G. Bertoni et al. Carbon 42 (2004) 440–443

Growth of multi-wall and single-wall carbon nanotubes with in situ high vacuum catalyst deposition

G. Bertoni [a,b], C. Cepek [c,*], F. Romanato [d], C.S. Casari [e], A. Li Bassi [e], C.E. Bottani [e], M. Sancrotti [b,c]

[a] Università degli Studi di Milano, via Celoria 16, I-20122 Milan, Italy
[b] INFM and Dip. di Matematica e Fisica, Università Cattolica del Sacro Cuore, I-25121 Brescia, Italy
[c] Laboratorio Nazionale TASC-INFM, Strada Statale 14, km 163.5, I-34012 Trieste, Italy
[d] Laboratorio Nazionale TASC-INFM, Lilit Group, Strada Statale 14, km 163.5, I-34012 Trieste, Italy
[e] INFM and Dip. di Ingegneria Nucleare, Politecnico di Milano, Via Ponzio 34/3, I-20133 Milan, Italy

Keywords: A. Carbon nanotubes; B. Chemical vapor deposition; C. Atomic force microscopy; X-ray photoemission spectroscopy; Raman spectroscopy

In the last few years, carbon nanotubes (CNTs) have attracted a great interest, due to their unique electronic and mechanical properties [1]. The growth via chemical vapor deposition (CVD) allows obtaining high quality CNTs at a large scale [2–8]. Generally a metal catalyst is needed for the synthesis and, by choosing the appropriate growth conditions, it is possible to obtain single- or multi-wall carbon nanotubes with controlled average diameter and length [1,2,5]. The catalyst metallicity is crucial for the CNTs growth, and generally the CNTs diameter depends on the catalyst cluster dimensions. The catalyst may be pre-deposited on the surface (*surface CVD*) before the CVD process [2–9], or may be introduced into the flowing carrier gas (*gas phase CVD*) [10–13]. In CVD with a supported catalyst film, it is possible to reduce the nanotubes diameter by reducing the catalyst film thickness: single-wall carbon nanotubes (SWCNTs) are obtained, even if they are generally mixed with multi-wall carbon nanotubes (MWCNTs) [9]. An efficient film for SWCNTs growth was obtained starting from a solution containing metal nanoparticles of the catalyst [3–5]. This method is time-consuming in the catalyst preparation, implying heating of the catalyst solution for hours and grinding into powder of nanometric scale. SWCNTs were observed during carbon evaporation on a thin pre-deposited catalyst film in ultra high vacuum conditions [17]. However the tubes grown with this method are very short (50 nm) and the resulting growth yield is low. The *gas phase CVD* [10–13] results also very efficient for SWCNT growth.

Here we describe an efficient procedure for the synthesis of multi- and/or single-wall carbon nanotubes. It is based on CVD process using merely acetylene as precursor gas and starting from a catalyst film deposited under high vacuum (HV) conditions (base pressure: $\sim 10^{-8}$ mbar) just before the CVD process. The use of HV is not favorable regarding the economics in a production process, however no hydrogen, ammonia or any other time-consuming pre-treatment of the catalyst film are needed. This reduces the total time (i.e. catalyst film preparation and CVD process) for CNTs synthesis to 15–40 min (principally depending on catalyst thickness, see below), which has to be compared to the typical time needed in the other methods based on a supported catalyst film (i.e. several hours [3]). Actually, in several CVD processes, the pre-treatment of the catalyst film with hydrogen and/or ammonia is crucial [15], and the CNTs grow if hydrogen and/or ammonia are used in well defined relative fluxes together with the hydrocarbon gas [16]. These pre-treatments act to reduce the thin oxide film of the catalyst to form metallic nanoparticles. For a deeper understanding of the role of the catalyst and of its oxidization state, and for a deeper control of the CNTs growth, we have compared the CVD growth of carbon nanotubes on metallic and oxidized Fe and Ni films. When the catalyst is oxidized, only an amorphous carbon film grows, consisting of carbon-coated particles with some embedded tubes. If the film is not oxidized, it is possible to grow the nanotubes also when the catalyst thickness is as low as 1 nm and in this case the grown CNTs are isolated SWCNTs.

The synthesis of CNTs was performed in the Analytical Division of the National Laboratory TASC-INFM (Trieste, Italy) on SiO_2 films (100 nm thick) grown on Si wafers. The metals catalysts (Fe and Ni, purity: 99.9%) were deposited in situ on the substrates by sublimation from direct heated filaments, just before the growth. The sublimation temperature was ~875 °C for Fe and ~925 °C for Ni, obtaining a deposition rate, as measured by X-ray photoemission spectroscopy

---

[*] Corresponding author. Tel.: +39-040-375-6436; fax: +39-040-226-767.

