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Structural Study of Micro and Nanotubes Synthesized by Rapid Thermal Chemical Vapor Deposition

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Abstract. The structures of micro and nanotubes obtained by pyrolysis of hydrocarbons, hold onto silicon (Si) substrates, are reported in this work. The tubes fabrication experiments were carried out by Rapid Thermal Chemical Vapor Deposition (RTCVD) using propane (C_3H_8) as carbon (C) precursor. Selection of parameters such as temperature of deposition, vacuum conditions or surface cleaning leads to the creation of tubular structures. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), selected area electron diffraction (SAED) and energy dispersive X-ray measurements (EDX) are the microbeam techniques that allow to characterize the tubes found in the studied specimens. Different tube configurations such as isolated nanorods, Y-type junctions or fiber-like layers are evidenced. Metallic catalysis seems to be the mechanism involved in the wires formation since Fe particles are present inside the CNT tubes. Other poly-crystalline inclusions are also evidenced by SAED. The composition of the nanotubes changes from tip to tail in an amorphous matrix. The growth mechanisms leading to tube formation are described.

Key words: Carbon nanotubes (CNT); rapid thermal chemical vapor deposition (RTCVD); transmission electron microscopy (TEM); scanning electron microscopy (SEM); energy dispersive X-ray microanalysis (EDX).

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Carbon nanotubes (CNT) are materials on fashion since electron microscopists discovered them in 1991 [1]. Indeed, tubular features in CNTs make them suitable to modulate conducting or insulating properties in opto and microelectronic devices [2], to enhance hydrogen diffusion using them as channels and to develop field emission displays acting as cathodes [3]. Also, these fibers have other fields of application in reinforced composite materials as for example nano-ropes [4]. The aim of this work is to demonstrate the synthesis of carbon micro and nanotubes by the reaction of propane with Si substrates surfaces and to show their structural characterization.

Experimental

The CNTs structures were fabricated in a RTCVD equipment that has previously demonstrated to be useful in the fabrication of silicon carbide (SiC) layers by carbonization of Si surfaces [5]. In this way, pieces of (111) Si wafers are loaded in the process chamber and subsequently the chamber is pumped down to a base pressure of 100 Pa. Previous cleaning of the surfaces to be treated consists of rinsing the samples for 5 min in diluted fluorhidric acid (5% HF in H_2O), acetone and ethanol respectively. The key factor in this CNT synthesis is that the reactor was not cleaned with flowing H_2 at high temperatures as usually is applied. In this way, remaining impurities that belong to the process chamber play an important role since the reactions occur inside an Incoloy MA956 (Fe/Cr/Al) alloy pipe heated by a resistance tubular furnace powered by 6 kW.

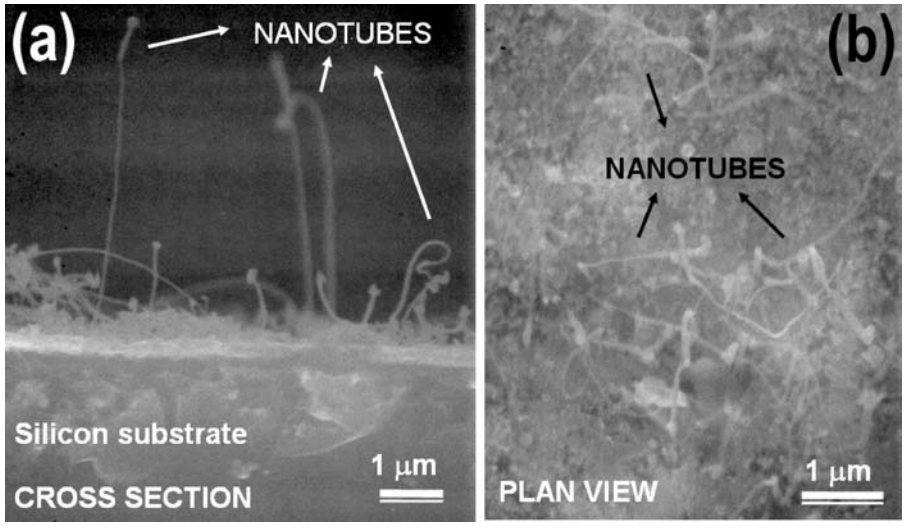

Fig. 1. Cross section (a) and plan view (b) SEM micrographs where the general structure of synthesized nanotubes is presented

