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Optimization of a carbon nanotubes manufacturing process by the technique of PECVD

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Abstract

Carbon nanotubes (CNT) are valuable for their application in nanotechnology, electrical properties and high surface area, and in our particular case, for the manufacture of nanosensors.
In this work the technique of Plasma Enhanced Chemical Vapor Deposition (PECVD) was used for the manufacture of CNT.
The process was conducted in a horizontal tube reactor using methane as precursor gas and an R.F. discharge of 1000w output power acting as ionizing medium. Having achieved the synthesis of CNT on copper (Cu) substrates, heated with an internal electrical resistance to a process temperature of 900 ºC, the substrates were coated with ferric nitrate $Fe(NO_3)_3$, which served as a catalyst and nucleation center. The heating system used differs from traditional methods by its internal heating. Growth of CNT was achieved on vertical walls on Cu substrates and perpendicular to it; a prerequisite for the manufacture of nanosensors, which is the main objective of this work, as well as to reduce as much as possible the diameter of the CNT, being its main features 5µm average length and 7 nm average diameter.

Keywords: Plasma CVD; nanotubes; nanosensors

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1. Introduction

This work shows a CNT production process (Lasorsa et al. 2010) for use in the manufacture of nanosensors (Perez et al. 2010), which constitute a basic tool in nanotechnology. A CNT based sensor is constituted by a network of CNT, and a pair of electrodes as signal transmitters (Fig.1). This is a kind of electrochemical sensor that is based in the charge's transfer from one electrode to another. Any alteration in the structure of the CNT will produce alterations in its electrical resistance, which will lead the modification of the signal, providing information about a change. The change could be chemical, as in gas sensors, or biological as in antigen/antibodies sensors (Fig. 2). This last kind of sensor is in advanced research stage (Lasorsa et al. 2010; Perez et al. 2010).

In previous work (Lasorsa et al. 2010) it was described the technique to produce CNT and other nanostructures, as well as the distinctive features of our process compared with conventional techniques. In that process the CNT and nanostructures are retrieved and dispersed in isopropyl alcohol, in spite of the growth of CNT between metal electrodes, preferably Cu, that was pending. With the purpose of physically building the structure of the nanosensor described previously, this growth process was done in this work.

This growth was achieved by employing as substrate a sample holder used in transmission electron microscopy (TEM), which played a dual role: one for observation of the CNT, and the other one to form the metal structure to support their growth, which would fulfill the role of the electrodes in the case of a nanosensor (Fig.1). It is important to note that their growth occurred without any contention, except for their attachment to the substrate, which shows the stiffness of its structure and, at the same time, that the lack of contention brought out its process of formation, giving rise to nucleation from a particle of *Fe* in a spherical shape with an outside diameter of 6nm to 12nm, and compact structure.

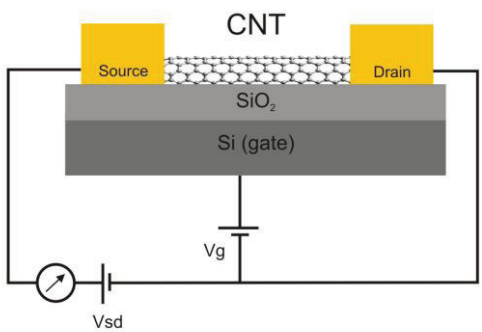

Fig.1: Structure of the biosensor.

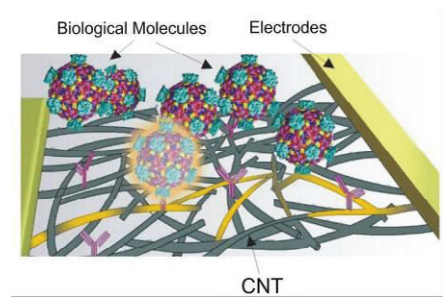

Fig. 2: Biological sensor.

The advantage of these nanodevices using CNT as a sensing element is that they have a huge specific surface which allows a great exposure, allowing the absorption of species that are still at very low concentrations and making these sensors elements of high sensitivity, with extremely fast response. This response is explained by the electronic configuration on the surface of the nanotube, leading to changes in the electrical current or voltage, when are exposed during a screening process to specific elements whose identification is sought. Applying this technology is intended to obtain sensors in micrometer scale. Achieving growth from a metal surface, and no other means of containment, is a decisive factor for the manufacture of nanosensors.

To the advantages described adds their small sizes (which in some cases do not reach the centimeter), low weight, in the order of grams, and low power consumption, which in some cases is limited to microwatts. While the actual sensors have a relatively high cost, it is legitimate to conclude that its standardization in the use will significantly decrease the cost, allowing its use in bulk. The growth of CNT directly on metallic structure of the sensor allows a large-scale industrial process that would enable this objective while avoiding the manipulation of CNT, which is a complex operation that requires special care and equipment.