E-mail address: cepek@tasc.infm.it (C. Cepek).

(XPS), of ∼0.3 and ∼0.5 nm/min, respectively. The films thickness, for both Fe and Ni, varied from ∼1 to 15 nm. The quality of the catalyst film and its oxidation states were studied by means of XPS in situ, just after the catalyst deposition. XPS data were measured using a non-monochromatized Al X-ray source ($h\nu = 1486.6$ eV) at normal emission geometry with an overall instrumental energy resolution of ∼1.1 eV.

Before CNT growth, the samples were pre-annealed for ∼10 min at ∼650–700 °C by direct heating. The annealing causes the coalescence of the metal film in nanometric islands, whose diameter distribution depends on the starting film thickness and on the annealing temperature [2,8]. After annealing, acetylene was introduced as carbon precursor gas from a nozzle (∼1 mm), with a nozzle-to-sample distance of ∼20 mm. During the CVD process the substrate has been kept between 650 and 700 °C. The acetylene flow was 100sccm, resulting in a background pressure of $\sim 1 \times 10^{-2}$ mbar. The time of growth varied from 5 to 100 min. The morphology of the films has been studied ex situ by using atomic force microscope (AFM), scanning electron microscopy (SEM), and Raman spectroscopy. Raman measurements have been performed in microconfiguration with a Jobin-Yvon T64000 spectrometer equipped with three 1800 gr/mm gratings and using the 532 nm line of a frequency-doubled Nd-YAG laser. A 100× objective lens allows a spatial resolution of ∼1 μm. The spectral resolution is below 3 cm^{-1}.

Fig. 1a and b shows the SEM images obtained from a sample grown using non-oxidized 8 nm Fe film as catalyst (Fe deposition time: 24 min, CNTs growth time ∼10 min). AFM images, taken ex situ on similar samples, showed that the annealing at 650 °C before the CVD process induces the formation of catalyst islands of ∼100 nm. We found that the thickness of the grown CNT *carpet* saturates after ∼10–15 min of growth. The so-grown sample is uniformly covered by *spaghetti-like* MWCNTs (confirmed also from Raman measurements, not shown), with an average tube diameter of 40 nm and length 25 μm. Similar results were obtained by using non-oxidized Ni catalyst under the same growth conditions.

Significant differences are obtained if the CVD growth is performed on oxidized catalyst films, obtained by annealing in air atmosphere ($T \sim 150$ °C) the films before the nanotubes growth. The XPS spectra of the thus-oxidized films showed typical features corresponding to oxidized Fe (FeO and/or Fe_2O_3) in the case of pre-deposited Fe film and oxidized Ni (NiO) for the pre-deposited Ni film. Fig. 1c and d shows the SEM images after exposure to acetylene at 700 °C of a Fe oxidized film (15 nm thick). In this case, it is clear that an amorphous carbon film primarily grows, consisting of big carbon coated particles with some isolated tubes.

