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Optical properties of nanotubes / Propriétés optiques des nanotubes

Carbon nanotubes based transistors composed of single-walled carbon nanotubes mats as gas sensors: A review

Transistors à nanotubes de carbone constitués de nattes de nanotubes de carbone à paroi simple. Leur utilisation comme détecteurs de gaz : Une monographie

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ABSTRACT

This contribution presents the main studies on the CNTFET based gas sensors obtained using Single-Walled Carbon Nanotubes mats (SWCNTs) as channel. Although these devices have allowed one to achieve sensors with an impressive sensitivity compared to existing technologies, the physical interpretation of the effect of interaction between the gas molecules and the CNTFETs has not yet been clarified. Concerning selectivity, we will deal with the main routes that have been proposed to overcome this problem: functionalization using polymers, electrodes metal diversification, metal decoration of SWCNT mats.

RÉSUMÉ

Parmi les détecteurs de gaz basés sur des transistors à effet de champ à nanotubes de carbone (CNTFET) ceux qui utilisent comme canal des nattes de nanotubes de carbone à paroi simple (SWCNT) sont passés en revue dans la présente étude. Bien que ces dispositifs aient permis de réaliser des détecteurs dont la sensibilité est impressionnante en comparaison avec les technologies existantes, l'interprétation physique de l'effet de l'interaction entre les molécules de gaz et les CNTFET n'a pas encore été clarifiée. En ce qui concerne la sélectivité, nous nous intéresserons aux diverses voies proposées pour surmonter ce problème : fonctionnalisation par des polymères, diversification des électrodes métalliques, décoration métallique des nattes de SWCNT.

1. Introduction

Carbon nanotubes are one-dimensional molecular structures obtained by rolling up one graphene sheet (Single-Walled Carbon Nanotube, i.e. SWCNT) or several (Multi-Walled Carbon Nanotube, i.e. MWCNT). Since their discovery in 1991 [1], many scientific teams have focused their interest on this material which shows extremely interesting physical properties. Concerning gas/chemical detection, sensors based on different working principles, have been fabricated thanks to SWCNTs: miniaturized ionizing gas sensors (also called "micro-gun" sensors) [2], CNT thin films with variable resistance as a function of the adsorbed gas properties [3–6] and finally Carbon NanoTube Field Effect Transistor (CNTFET) based sensors. The main

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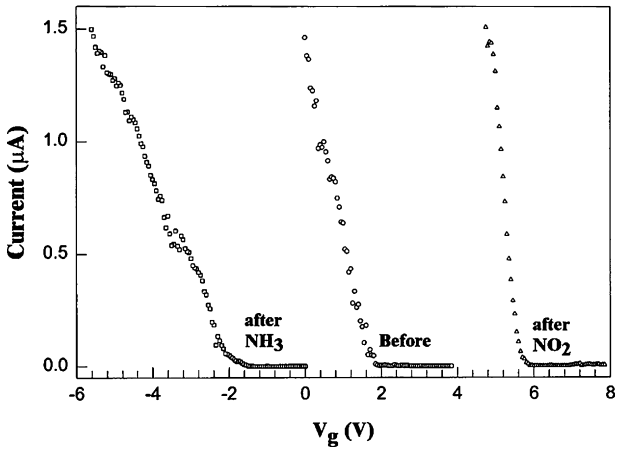

Fig. 1. CNTFET transfer characteristic change after exposure to NO_2 and NH_3 [7].