The growth process consists of rapid thermal heating of Si surfaces at the same time that a mixture of $0.5\,\mathrm{L\,min^{-1}}$ of H_2 (carrier gas) with a low percentage of C_3H_8 (0.01–0.03%) is flowing. The fixed temperature inside the reactor tube is about 1200 °C and the reaction lasts 1.5 minute. In this course, the samples change from ambient temperature to 1000 °C where the corresponding heating ramp rate is about $10\,^{\circ}\mathrm{C\,s^{-1}}$. These conditions are sufficient to allow the rupture of the hydrocarbons molecules and the deposition of carbon on the Si surfaces.

The structural studies of the fabricated tubes were executed by transmission electron microscopy in both conventional and high-resolution modes (CTEM-HRTEM), scanning electron microscopy (SEM), selected area electron diffraction (SAED) and energy dispersive X-ray (EDX) measurements. In order to carry out TEM analysis, samples prepared in cross section mode (XTEM) were joined on grids that allow the direct TEM visualization without further preparation because the incident electron beam remains parallel to the grown surface plane. For plan view TEM analysis (PVTEM), the sample was prepared by classical methods of mechanical thinning and ion milling. Specimens were not subjected to any sample preparation for the rest of techniques. CTEM and SAED experiments were carried out in a JEOL JEM-1200EX electron microscope and a JEOL JEM-2000EX/THR was used for HRTEM experiments. The equipment used for SEM and EDX is a JEOL 820 JSM electron microscope equipped with a "LINK" commercial system for microanalysis.

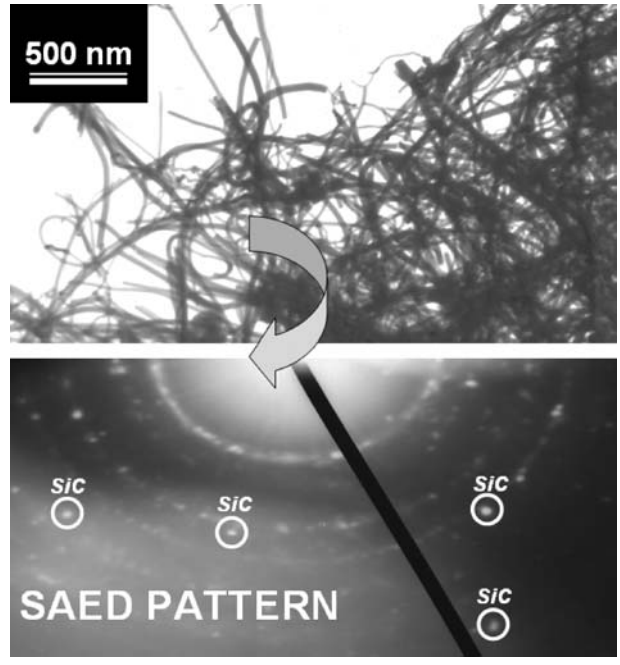

Fig. 2. A TEM micrograph of a fiber-like structure (a) and a SAED pattern of a similar region (b) that shows rings and isolated diffraction dots corresponding to dispersed poly-crystals. Spots encircled in this pattern are associated to poly-crystalline SiC

Results and Discussion

Different tubes configurations were observed in the experiments. Figure 1 shows a cross section SEM image (a) and a plan view SEM image (b) with some of these arrangements. From these micrographs, it is concluded that the tubes sizes are variable growing until some microns in length and tens of nanometers in width. Figure 2(a) is a PVTEM image of a fiber-like region where a lot of tangled nanotubes are shown. Figure 2(b) is a detail of a SAED pattern registered from a region near the surface from a XTEM preparation. This pattern possesses a lot of isolated diffraction dots and rings that give an idea of the poly-crystalline nature of this base region. These diffraction spots are due to cubic and hexagonal poly-types of SiC crystallites (see examples as encircled spots) and other phases that could not be assigned unambiguously. The bigger poly-crystals

