CNTFETs fabricated using an Original Dynamic Air-Brush technique for SWCNTs deposition : application to gas sensing

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ABSTRACT

This contribution deals with Carbon Nanotubes Field Effect transistors (CNTFETs) based gas sensors fabricated using a completely new dynamic air-brush technique for SWCNTs deposition. The extreme novelty is that our technique is compatible with large surfaces, flexible substrates and allows to fabricate high performances transistors exploiting the percolation effect of the SWCNTs networks achieved with extremely reproducible characteristics. This technique is extremely interesting considering that it is suitable for industrial transfer. More precisely, we have developed a machine which allows us the dynamic deposition on heated substrates of SWCNT solutions, improving dramatically the uniformity of the SWCNTs mats. The CNTFETs have been developed for gas sensing applications. Indeed we have fabricated arrays of CNTFETs achieved using different metal electrodes to exploit the change of metal/SWCNTs junction characteristics as a function of the gas detected in order to identify a sort of lectronic fingerprinting. This phenomenon is related to the change of the metal work function and so of the Schottky barrier and seems to be extremely selective. Although the deposition technique has been developed to fabricate CNTFETs, this technique is extremely versatile and can be used for other kinds of applications such as fabrication of bolometers (e.g. nanotubes), replacements of ITO layers (e.g. nanotubes, graphene), in OLED (e.g. graphene), for light and cheap ultracapacitors on flexible substrates (e.g. using carbon nanotubes or nanohorns). This technique could really allow these nanomaterials to strike the market on these applications. During the presentation examples, for all these applications, will be shown.

1 INTRODUCTION

The first paper demonstrating the efficiency of Carbon Nanotubes Field Effect transistors (CNTFETs) for gas sensing applications was published in 2000 by Kong et al. [1]. Since then, many teams have obtained very interesting results concerning the sensitivity of this new kind of sensors. We can mention, for example, the results obtained by Qi et al. in 2003 [2] which were able to detect 1ppt of NO_2 (using functionalized CNTFETs) and, the same year, Snow and co-workers that were able to detect 1ppm of Di-Methyl-Methyl-Phosphonate using carbon nanotubes networks based transistors [3-4]. These results seem to prove that the main issue for this kind of sensors is not the sensitivity. Indeed the real concern consists in finding a suitable technique to achieve an highly selective sensor that could be used in every-day life applications or in operational context. Various methods have been proposed so far. Among these methods, the deposition of polymers on the CNTFETs (functionalization) is extensively studied and very promising results have been already obtained [see *e.g.*, ref. 2]. 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. Another approach is the bio-functionnalisation, using DNA sequences of the Single-Walled-CNTs (i.e. SWCNTs) to improve the sensitivity for specific gases, performed by researchers at Pittsburg University [5]. Finally we can mention the approach developed jointly by researchers at Nanomix Inc. and Pittsburgh University [6-7]. They deposed nanoparticles of different metals on networks of SWCNTs connecting, by percolation, two Pd electrodes (i.g. "metal decoration"). Therefore they fabricated an array of CNTFETs each one characterized by a different metal "decoration". They exposed this array to several gases (NO, H_2, CO, CH_4, H_2S, NO_2, NH_3) and they observed a specific change of the transfer characteristics of each transistor as a function of the nature of the nanoparticles and of the gas. These results made researchers think that large array of "metal-decorated" CNTFETs could be used in order to recognize univocally the gases identifying their electronic fingerprinting. All the approaches that we have presented appear to be very interesting from a scientific point of view but the technological steps for the fabrication of the sensors (e.g. polymer/bio-fonctionnalisation or metal decoration) are quite complex and the their industrial exploitation has not been achieved yet. Our approach for solving the selectivity problem, is to achieve a sensor comprising an array of SWCNT-based transistors where each transistor will be fabricated using different metals as source/drain electrodes. 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 SWCNTs based mats instead of individual SWCNTs results in percolation networks with a better overall electrical control of the system. Secondly, using dynamic spray-gun technique (patented by Thales) we can achieve uniform and highly controlled SWCNT densities which allows us to obtain CNTFETs with highly reproducible electrical characteristics [8-9]. Only two conditions must be fulfilled : the distance between the two electrodes must be larger than the SWCNT length (otherwise metallic nanotubes could cause a short-circuit) and the areal density of the SWCNT mat has to exceed slightly the percolation threshold. Actually, for too high densities, the conduction can reach an ohmic trend with no gating effect. This technique allows us to fabricate large array of sensors with a method very simple, rapid, totally compatible with existing CMOS technology and so suitable for industrial exploitation and relatively low-cost. We have chosen to diversify the metals electrodes in order to exploit the different effect of the interaction of the gas with the metal/SWCNTs junction on the Schottky barrier. As a consequence after gas exposure the Fermi level alignment between metal and CNT at the contact, will change and therefore the characteristics of the Schottky barrier at the junction. In fact we cannot talk about a "classical" Schottky barrier because in our case we do not deal with a junction with an intimate contact (like classical Schottky barrier between semiconductor and metal where the Fermi Level is pinned by interface defects as explained by F.Leonard et al. in 2000 [10]). In our case we have a "non-intimate" contact because the SWCNTs are simply deposited on the metal electrodes without annealing to achieve a better contact. This model was firstly suggested by T.Yamada of the Ames Research Center in 2004 [11-12] for Au/SWCNT contacts, generalized by P.Bondavalli et al. [13] to all the metal/ SCWNT junctions and, for network based CNTFETs, improved by F.Peng et al. in 2009 [14]. In this contribution we will demonstrate that, after being exposed to different gases (NO_2, NH_3 and DMMP) at concentration from 10ppb to 10ppm, each transistor will be influenced in a very peculiar way : this influence on the barrier is strictly related to the interaction between a specific gas and a specific metal/CNT junction [15]. Indeed, the gas will change the metal work function and so the junction electrical behaviour. This is not possible in traditional for semiconductor/metal junction because the Fermi level is pinned by, as told previously, interface defects. Using this method, we will be able to demonstrate that each gas can be "fingerprinted" and so unambiguously identified.