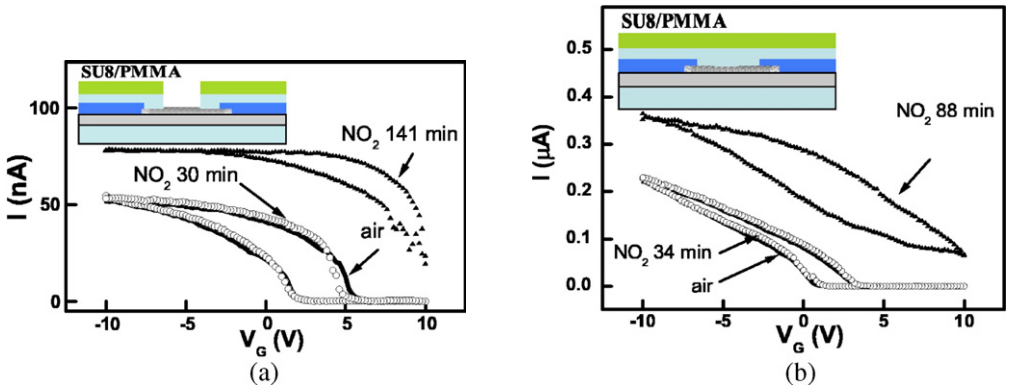

Fig. 2. Transfer characteristics change for a CNTFET in contact-covered configuration (a) and totally covered (b) for different exposure times to NO_2 [8].

advantages of CNTFET based sensors, compared to existing technologies, are: devices can be made ultra compact, effective at room temperature, with low power consumption (< 1 mW), very fast response (< 10 sec), low recovery time (few minutes) and show a good versatility. Moreover, they are relatively low cost fabrication devices considering that they are based on CMOS compatible technology.

This article deals with the state of the art in the domain of CNTFET based gas/chemical sensors obtained using SWCNTs mats and intends to review the main routes developed to improve selectivity, which is the main issue.

2. CNTFETs as sensors: how do they work?

The first paper showing the great potentiality of CNTFETs for gas sensing applications was published in 2000 [7]. In this paper Kong et al. at Stanford University observed that a single SWCNT used as a transistor channel between two gold electrodes, fabricated on a SiO_2/Si substrate acting as a bottom gate, interacted with gas molecules, changing the CNTFET transfer characteristics (source/drain current as a function of the gate voltage). The gases used for tests were NO_2 and NH_3 with concentrations between 2 and 10 000 ppm. These gases were chosen because they exhibit two opposite electronic behaviors as a consequence of their chemical affinity: the first one is an “electron withdrawing” and the second one an “electron-donor” gas. The experimental results pointed out an increase and a reduction of the p-type CNTFET conductance for NO_2 and NH_3 respectively (Fig. 1). Therefore the effect of the gas on the CNTFET was assimilated to a sort of “molecular gating” on the carbon nanotube due to the gas molecules adsorption and so to a sort of doping of the SWCNT.

In this context, one of the most interesting studies has recently been published by Georgestown University [8]. In 2006, they fabricated CNTFETs using two Pd electrodes on a SiO_2/Si substrate (bottom gate configuration). In order to evaluate the effect of metal/SWCNT contacts, they covered these with a 200 nm of polymethyl-methacrylate (PMMA) and a 2 μm layer of SU8 (Fig. 2). After having exposed the CNTFET to a concentration rising up to 150 ppm of NO_2, they did not register any change of the transfer characteristic, compared to the results in ambient air. However, after 30 min of exposure to a concentration of 200 ppm, the transfer characteristics changed as a consequence of the diffusion of the gas molecules through the polymer layers. The same result was obtained for a whole covered device, demonstrating that the NO_2 molecules had no effect on the channel doping of the CNTFET. For these measurements, the total recovery time was around one day of CNTFET