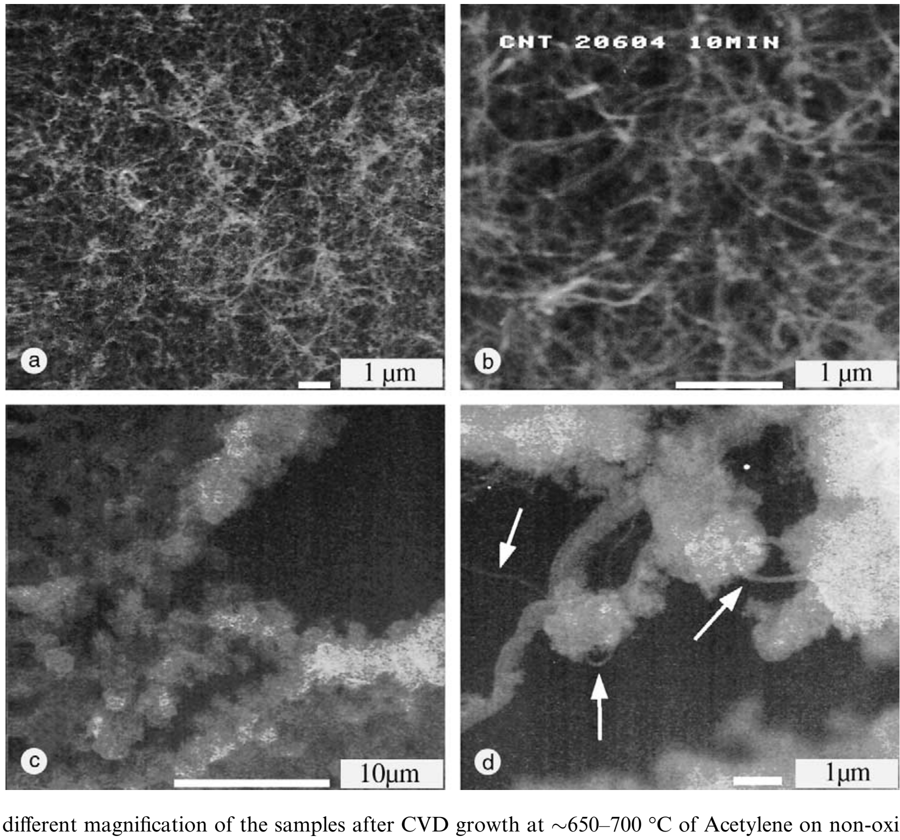

Fig. 1. SEM images at different magnification of the samples after CVD growth at ∼650–700 °C of Acetylene on non-oxidized (a, b) and oxidized (c, d) Fe film (thickness: ∼8 nm). Note that tubular growth is significantly suppressed when the catalyst is oxidized.

The effect is dramatic for the growth on oxidized Ni film. In this case we observed a drastic reduction of tubular structures or no tubular structures at all.

We synthesized SWCNTs by CVD just by reducing the catalyst thickness and by paying particular attention to its metallicity. Fig. 2 shows AFM images collected in non-contact mode of a sample grown on a non-oxidized Fe film of thickness 1.2 nm (Fe deposition time: 4 min). The sample has been grown for 5 min at the same growth conditions of sample of Fig. 1a. In this case the AFM images shows very thin and long isolated CNTs, with average height of 2 nm and lateral dimension of 15 nm, compatible with SWCNTs. Micro-Raman spectroscopy confirms the single-walled nature of the tubes. Fig. 3A shows the tangential modes frequency range (TM) in the Raman spectrum for the sample grown on 1.2 nm thick Fe film. The typical features of SWCNTs [18] (A_{1g}, E_{1g}, E_{2g} modes) are observed. Fig. 3B shows the radial breathing modes frequency range (RBM). Each measurement reveals one or at most three RBMs, showing that the Raman signal comes from isolated SWCNTs with different diameters. The diameter d of isolated tubes can be calculated from the RBM wavenumber ν according to the relationship [14]: $\nu\ (\mathrm{cm}^{-1}) = 248/d$ (nm). In our case the tube diameters are in the range 1.4–1.8 nm, in agreement with the AFM measurements. The significant larger lateral dimension of the tubes observed in the AFM images is due to the convolution of the AFM tip (of finite size) with the CNTs.

In summary, we have described an efficient method for the synthesis of isolated SWCNTs by CVD starting from a film of catalyst metal. The catalyst film is grown

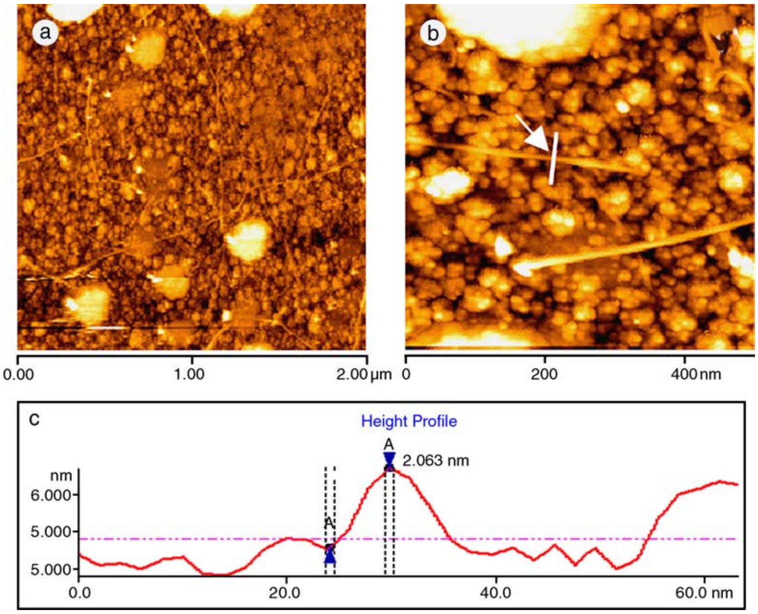

Fig. 2. AFM non-contact mode images of the CNTs grown at 650 °C on the ~1 nm thick Fe film: (a) 2 µm × 2 µm topographic image. (b) 500 nm × 500 nm topographic image. (c) Height profile for the line indicated by the arrow of Fig. 2b.

