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Oriented growth of suspended single wall carbon nanotube by Hot Filament CVD

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Abstract

The feasibility of the Hot Filament assisted CVD (HFCVD) technique to favor the catalytic growth of carbon nanotubes has been investigated. Single wall nanotubes (SWNT) with a high degree of crystallinity and purity have been grown with a density which could be varied by changing either the catalyst thickness or the synthesis conditions. In particular, one aspect of the technique was to allow self assembling of suspended bundles or isolated SWNTs.

Keywords: Carbon nanotubes; Catalytic hot-wire CVD; Atomic force microscopy; Raman spectroscopy

1. Introduction

SWNTs are formed by rolling up a graphene sheet. One of their characteristics is their high aspect ratio with diameter in the nanometer range, but length which can reach a few hundreds micrometers. A second characteristic is that they can be either semiconducting or metallic, depending on their diameter. As 1D molecule, SWNTs are very attractive both in the field of nanoscience and nanotechnology.

Since the discovery of carbon nanotubes by Iijima [1], SWNTs have been mass-produced by arc evaporation [2] and laser vaporisation [3] of graphite with embedded catalyst particles. Recently the possibility to grow SWNTs by CVD techniques using catalyst particles deposited on a surface has opened up the ability to localize SWNTs at determined placement [4,5] and thus to prepare devices by a self assembling process [6].

Up to now, the HFCVD technique was mostly used to grow MWNTs, either plasma assisted [7] or not [8]. There are very few results reporting the HFCVD growth of SWNTs. The continuous generation of SWNTs has been obtained by HFCVD [9]. However, the use of ferrocene as the gas precursor for the catalyst did not allow the nanotube growth with specific surface placement.

In this letter, we show that the HFCVD technique not only leads to the growth of well crystallized SWNTs, but has also the ability to localize and self assemble suspended isolated SWNTs [10].

2. Experiment

The HFCVD apparatus has been built for diamond thin film growth [11]. For the synthesis of SWNTs, substrates have been covered with a 0.5–4 nm thick Co catalytic layer deposited by standard evaporation techniques and the synthesis parameters have been adjusted. Typical deposition parameters were a 5–20 vol.% CH_4 proportion in hydrogen, a 750–850 °C substrate temperature and a 30–100 mbar total pressure. The tungsten filament, placed 1 cm above the substrate, was heated up to 1900–2100°C.

During the synthesis, in situ measurements of the reflectivity and elastic scattered light of a 633 nm laser radiation gave insight into real time growth kinetics.

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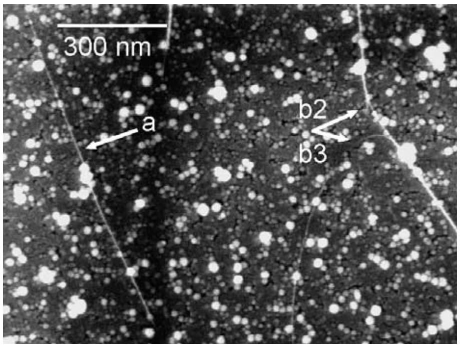

Fig. 1. SEM image of SWNTs grown on a thermally oxidized Si substrate with a 2-nm thick cobalt layer. Arrows underlined the position of the SWNTs: a straight one (a) and a small bundle (b_1) which splits off into two thinner ones (b_2, b_3).

Raman characterization was undertaken using a Dilor LabRam Infinity microRaman spectrophotometer equipped with a 633 nm laser focused on a ~1 μm^2 area.

Imaging of the sample was undertaken with a LEO 1530 HRSEM and a Digital Dimension 3100 AFM apparatus.

Observation of our CNTs has been achieved by HRTEM at ONERA. It was performed on a Philips CM20 microscope with an acceleration voltage of 200kV.

Starting substrates were silicon wafers covered with a thin 0.5–4 nm Co layer deposited at room temperature. Depositions were undertaken either on flat substrates or on patterned ones with 130 nm high Si pillars with size 200 nm and different interdistances.

