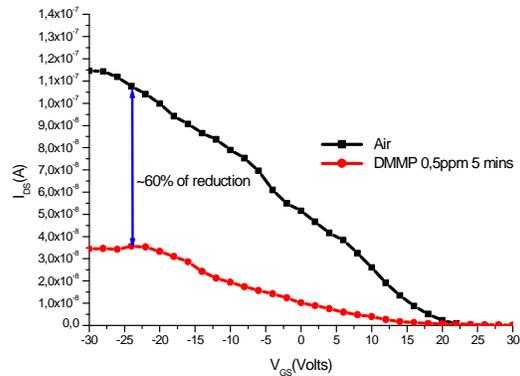


Figure 3:  $I_{DS}$  (as a function of  $V_{GS}$ ) change after gas exposure for CNTFETs achieved using Pd for metal electrodes.

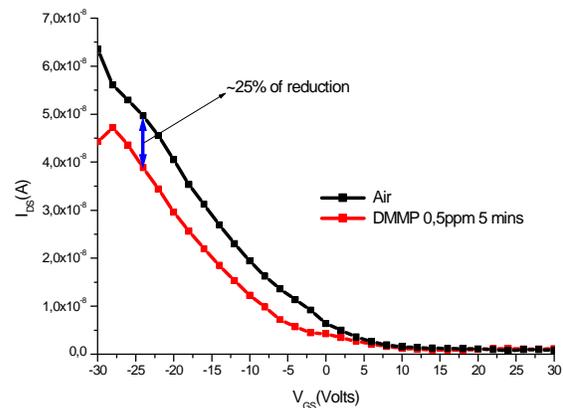


Figure 4:  $I_{DS}$  (as a function of  $V_{GS}$ ) change after gas exposure for CNTFETs achieved using Mo for metal electrodes.

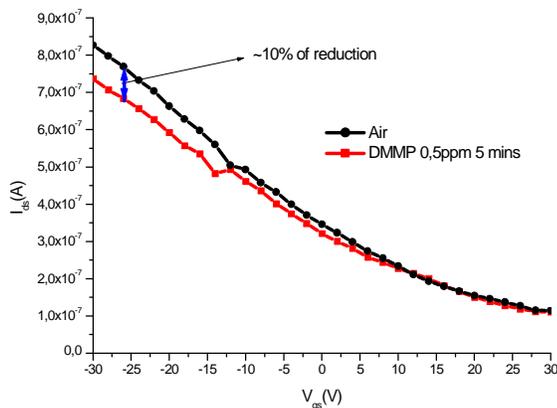


Figure 5:  $I_{DS}$  (as a function of  $V_{GS}$ ) change after gas exposure for CNTFETs achieved using Pt for metal electrodes.

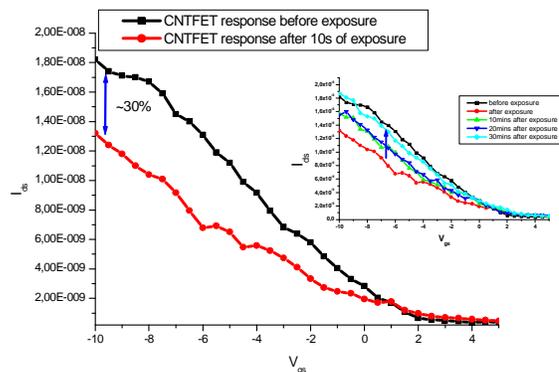


Figure 6:  $I_{DS}$  (as a function of  $V_{GS}$ ) change after exposure after exposure to Acetic anhydride for CNTFETs achieved using Pd for metal electrodes.

Metals	$I_{DS}$ current reduction % after exposure (0.5 ppm DMMP)
Ti/Au	60
Ti	25
Ti/Pt	10

Table 1 : Summary of the results and number of transistors tested for each different metal electrode.

#### 4 TESTS USING DRUG PRECURSORS (SPRAY-GUN DEPOSITION TECHNIQUE)

Another important application related to security is the detection of drug precursors. For this reason we have performed preliminary tests using Acetic anhydride  $((CH_3CO)_2O$ , an heroin precursor. The results show, for example, a sudden change of  $I_{DS}$  as a function of the gate voltage, after 10secs of around 30% of the initial current using Pd metal electrodes (Fig.6). In this case we observed a recovery time of around 30mins (see inset Fig.6). These tests will performed also using a heating substrate in order to study the de-adsorption time as a function of different chemical species and metal electrodes. Actually, de-adsorption time could be another parameter to improve selectivity of this kind of sensors.