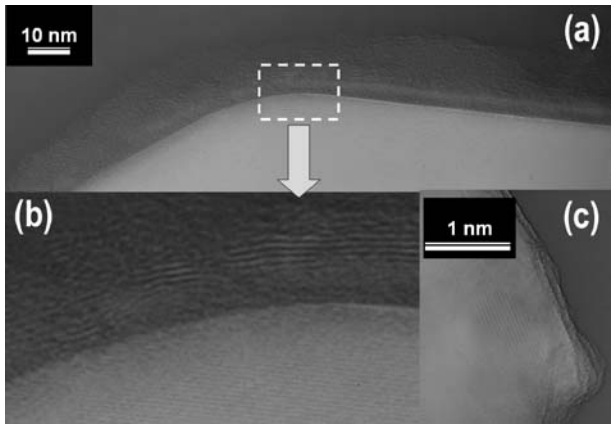

Fig. 3. HRTEM images of two different poly-crystalline structures (a and c) found among the tubes structures. Part (b) of this figure is a magnified detail of the region labelled in (a) where planes corresponding to the inclusion network are clearly visible

are deposited among these fibers but do not belong to the CNT inner structures. Figure 3(a) and (c) show two HREM micrographs taken from two of these dispersed inclusions and Fig. 3(b) is a detail of the area labeled into a dotted line square in part (a) of Fig. 3. In the latter structure, planes having a lattice parameter of 0.29 nm are visible.

In some cases, there is a clear accumulation of characteristic features in the tubes tips. From this point, these features will be named ''heads''. A detailed TEM study of the inner part of these heads let us to discover that just inside the heads there are placed big poly-crystals, if they are compared with the tube width. Figure 4(a) exhibits two of these long nanowires and a mesh composed by tubes near the surface. Part (b) of this figure shows a detail of one of these heads with the contrast inverted to allow a better visualization. In this image, the crystal placed on top of the tip is clearly displayed and small crystallites near the head are also visible. Figure 4(c) is a HREM image focused at one of these heads. Here, a cylindrical structure about 70 nm of diameter is placed inside an amorphous matrix. This amorphous structure is associated with the carbon that is filling the tube skeleton and can be seen as typical amorphous contrasts inside the tubes structures of the same image.

EDX analysis of the tip region of one of the bigger nanotubes showed the presence of Fe in these structures. In this way, thermal catalytic CVD is the accepted mechanism for explaining the wires formation. Fe particles due to contamination are essential precursors in the growth of non-aligned carbon nanotubes. Other researchers have previously shown that 750 or 1100 °C are the minimum temperatures needed for similar Fe catalyzed processes using C_2H_2 or C_2H_4 respectively [6]. In the present experiments, a temperature of 1000 °C is sufficiently high for CNT