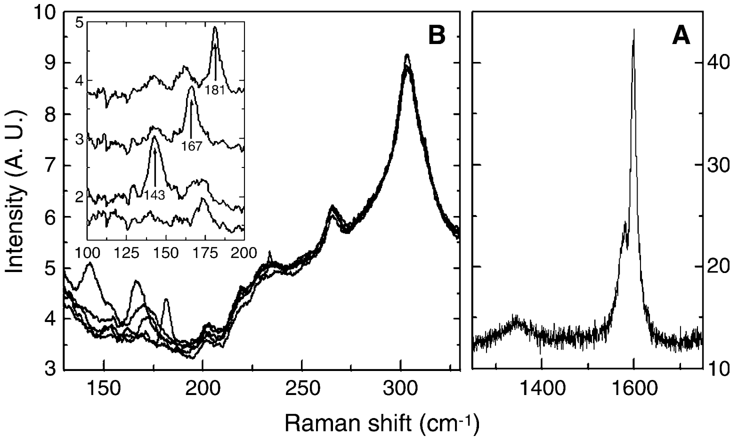

Fig. 3. Raman spectra for the sample of Fig. 2. (A) Tangential Mode (TM) frequency range revealing the typical features of SWCNTs. (B) Comparison of the Radial Breathing Modes (RBM) from different regions of the sample (i.e. from different nanotubes). The 303 cm^{-1} peak coming from the silicon substrate has been used for calibration purposes. Results of the substrate signal subtraction is showed in the inset.

in HV conditions, just before the growing process. This prevents the catalyst oxidation, responsible for the reduced yield of tubes in the growth. No hydrogen and/or ammonia or other time-consuming pre-treatments are needed. Isolated SWCNTs are obtained starting from a 1 nm thick catalyst film. These results make the technique here described an efficient method (the total time of growth, including catalyst preparation, is ~40 min for MWCNTs and ~15 min for SWCNTs in our used catalyst deposition rate, see above), and a promising way for the growth of nanotubes.

Acknowledgements

This research was partially funded under the FIRB project "Carbon-based nanostructures and microstructures". The authors would thank F. Capotondi and M. Tonezzer for the SiO_2/Si substrates preparation, and M. Lazzarino for the help in using the AFM of the TASC facility.

References

[1] See for example Dresselhaus MS, Dresselhaus G, Avouris Ph. Carbon nanotubes. Synthesis, structure, properties, and applications. Springer; 2001.

[2] Wei YY, Eres G, Merkulov VI, Lowndes DH. Appl Phys Lett 2001;78(10):1394–6.

[3] Hafner J, Bronikowski M, Azamian B, Nikolaev P, Colbert D, Smalley R. Chem Phys Lett 1998;296:195–202.

[4] Kong J, Soh HT, Cassel AM, Quate CF, Dai H. Nature 1998;395:878–81.

[5] Li WZ, Wang DZ, Yang SX, Wen JG, Ren ZF. Chem Phys Lett 2001;335(3–4):141–9.

[6] Su M, Zheng B, Liu J. Chem Phys Lett 2000;322:321–6.

[7] Flahaut E, Govindaraj A, Peigney A, Laurent C, Rao CN. Chem Phys Lett 1999;300:236–42.

[8] Colomer J-F, Stephan C, Lefrant S, Van Tendeloo G, Willems I, Kónya Z, et al. Chem Phys Lett 2000;317(1–2):83–9.

[9] Homma H, Kobayashi Y, Ogino T. Appl Phys Lett 2002;81(12):2261–3.

[10] Nikolaev P, Bronikowski MJ, Bradley RK, Rohmund F, Colbert DT, Smith KA, et al. Chem Phys Lett 1999;313(1–2): 91–7.

[11] Cheng H, Li F, Su G, Pan H, Dresselhaus M. Appl Phys Lett 1998;72:3282–4.

[12] Satishkamar BC, Govindaraj A, Rao CNR. Chem Phys Lett 1999;307(3–4):158–62.

[13] Singh C, Shaffer MSP, Windle AH. Carbon 2003;41(2):359–68.

[14] Jorio A et al. Phys Rev Lett 2001;86(6):1118–21.

[15] Franklin NR, Li Y, Chen RJ, Javey A, Dai H. Appl Phys Lett 2001;79(27):4571–3.

[16] Ren ZF, Huang ZP, Xu JW, Wang JH, Bush P, Siegal MP, et al. Science 1998;282:1105–7.

[17] Hövel H, Bödecker M, Grimm B, Rettig C. J Appl Phys 2002;92(2):771–7.

[18] Rao AM, Richter E, Bandow S, Chase B, Eklund PC, Williams KA, et al. Science 1997;275:187–91.