2 CNTFET FABRICATION

Our CNTFET arrays have been fabricated using n-doped Silicon substrates covered with 50nm of thermally grown SiO_2. The electrodes have been defined by UV photolithography: the metal has been deposited by thermal evaporation followed by lift-off. This step has been repeated sequentially for each metal in order to achieve a final chip (0.5x0.5cm²) composed by 16 couples of electrodes. We have achieved two series of 8 couples of electrodes with a distance of 10µm and a length respectively of 1 and 3mm. The metal electrode thickness was 35nm. A 5nm thick layer has been added in order to improve the layer adhesion of Au, Pd, Pt and Ti layers on the substrate.

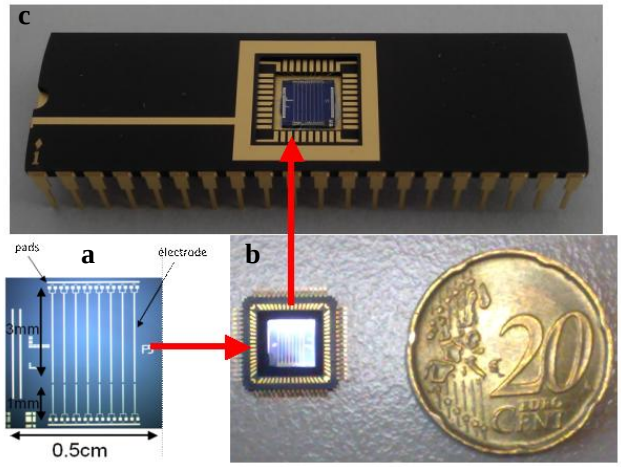

Fig.1: a) chip containing 16 CNTFETs achieved using 4 different metals as electrodes (4 for each metals) b) chip dimensions compared to a 20 cents coin c) chip mounted on the C-DIP used for tests.