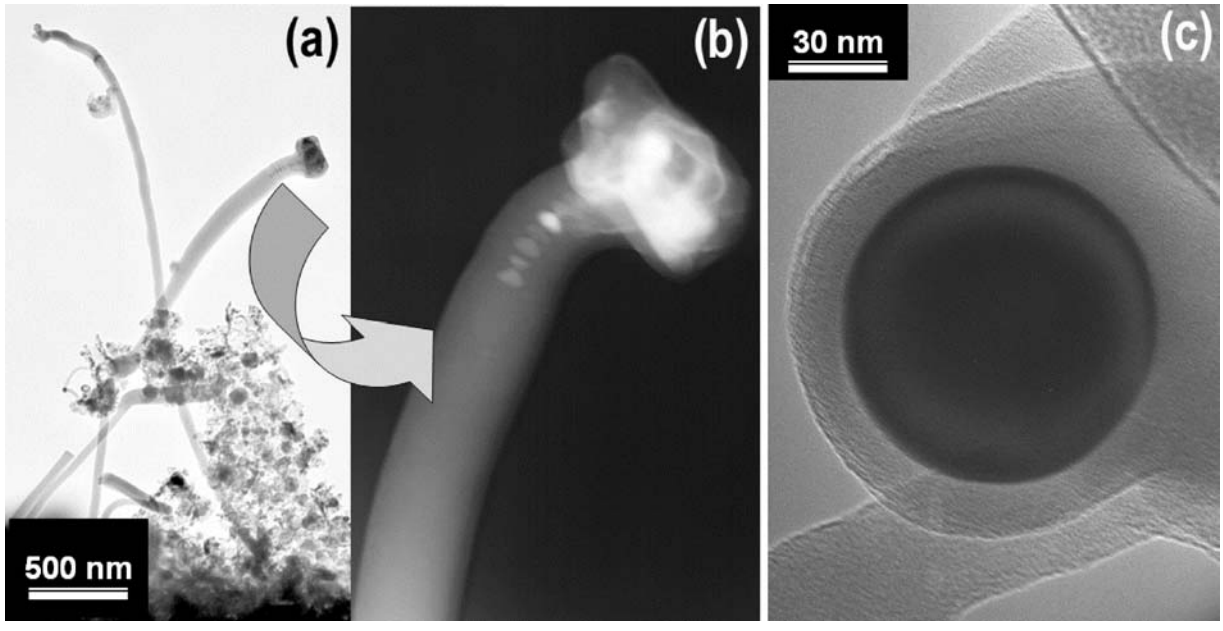

Fig. 4. TEM image (a) and detail (b) that show a big crystal placed inside a carbon nanotube head. The HRTEM micrograph (c) shows other particle located in a tip and the amorphous structure of carbon that fills the entire tubes

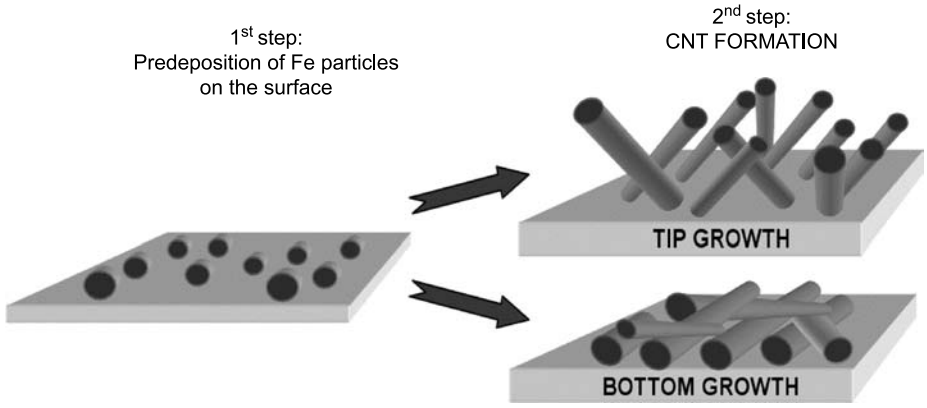

Fig. 5. Schematic overview of the mechanisms involved in both ''tip'' and ''bottom'' growth

formation. According to the literature [6], metallic particles keep deposited onto the Si substrates and they act as nucleation sites on the surface, promoting the rupture of hydrocarbons molecules. Later on, carbon atoms firstly diffuse towards the inner part of the metallic phases and subsequently raise the substrate by an enhanced thermal gradient. If metal particles remain adsorbed on the substrate, fiber-like films as the shown in Fig. 2(a) are created. This behavior is called ''bottom growth''. On the contrary, if a Fe particle is lifted up from the substrate, remaining in the head of the growing nanotube (see for example Fig. 1(a) or Fig. 4(a)), then the ''tip growth'' is obtained. In both cases, the dimensions of the tubes are highly marked by the metallic particle size. These mechanisms of formation are briefly summarized in the schematic picture of Fig. 5.

Conclusions

In conclusion, thermal catalytic chemical vapor deposition has demonstrated to be a useful method to fabricate carbon nanotubes on Si substrates.

Electron beams analysis techniques as TEM, SEM and EDX proved to be appropriate for characterizing these kinds of structures created by employing the catalytic activity of Fe impurities.

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