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Growth kinetics of low temperature single-wall and few walled carbon nanotubes grown by plasma enhanced chemical vapor deposition

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Abstract

Single-wall, double walled or few walled nanotubes (FWNT) are grown by electron cyclotron resonance plasma enhanced chemical vapor deposition (ECR-PECVD) at temperature as low as 600 °C. Most of these structures are isolated and self-oriented perpendicular to the substrate. The growth mechanism observed for single-wall and few walled (less than seven walls) nanotubes is the "base-growth" mode. Their grow kinetics is investigated regarding two parameters namely the growth time and the synthesis temperature. It is shown that nucleation and growth rate is correlated with the number of walls into FWNT. It also provides an evidence of a critical temperature for FWNT synthesis.

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1. Introduction

Carbon nanotubes (CNTs) have become one of the most promising nanostructure in the emerging field of nanosciences. Taking advantage of the exceptional properties of CNTs, nanoscale prototypes as bio or gas sensors, nano electro mechanical systems (NEMS) or CNTs transistors have already been achieved [1–3]. One of today's challenges is to succeed the direct CNTs growth following nanoarchitectures with a precise location control. Mastering this process would open new perspectives in CNTs-based devices production. Another important challenge is to decrease the growth temperature to ensure compatibility with MOS technology.

For these two reasons, plasma-enhanced chemical vapor deposition (PECVD) appears as a very attractive process especially for its ability to grow CNTs at low temperature (<600 °C) [4] on patterned catalyst particle [5]. In addition, PECVD allows the growth of CNTs oriented perpendicular to the substrate thanks to the intrinsic electrical field into the plasma sheath [6]. But, until recently, PECVD process has been only dedicated to the synthesis of multi-wall nanotubes (MWNT). However, single-wall nanotubes (SWNT), double-walled nanotube (DWNT) or other few walled nanotube (FWNT) are of greater interest due to their important potential application. Newly, it has been shown that with standard plasma configurations, FWNT growth can be somewhat thwarted by plasma species [7]. This can explain why other works usually report the use of a remote plasma for SWNT grown by PECVD process [8–10]. Nevertheless, without biasing the substrate, SWNT do not exhibit the self-alignment and are organized as bundled "spaghetti-like" [8]. In addition, most of these studies are performed on catalyst-supported powders that inhibit any preferential orientation [9,10].

In this work, CNT synthesis is performed by electron cyclotron resonance-PECVD (ECR-PECVD). Isolated and self-vertically oriented SWNT, DWNT or FWNT are grown successfully at several temperatures, as low as

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600 °C. Hydrogen, used here as dilution gas seems to be more appropriate than NH_3 for FWNT synthesis [7]. Therefore we use C_2H_2/H_2 mixture in order to study FWNT growth kinetics regarding two parameters namely the growth time and the synthesis temperature.

2. Experimental

CNTs are grown on thermal oxidized silicon flat substrate in a vacuum chamber with a typical residual pressure below 2.10^{-5} Pa. Permanent magnets coupled with micro-wave (2.45 GHz) injected trough an antenna ensure the ECR effect and generate thus a low pressure (0.2 Pa) high density ($n_e = 10^{10}\,cm^{-3}$) plasma at the top of the chamber. A biased grid, located downstream the ECR source controls the plasma diffusion in front of the grounded heated substrate holder. Both steps, catalyst preparation and nanotube growth, take place in this same reactor following the process described in detail elsewhere [11]. Briefly, the steps are summarized below.

1. Pure ammonia plasma sputters a cobalt wire (biased at −300 V) located over the substrate during 5 min. An ultra-thin Co film is obtained with a thickness ~1.5 nm evaluated by X-ray photoelectron spectroscopy (XPS). The substrate holder is then heated up to the synthesis temperature (500–700 °C). The catalyst thin film is therefore reshaped into nanoscale particles with an average diameter of 3–4 nm (measured by transmission electron microscopy—TEM).
2. Without breaking the vacuum, 1.2 sccm of C_2H_2 diluted in 13.1 sccm of H_2 (1:12) is introduced in the chamber. An ECR plasma is then generated for nanotube growth at 0.2 Pa and 250 W. Plasma potential is set by the grid, biased at 200 V.