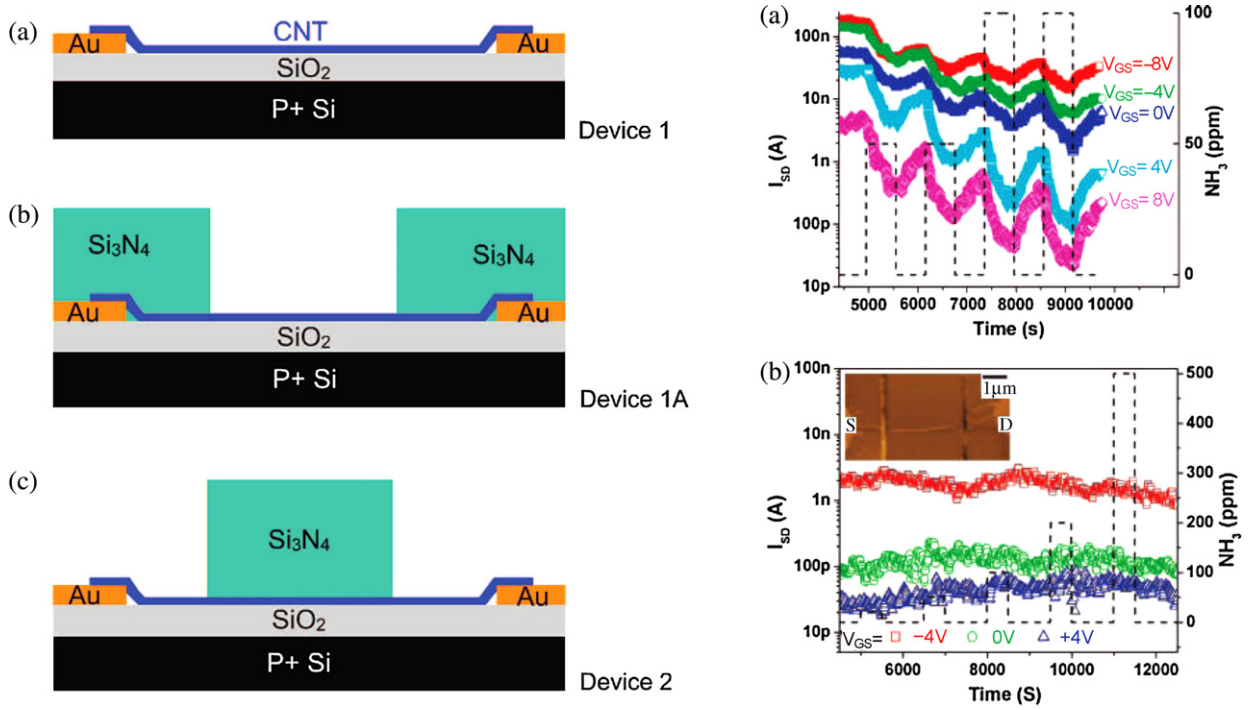

Fig. 3. (Left column) Schematics for (a) device 1, as-prepared CNTFET; (b) device 1A, the contacts passivated by Si_3N_4, and (c) device 2, the central CNT channel passivated by Si_3N_4. (Right column) Real time detection of NH_3 at room temperature under various gate voltages (a) before (device 1) and (b) after the contacts passivation (device 1A), respectively. Inset: an atomic force microscope (AFM) image of device 1A after the passivation [9].

exposure to ambient air. Similar measurements have been recently performed at Nanyang Technological University in 2009, by Peng et al. [9] using SiN_3 as passivation layer. These tests have confirmed that at room temperature the CNTFETs are not sensitive to gas exposure if the contacts (SWCNT/metal) are covered. However they observed a change in the transfer characteristics when the substrate was heated at 150 °C. This phenomenon seems related to the fact that NH_3 can be more easily adsorbed on SCWCNT defects thanks to oxygen. Indeed, the same test using N_2 as the streaming gas, did not show any change in the sensor response (Fig. 3).

3. CNTFET based sensor using SWCNT mats

The previous paragraphs have dealt with tests performed using CNTFET based sensors fabricated using individual SWCNT. However, the utilization of a single SWCNT presents some important issues. Firstly, considering that no method up to now exists to fabricate only semiconducting SWCNTs, we cannot predict if an SWCNT is metallic or semiconductor. Secondly, it is quite laborious to identify the position of one single SWCNT using the Amplitude Force Microscopy (AFM) technique. From an industrial point of view it is not a suitable solution for batch sensor fabrication.