3. Results and discussion

3.1. SWNT growth

Fig. 1 shows a typical SEM image of the sample morphology for HFCVD deposition on thermally oxidized silicon substrates with a 4 nm Co layer. A few CNTs are observed among numerous particles. Some are very straight (see the CNT identified as a in Fig. 1) with sections that are clearly visible, other merged in the substrate surface. Surrounding particles are also often observed. Small bundles appear generally to be wavy (b_1 in Fig. 1) and sometimes present the peculiarity to separate into branches (b_2, b3 in Fig. 1).

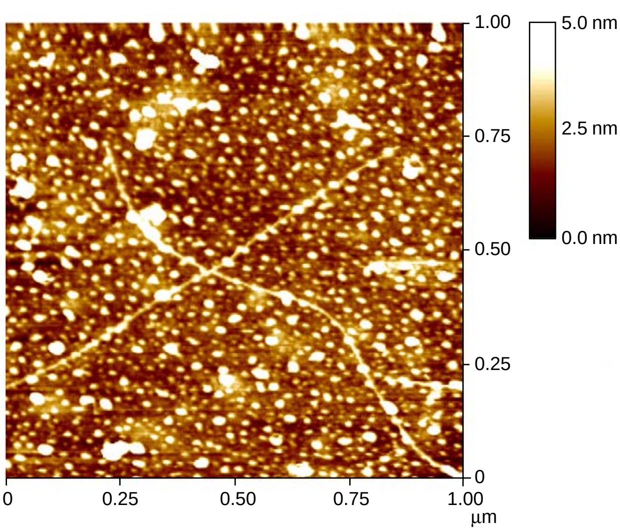

Fig. 2. AFM topography of SWNTs grown on a thermally oxidized Si substrate which puts forward two crossing nanotubes surrounded by catalytic particles.

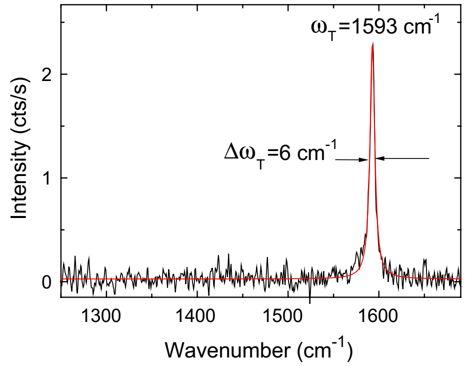

Fig. 3. Raman signal corresponding to the tangential modes of SWNTs deposited on thermally oxidized Si substrate and its Lorentz fit into three peaks at 1599 cm^{-1}, 1590 cm^{-1}, 1581 cm^{-1} with 5–7 cm^{-1} width at half maximum.

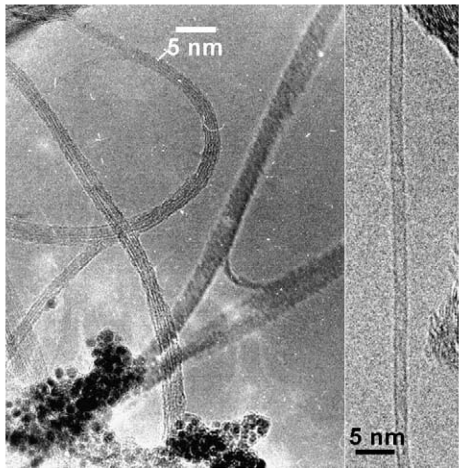

Fig. 4. TEM observations of an isolated SWNT and small SWNT bundles synthesized on Mo grids covered with a 2-nm thick Co layer.

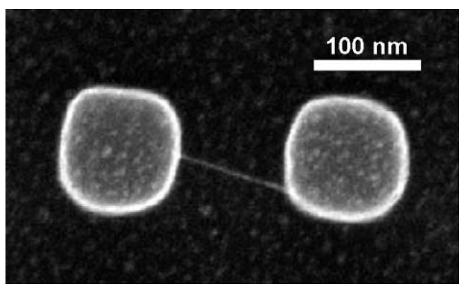

Fig. 5. SEM images of suspended SWNTs (in the limit of an isolated SWNT) self assembled by HFCVD between thermally oxidized Si pillars with a 200-nm interdistance and capped with a 2-nm thick Co layer.