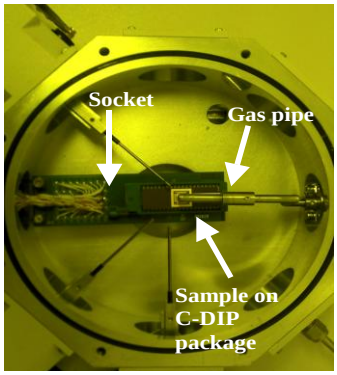

Fig.2: Detail of the chamber used to perform measurements

3 RESULTS

After fabricating chips, we have performed measurements, exposing chips to three different gases NO_2, NH_3 and DMMP. We have exposed each time one single chip to the gas. In this way, we were able to record the changes of the transfer characteristics of four CNTFETs, composed by four different metals (Au, Pt, Pd, and Ti) as electrodes, at the same time. The first measurements have been performed exposing the CNTFETs to concentration values varying from 100ppb to 10ppm for NO_2 and NH_3. In this way we have tried to evaluate the limit of sensitivity of

each metal. The variations of the I_{DS} current during the exposure cycles (for V_{GS} =–16V and V_{DS}=1,6 V) are shown in Figs.3-4 for NO_2 and Fig.5 for NH_3. The exposure time was of 300 sec to the particular gas specie and 600 sec to air.

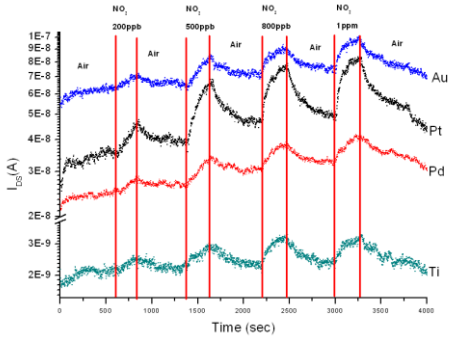

Fig.3: Change of the I_{DS} current as a function of time for V_{GS}=-16V and V_{DS}=1,6V for concentrations between 100ppb to 1ppm of NO_2.

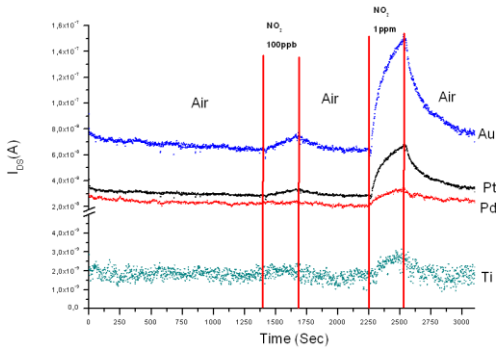

Fig.4: Detail of the change of the IDS current as a function of time for VGS=-16V and VDS=1,6V at 100ppb and 1ppm.

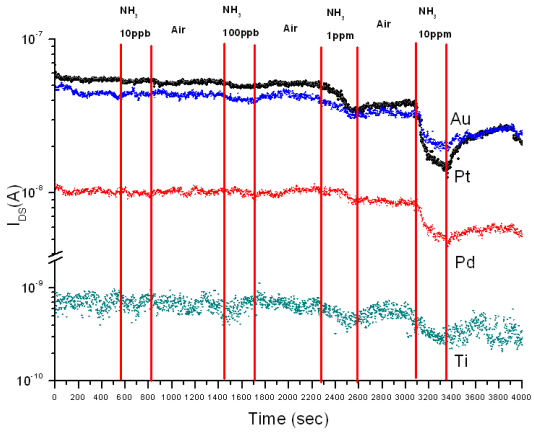

Fig.5: Change of the I_{DS} current as a function of time for V_{GS}=-16V and V_{DS}=1,6V for concentrations between 10ppb to 10ppm of NH_3.

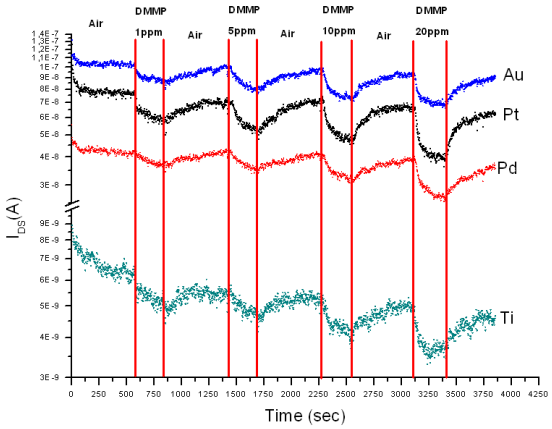

Fig.6: Change of the I_{DS} current as a function of time for V_{GS}=-16V and V_{DS}=1,6V for concentrations between 1ppm to 20ppm of DMMP.