For these reasons, several research teams have focused their work on CNTFET using SWCNT mats as channels. Indeed, as far as random networks are concerned, it has been shown that, through a percolation effect, an overall semiconductor behaviour can be obtained for carefully controlled areal densities [10–13]. 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 [14].

One example of CNTFET based sensor achieved using SWCNT mats, has been proposed by Snow et al. of the Naval Research Laboratory [15,16]. They fabricated a sensor using lithographically-patterned SWCNT networks between Ti drain and source contacts on a SiO_2 layer and Si substrate in a bottom gate configuration (Fig. 4). These sensors were exposed to saturated vapour of dimethyl-methyl-phosphonate (DMMP) [17], which is a nerve agent stimulant. The researchers found a V_{ON} negative shift, compared with results obtained in air, which was compatible with the “electron donating” character of DMMP. The phenomenon was explained as a consequence of the electron transfer from DMMP to the SWCNT. The observed recovery time was of several hours of merely exposure to air, but could be dramatically reduced simply applying an inverse bias for around 200 seconds (Fig. 5). Researchers thought that the interaction between the negative charges induced in the channel by the gate voltage (positive), removed the DMMP reducing the desorption barrier.

An integrated sensor based on CNTFET transistors has been manufactured by researchers from the NASA Ames Research Centre [18]. They fabricated a sensor composed by interdigitated Pt electrodes (with finger distance ranging from

Fig. 4. CNTFET (A) fabricated using carbon nanotubes networks (B) [15].

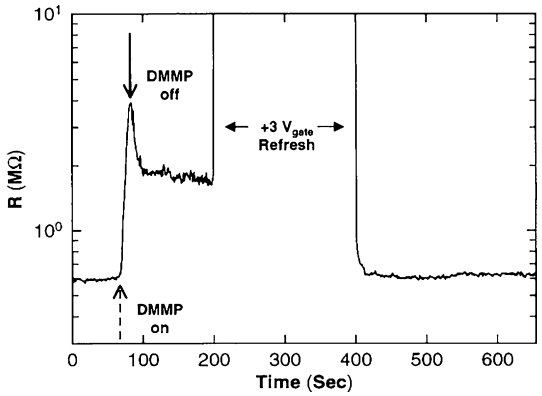

Fig. 5. Effect of the bias gate inversion on the resistance change related to DMMP exposure [15].

4 to 50 µm) with carbon nanotubes chains, grown using an in situ chemical vapour deposition process (CVD) [19], as the transistor channel. This final device, composed by twelve CNTFETs, shows a very promising sensitivity for NO_2 and NH_3 concentrations, respectively between 400 ppb and 10 ppm, 4 and 50 ppm in air. The great originality of this microsystem lies in the fact that an embedded heating layer is achieved between the substrate and the dielectric layer (Si_3N_4). This one can be used to reduce the recovery time desorbing more rapidly the gas molecules (Fig. 6). This microsystem is particularly interesting because it allows us to identify the principal issues to move from a lab prototype to a device for real life applications, introducing at the same time some solutions for the final device packaging.

4. Routes to improve selectivity

We have shown in the previous paragraphs that CNTFET based sensors obtained using SWCNT can be very sensitive to gas exposure. However, the real issue remains to demonstrate a suitable selectivity.