As-grown nanotubes are characterized by scanning electron microscopy (SEM), performed on JEOL JSM 6400 F1 apparatus. Samples are micro-delaminated with a diamond tip and directly transferred on the TEM grid. The CNTs structure is analyzed with a field emission gun transmission electron microscopy (FEG-TEM; Hitachi HF 2000) operating at 200 kV.

3. Results

For two synthesis temperatures (700 and 600 °C) we have studied the evolution of FWNT at different moments: after 15 and 60 min of C_2H_2/H_2 plasma. We have also decreased the synthesis temperature down to 500 °C.

After 15 min of C_2H_2/H_2 plasma discharge at 700 °C, SEM characterization shows dispersed and quite vertically oriented CNTs (Fig. 1(a)). From these SEM pictures one can easily estimate CNTs length, but not their diameter due to the limited resolution of the microscope (~10 nm). Even if some 400 nm long CNTs can be observed, a large majority of CNTs has lengths between 150 and 200 nm. From these results, we can get an estimation of the growth rate of ~2 Å s^{-1}. Such growth rate enables us to analyze the early stages of the CNTs synthesis, as it was done for another gas mixture (C_2H_2/NH_3 plasma [7]). TEM images reveal predominantly SWNT (Fig. 1(c)) and DWNT (Fig. 1(b)) with an average diameter of 2 and 1.9 nm, respectively (inner diameter for DWNT). Most of CNTs are isolated, but some small SWNT bundles can also be observed (Fig. 1(b)). Otherwise, many catalyst particles surrounded by turbostratic carbon are identified around the bottom end of the CNTs (Fig 1(b)). From these TEM observations, it is difficult to assert if they are poisoned or if they represent MWNT nuclei in the early stages of a "tip-growth" mode.

Decreasing the temperature at 600 °C but keeping unchanged the others plasma parameters (15 min synthesis time, C_2H_2/H_2, etc…), very few nanotube structures can be observed (Fig. 2). Only nanoparticles surrounded by turbostratic carbon are distinguished by TEM (not shown).

Let us now increase the synthesis time to 60 min. At 700 °C, nanotubes observed by SEM are quite long (average length ~250–350 nm) and exhibit preferential vertical alignment (Fig. 3(a)). TEM analysis shows many well-graphitized DWNT (Fig. 3b and c) and other FWNT with more walls (Fig. 3(b)) without any catalyst particles on their tip. Seven walls can be counted for the larger well-graphitised FWNT observed by TEM. The majority of FWNT is isolated even if some bundles composed by few nanotubes can also be observed (Fig. 3(c)). In fact, FWNT surface density is quite high, and lateral Van der Walls interactions become significant with respect to vertical attraction due to the plasma sheath. Besides, very short (<50 nm) MWNT and nanofibers with large diameters ($10<d<25$ nm) following the "tip-growth" mode are also distinguished. Contrarily to FWNT, the number of wall into these structures seems to be unbounded (15–20 walled nanotubes are typically observed).

In comparison with sample obtained after 15 min, we can see after 60 min at 700 °C an elongation of CNTs structures. However, the average growth rate is twice lower than during the first quarter of hour (only ~1 Å s^{-1}, assuming a constant growth rate over the 60 min of plasma synthesis), indicating a nonlinear behavior of the SWNT and DWNT growth.

Concerning the sample performed at 600 °C after 1 h of C_2H_2/H_2 plasma discharge, we can observe a very scarcely growth of FWNT ($<5\,\mu m^{-2}$). Nevertheless, one can note their very straight perpendicular orientation to the substrate when sample is tilted at 90° (Fig. 4(a)). TEM investigation reveals that isolated FWNT coexist with a large majority of catalyst particles surrounded by turbostratic carbon. (Fig. 4(b and c)). Decreasing the synthesis temperature at 500 °C, none nanotube structures could be detected, but only nanoparticles embedded into amorphous/turbostratic carbon similar to those already observed at 600 °C (Fig. 4(b)).