The CNT are constituted by tubular structures whose diameter ranges from one to several nanometers, being the first single wall, and therefore the greatest sensitivity, and those beyond four or five nanometers are generally multiple wall, considering as the product of the winding of a sheet of carbon hexagonal structure (Fig. 3) on itself and in concentric form. CNT are an allotrope of carbon such as graphite, diamond, or fullerenes. The diameter and internal geometry depend on the method of manufacture, and of the variables used in the same (O'connell 2006; Tanaka et al. 1999). In our case the CNT were fabricated by plasma CVD technique (Lasorsa et al. 2010), and the applied variables are detailed in section 2. Fig 4, obtained by SEM, displays a set of CNT, the approximate dimensions of the CNT are: 8.5nm to 12nm in diameter and 1.5µm to 3 µm in length, showing the typical structure in the form of bamboo.

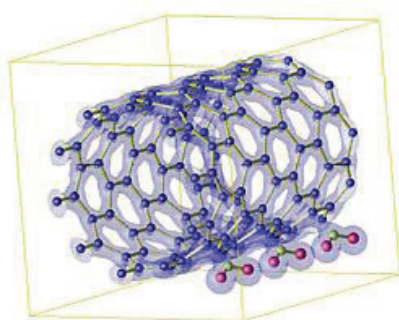

Fig. 3: Structure of a single wall carbon nanotube (SWCNT).

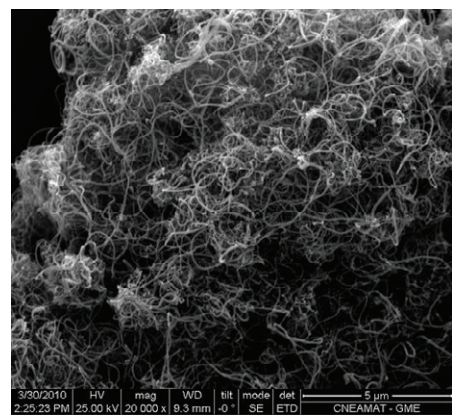

Fig.4: SEM. Cluster of CNT.

2. Experimental procedure

2.1. PECVD reactor

A PECVD reactor with a radiofrequency source of 13.56 MHz and output power of 1200 watts with an inductive coupling and impedance matching was used. Equipment characteristics are illustrated in Fig.5. It was designed and built expressly for this work. The vacuum chamber is formed by a pyrex glass tube 90 cm long and 15 cm internal diameter, at its ends possesses two closing bronze plates with manholes corresponding to entry of gases , systems access measurement, and a process gas diffuser built in a 0.10 cm diameter tube steel AISI 316. The diffuser was located on the samples at a distance of 8cm. The sample holder was constructed with a steel AISI 316 tube with a diameter of 0.5 cm, and heated internally with a

resistive cartridge (Termical). Unloading is effected by a system of two vacuum pumps acting in parallel to the effects of producing a dynamic vacuum, which ensures a permanent flow of methane.

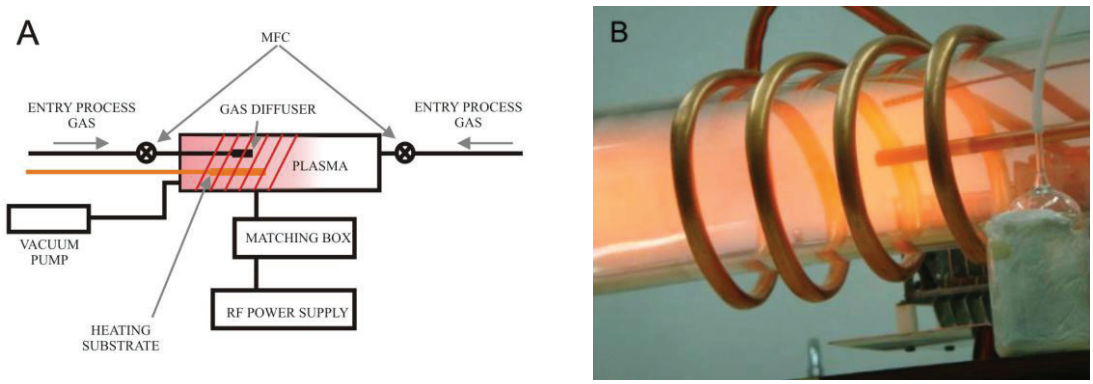

Fig.5: (a) Diagram of equipment used; (b) Photograph of the equipment in service.

Methane flow was controlled with an MKS mass flow controller. Methane of ultra high purity (UAP) was used. The initial pressures and work were measured with a capacitive Cindelvac. Morphology and dimensions were determined using a scanning electron microscope and transmission electron microscope (Klie et al. 2004; Liu and Cowley 1994; Liuand John M 1994).