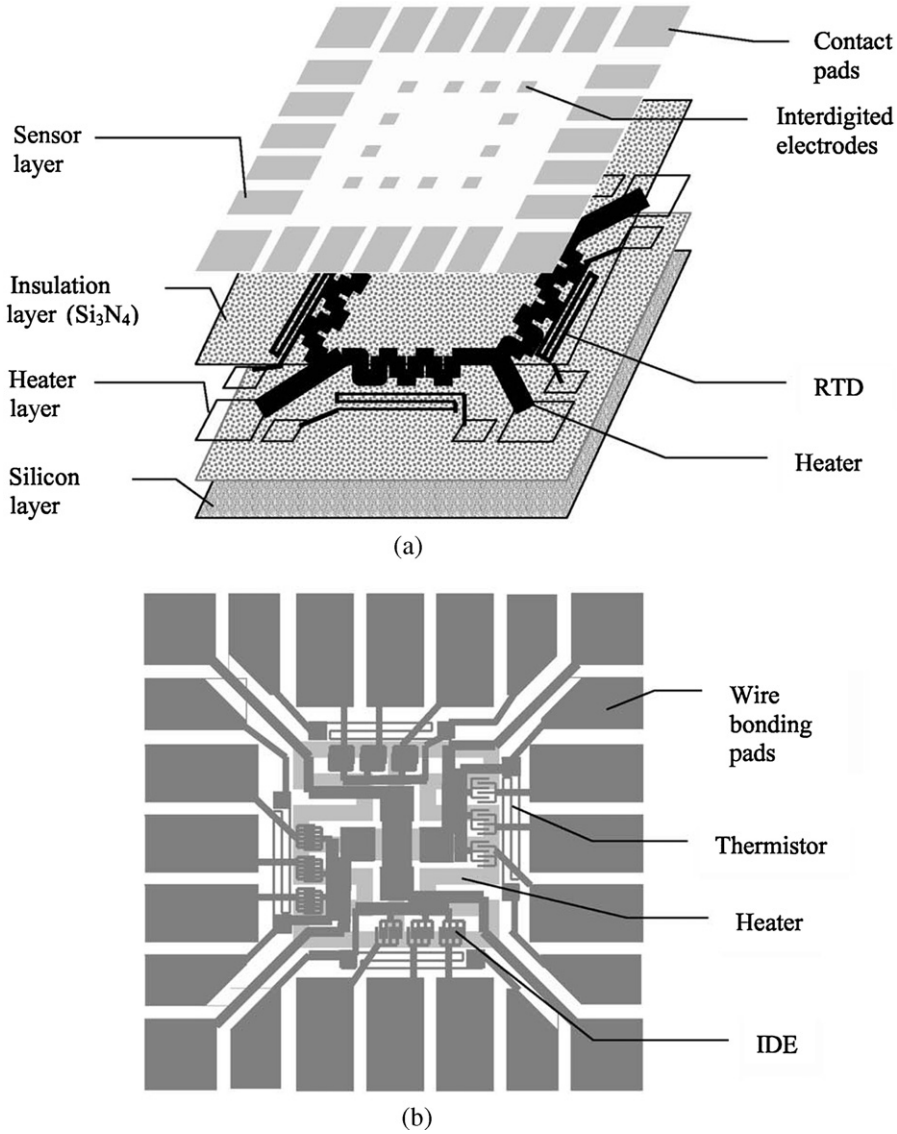

Fig. 6. Schematic view of the different layers composing the integrated sensor [18].

One approach to improve selectivity of CNTFET fabricated using SWCNTs mats, is to diversify the CNTFET metal electrodes. This concept has been developed by a joint-research team of Thales and École polytechnique in France (Nanocarb Lab.) [20–23]. More precisely, they exploited the mechanism described by IBM researchers, the modulation of the metal work function operated by gas exposure, to get the fingerprinting of a particular gas using a large network of CNTFETs. These last were fabricated using different metals for the contacts: the change of transfer characteristics of each transistor after gas exposure can identify a gas unambiguously. As prove-of-concept, the Nanocarb team manufactured CNTFETs composed by four different metals as electrodes: Au, Pd, Pt and Ti. The work functions for these metals are respectively 5.1 eV for the first two, 5.65 and 4.33 eV for the last [24–28]. They employed these metals in order to verify if the gas interaction was strictly related only to the initial work function difference between the different metals or if it depended on the nature of gas and electrode interaction.