All the CNTFETs fabricated show a p-type behavior because the metal work functions are larger than the sum of the CNT's electron affinity + half the band gap. Ti has a lower marked p-type behavior because its gap approaches the CNT one. Moreover Ti-based electrodes are naturally oxidized and so the current is quite low compared to the other metals. From the measurements, it is highlighted, as shown in literature, that the current variation of the CNTFETs is exactly the opposite in the case of the NH_3 and NO_2. As shown in previous papers [13-15] when channel length is less than 100µm and gas concentration lower than around 200ppm (for the most reacting gases [20]), the main effect of gas on the CNTFET is at the junctions metal/CNT. Indeed considering that NH_3 is a so-called "electron-donating" gas, it creates an interface dipole that decreases the work function of the metal, at the contact, (for all the metals), thus favoring electron injection from the contacts and so it reduces the hole passing current. Exactly the opposite behavior is observed for NO_2, which is an "electron-withdrawing" "acceptor" gas (the interface dipole is oriented in the opposite direction and the Schottky barrier is reduced for hole injection). We can also see that the CNTFETs seem to be more sensitive to NO_2. We can observe a clear change in the I_{DS} for concentrations as low as 100ppb for Pt and Au, and for all the metal at 200ppb. In case of NH_3, Au and Pt show a change in I_{DS} for 100ppb but in order to see a clear change for all the CNTFETs, we have to reach a concentration of 1ppm. These results are at the state of the art considering that our chip has not been functionalized (using chemical or biological analytes) and the measurements have been performed using gas as carrier gas at ambient pressure.

4 TESTING SELECTIVITY

The most important issue for gas sensors is the selectivity. Our approach is to use different metals as electrodes because the interaction of each gas with each metal is specific. In this way we are able to identify a sort

of fingerprinting for each analyte. This idea is not simply based on the fact that for short channel configurations the main effect of the gases is on the metal/SWCNT junctions. Indeed, considering that the channel (composed by SWCNT based mats) is the same one for each transistor, the only difference in the reaction of the gas with the CNTFET array can be originated by the junctions (fabricated using different metals as electrodes). In order to verify this hypothesis, we have to checked that the response of the chip is not only different for two gases of two different families, classified as electron donating or withdrawing (like NH_3, NO_2), but also for gases with the same electronic character. For this reason we have performed different measurements exposing the same chip to Di-Methyl-Methyl-Phosphonate (DMMP), which is an "electron-donating" gas (like NH_3). To obtain concentrations from 1ppm to 20ppm, we have bubbled the gas which gas?? through a liquid. We have not been able to test the sensitivity for lower concentrations, because the saturation pressure of DMMP is 1600ppm at ambient conditions, and with our system (max dilution of 1/1000) we can reach at maximum a concentration around 1.6 ppm. The results of several exposure cycles are shown in Fig. 6.

5 CONCLUSIONS

In this work, we have demonstrated that the NO_2, NH_3, DMMP gases interact differently with each metal/CNT junction. This is because each gas changes the metal work function of the metal electrodes in a specific way and therefore the transfer characteristics of the CNTFETs. This effect does not depend on the initial metal work function. In fact, if we analyze the relative change of the conductance, we have observed that it is not correlated to the starting working function and it is different for each gas. From these results, we think that CNTFET based array could be potentially used to obtain an electronic fingerprinting of specific gases and therefore to perform selective sensing using very simple, relatively low-cost devices. The results obtained in this contribution, concerning the sensitivity of all the transistors on the same chip (200ppb for NO_2, 1ppm for NH_3 and around 1ppm for DMMP), are at the state-of-the-art considering that we have not functionalized chemically or biologically our devices. Moreover we have tested CNTFETs, fabricated using SWCNT mats as channels deposited with a new deposition technique, for the transistors at ambient conditions. New studies must be performed in order to study the effect of each gas on the metal work functions and so to rely this effect to the change of the Schottky barrier at the metal/CNT junction. This studies could permit to understand deeply the effect and the origin of the gas interaction on the electrodes and to define a clear quantitative model.

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