All of our measurements have been performed at ambient conditions. New measurements of response after other drug precursor (Piperonal, Phenylacetone) exposure, using different metal as electrodes, will be presented during the conference.

#### 5 PRELIMINARY TESTS ON SELECTIVITY (DROP-CASTING TECHNIQUE)

As told previously, the deposition technique using Spray-gun has been only recently developed so we have performed preliminary tests on selectivity using CNTFET achieved using drop-casting technique. We started the test performing measurements of the electrical behavior of the different CNTFETs. In our case the most important characteristics is the evolution of the current between drain and source as a function of the gate voltage ( $I_{DS}(V_{GS})$ ). We exposed the CNTFETs inside a chamber to a concentration of 1ppm of DMMP and 10ppm of  $NH_3$ . The carrier gas was the ambient air. We measured the change of  $I_{DS}(V_{GS})$  for each transistors using specific point probes. The measurements have been achieved after an exposure of half an hour to the targeted gases. We observed that the change of the transfer characteristics was different for the CNTFETs fabricated using different metals: the  $I_{DS}$  for Pd, Au, and Mo is reduced respectively of 90%, 80% and 65% of their initial values measured in air (for a  $V_{DS}=0.5V$ olt) for 1ppm of DMMP and respectively 50%, 65% and 50% for 10 ppm of  $NH_3$ . These reductions are reached for a value of the gate voltage of 15 Volts.

In this work we have demonstrated that CNTFET based array could be potentially used to obtain an electronic fingerprinting of specific gases. Actually, we have observed that the ratio of the  $I_{DS}$  current before and after gas exposure is different for 1 ppm of DMMP and 10 ppm of  $NH_3$ . The ratio changes in a different way for each gas as a function of the metal electrodes. The results are summarized in Table II.

Table II. Relative change of $I_{ds}$ as a function of the metal electrodes after gas exposure			
	Ti/Pd	Ti/Au	Ti/Mo
DMMP	90%	80%	65%
NH <sub>3</sub>	50%	65%	50%

Table II : Relative change of  $I_{ds}$  as a function of the metal electrodes after gas exposure for DMMP and NH<sub>3</sub>.

## 6 CONCLUSIONS

In this work we have demonstrated that CNTFET based array could be potentially used to obtain an electronic fingerprinting of specific gases. Actually, we have observed that the ratio of the  $I_{DS}$  current before and after gas exposure is different for 1 ppm of DMMP and 10 ppm of NH<sub>3</sub>. The ratio changes in a different way for each gas as a function of the metal electrodes, as summarized in Table 1.

Recently, we have also demonstrated that we can obtain high performances CNTFETs using Spray-gun technique deposition, with high and reproducible On/Off ratio. These CNTFETs have been exposed to Acetic Anhydride and have shown extremely interesting results (Fig.6). During the conference more results using this kind of CNTFET will be shown.

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**Dr. Pierre Legagneux** was awarded his PhD from the University of Orsay in 1989 and joined the Central Research Laboratory of Thomson CSF which is now Thales Research & Technology. His research interests include the design and fabrication of nanotube and nanowire based devices for electronic applications. He was the coordinator of two European projects which relate to the study of nanotube for field emission applications (Nanolith and Canvad). P. Legagneux is the author/co-author of more than 60 papers and 15 patents including 6 on nanotube based devices. He is the head of Nanostructures Laboratory at Thales R&T.

**Dr. Didier Pribat** graduated from Grenoble University in 1977. He worked for 23 years within the Central Research Laboratory of Thomson-CSF (now Thales Research & Technology) on various subjects of materials science and semiconductor technologies (heteroepitaxy, solid electrolytes, III-V materials and devices...). In 1991 he started a group on Large Area Electronics and has been particularly involved in low temperature polysilicon technology, including polysilicon synthesis by excimer laser crystallisation, thin film transistors (TFT) fabrication, characterisation and modelling, as well as circuit design and simulation. He joined CNRS/Ecole Polytechnique in 2001 and started the activity on carbon nanotubes for molecular electronics. He is currently Director of the Masters Programmes at Ecole Polytechnique, consultant to the LETI in Grenoble and expert to the EC and the EPSRC (London). D. Pribat has published or presented more than 150 papers. He is also co-author of a book chapter and author or co-author of more than 50 patents.