The joint team performed several measurements using different electrode designs and these results were in close agreement with the initial hypothesis: it seemed that the sensor sensitivity was not influenced by the number of nanotubes linking the electrodes. The results obtained after exposure of CNTFETs transistors to 1 ppm DMMP at ambient conditions are shown in Table 1. From these measurements, researchers formulated the hypothesis that different metals interact in a different way with the DMMP. Particularly interesting was the result showing that the Pd and Au transfer characteristic changes were very different. This seemed to confirm that the effect of gas on CNTFET characteristics was not simply related to the initial metal work function but probably to a specific chemical interaction between the metal and the gas: apparently the DMMP molecules influence the metal work function in a specific way and thus the electric response of the transistor.

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

Current reduction after DMMP exposure	
Metals	I_{DS} current reduction % after exposure (1 ppm DMMP) error ± 5%
Ti/Pd	90
Ti/Au	65
Ti	50
Ti/Pt	20

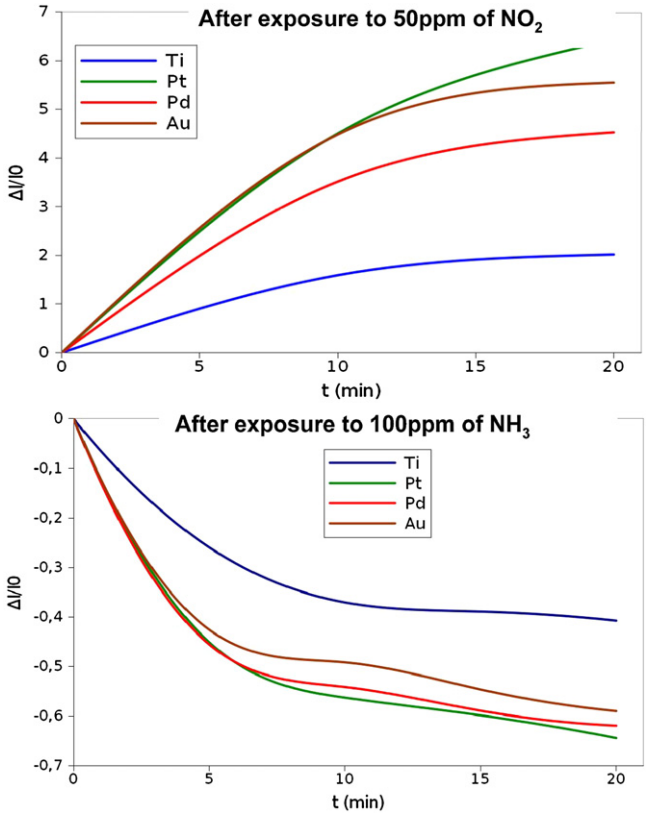

Fig. 7. Current change as a function of exposure time for two series of CNTFETs achieved using different metals as electrodes. The current ratio between after (I) and before gas exposure (I_0) is evaluated for $V_{ds} = 1$ Volt [29].

Recently new measurements have been performed using different gases: NH_3, NO_2. The results shown in Fig. 7, confirm that each gas seems to interact in a specific way with each CNTFETs characterized by different metal electrodes [29].

Another very interesting approach has been developed by researchers at Nanomix Inc. and Pittsburgh University. They exploited an idea firstly introduced in 2001 by J. Kong et al. of Stanford University [30]: to decorate the SWCNTs constituting the channel of a CNTFET with metal nanoparticles. They deposed nanoparticles of different metals on networks of SWCNTs connecting two Pd electrodes (Fig. 8). Therefore they fabricated an array of CNTFETs each one characterized by a different metal "decoration" [31,32]. They exposed this array to several gases (NO, H_2, CO, CH_4, H_2S, NO_2, NH_3 [32]) 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 a large array of "metal-decorated" CNTFETs could be used in order to recognize univocally the gases by identifying their electronic fingerprinting.