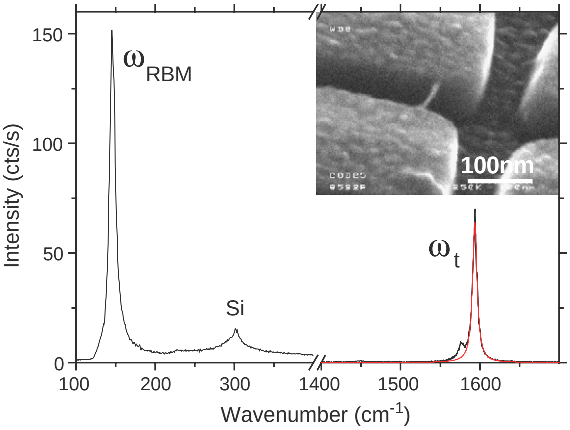

Fig. 6. Raman spectrum of suspended SWNTs between Si pillars with a 100 nm interdistance and capped with a 2-nm thick Co layer. The RBM peak at $\omega_{\mathrm{RBM}}=145$ cm^{-1} with the narrowness of the tangential peaks (at $\omega_t=1594$ cm^{-1} and 1594 cm^{-1} with 7–9 cm^{-1} width at half maximum) point out a semiconducting SWNT. The Raman band at 302 cm^{-1} originates from the Si pillars. In inset is shown a typical SEM image of the template.

Fig. 2 shows a topographic AFM image of a sample prepared under same conditions as in Fig. 1. It puts forward two crossing CNTs surrounded by catalyst particles. CNTs and particle diameters have been estimated from height analysis of the AFM images (Fig. 2). Typically, CNT heights are in the 1–3 nm range, which is compatible with the formation of isolated SWNTs or small SWNT bundles. The particle heights are of the same order, but extend to higher values (1–5 nm).

The formation of SWNTs is also reinforced by the Raman spectrum shown in Fig. 3. The Raman peak at 1593 cm^{-1} corresponds to the tangential modes of a SWNT [12]. The narrowness of the band (6 cm^{-1} width at half maximum) with indiscernible Raman signal around 1325 cm^{-1} originating from disordered graphite is a strong indication of the high crystallinity and purity of the SWNTs.

Finally, the HFCVD growth of SWNTs which can be either isolated or packed in small bundles has been definitely demonstrated by TEM observations of deposits on Mo grids with a Co top layer (Fig. 4).

3.2. Self assembled SWNT on Si pillars

With the objective to prepare devices, HFCVD syntheses have been undertaken on templates composed of Si pillars encapsulated with Co.

As shown in Fig. 5, adjustment of both the catalyst film thickness and synthesis parameters has allowed the growth of SWNTs which are suspended between neighbouring pillars. They appear so thin that it suggests they are isolated or in small bundles.

The formation of isolated SWNTs is reinforced by the narrowness of the tangential Raman mode at 1593 cm^{-1} (Fig. 6) with a 7 cm^{-1} width at half maximum. Moreover, it has been observed that one characteristic of suspended SWNTs was the strong intensity of the Radial Breathing mode (145 cm^{-1} in Fig. 6) which was rarely observed for sparse SWNTs in van der Waals interaction with a substrate.

Similar carbon nanotube growth morphology has recently been obtained by Homma et al. [5] by means of methane CVD on ultrafine oxidized silicon patterns recovered by a thin Co or Fe layer. Connection of the nanotubes between nearest neighbour pillars was attributed to the swing of the growing nanotubes and their connection to a catalyst particle in liquid phase.

4. Conclusion

The HFCVD technique appeared to be powerful to grow highly crystalline and pure SWNTs by taking advantage of the catalytic properties of a thin cobalt layer. In particular, adjustment of the substrate preparation and synthesis conditions allowed to self assemble isolated SWNTs which can be suspended between Si pillars. The HFCVD technique is thus very well adapted for batch processing of devices.

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