2.2. CNT manufacture

On the heated central electrode of the reactor, provided with an internal resistive heating, were placed the sample holders of Cu (six in total per process), which were impregnated with a solution of ferric nitrate in isopropyl alcohol. The ferric nitrate solution was previously double filtered with paper filter (0.1 micron pore size and 47 mm diameter membrane from Omnipore. The sample holders were placed on the reactor, and proceed to the thermalization of the samples at 900 °C for thirty minutes in hydrogen plasma at a pressure of 400Torr. Completed the heating step, the process with the plasma of methane and hydrogen began, which enter through the same diffuser unlike what was done in our work cited previously (Lasorsa et al. 2010)#, establishing a working pressure of 650 Torr for six hours, and these conditions remaining constant throughout the process.

3. Results and Discussion

The CNT growth occurred inside the hollows of the sample holder, as well as in all zones impregnated with ferric nitrate solution, including the upper face. Thereof,, evidencing that the growth of the CNT depends on the location of the nucleating element (particles of Fe from the ferric nitrate) and the temperature. The plasma of methane and hydrogen acts indifferently in all zones of the sample holders exposed.

On the vertical faces of the substrate, the growth of CNT is in perpendicular direction to them (Fig.6, 7, 8, and 9). Growth in the upper faces of the substrate is in direction parallel to them (Fig.6). The morphological and dimensional characteristics of the CNT obtained were as follows: Multiple Wall, average length 5 μm, average diameter 7nm, carbon constituent element.

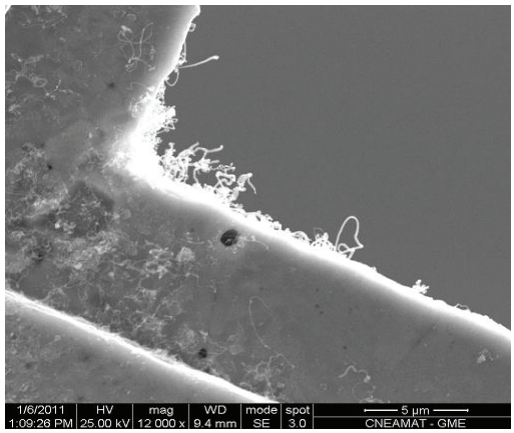

Fig.6: TEM image of the CNT grown on the upper side surface and lateral wall of the sample holder.

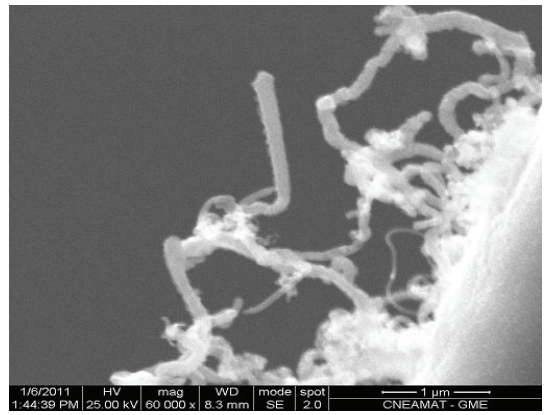

Fig.7: TEM image of the CNT grown on the lateral wall of the sample holder and perpendicular to the same.

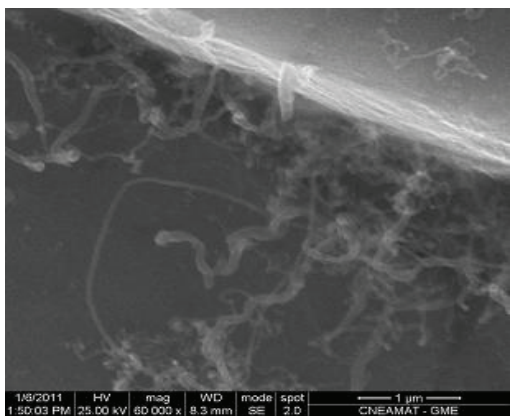

Fig.8: TEM image of the CNT grown in cell sample holder wall of Cu.

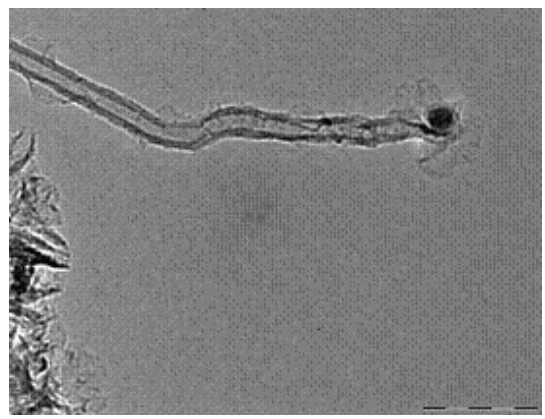

Fig.9: TEM image of the CNT grown in the sample holder wall with the particle of Fe on which has nucleated. Esc. 50nm. (Devaux and Vergnat 2008)

4. Conclusions

Once achieved the CNT growth on metallic substrates of vertical wall, the construction of the basic structure of the nanosensor in a single step was allowed. The possibility of incorporating CNT in a single process avoids manipulation, which is a complex operatory. Finally, an adequate size and geometry of the plasma reactor gives the possibility of producing a large number of structures of sensors in the same operation, which could allow introduce the production of these sensors on industrial scale.

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