Regarding the physics of the phenomenon, researchers from Stanford, who had analyzed the electrical behaviour of one CNTFET decorated with Pd nanoparticles after exposure to H_2, stated that the H_2 dissociated on the Pd surface lowered the Pd work function. This reduction gave rise to an increased transfer of electron from Pd to SWCNT, naturally p-type, reducing the channel conductance. This hypothesis could explain the experimental results for H_2 but could not be applied for other gas species.

Kauffman et al. [32], failed to try an exhaustive explanation for the phenomenon but made a very interesting analysis. They underlined the main difference between the interaction of metal nanoparticles/SWCNTs and metal electrodes/SWCNTs. In the first case without any molecular interaction (exposure to gas), the nanoparticles acted exactly as inert hole scattering

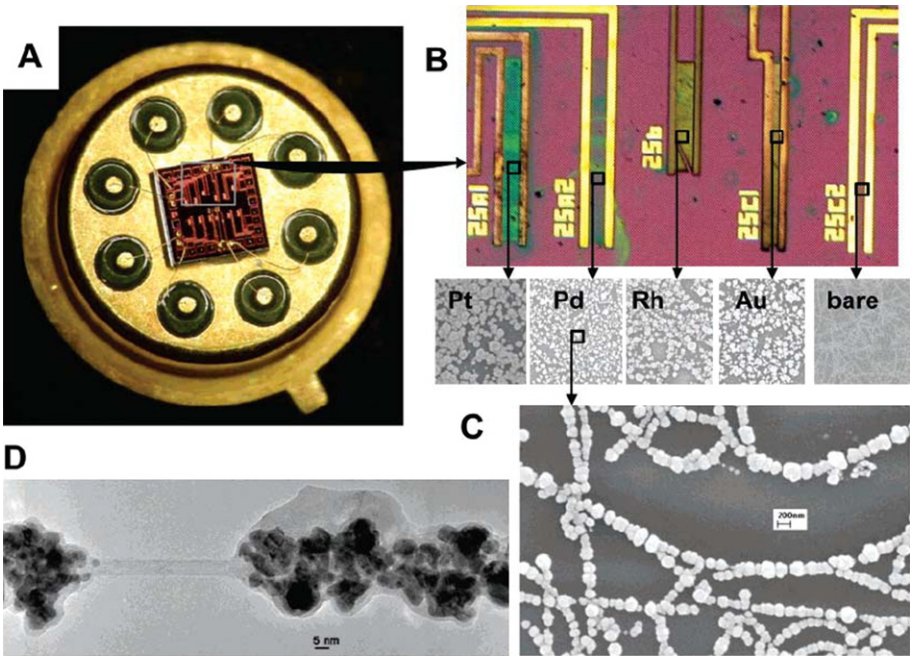

Fig. 8. (A) CNTFET based sensor chip. (B) Array of CNTFETs decorated using different metals. (C) SEM image of CNT with metal particles on their surfaces. (D) HRTEM image of Pd decorated CNTs [31].

sites, reducing mobility. Only upon molecular interaction their behaviour was exactly the same of the metal electrodes (Schottky barrier modulation caused by work function change).

5. Conclusions

In this article we have exposed different recent scientific works dealing with CNTFETs based gas sensor achieved using SWCNTs mats as channel. These devices show very promising performance for striking hugely the sensor market in the next years. Many advantages could be advanced: the extreme sensitivity, the very short response and recovery time, efficiency at room temperature, the low power consumption, the CMOS technology compatibility (relatively low cost). However we must demonstrate definitively the higher selectivity compared to existing technology. Different routes to improve selectivity, showing promising results, have been proposed. They are mainly based on the electrode metal diversification, metal particle deposition on the SWCNT mat. The common thing in all these approaches is the tendency to multiply the parameters (e.g. the metal electrode nature, the metal particles on the mat, the desorption rate) in order to develop a sort of matrix that will allow the accurate identification of the gas. This seems to be a suitable route to achieve a sort of selectivity with this kind of device. We could suggest that the utilization of these approaches jointly could improve dramatically the final device selectivity.

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