STUDY OF THE EARLY STAGES OF NANOTUBE GROWTH BY CVD OF AEROSOLS

M. Pinault[1], M. Mayne-L'Hermite[1], B. Bouchet-Fabre[1], C. Reynaud[1], V. Pichot[2], P. Launois[2], J.N. Rouzaud[3], C. Clinard[3], D. Ballutaud[4].
[1]Laboratoire Francis Perrin (CNRS URA 2453) CEA Saclay DSM-DRECAM-SPAM, Bat. 522, 91191 Gif sur Yvette Cedex, France
[2]Laboratoire de Physique des Solides (UMR CNRS 8502), bat. 510, Université Paris Sud, 91405 Orsay cedex, France
[3]CRMD, CNRS Université d'Orléans, France
[4]LPSC-CNRS (UMR 8635), Meudon, France
E-mail: pinault@drecam.cea.fr

Since the original work of Iijima [1] in 1991, carbon nanotubes (CNTs) have attracted much attention because of their promising properties. In this context, it is important to control their production regarding their quality, quantity and arrangement.
Growth of well aligned carbon nanotube carpets by Chemical Vapor Deposition (CVD) represents an effective technique for NT production, and has been studied by several groups [2-8] trying to optimize the parameters of this process for applications such as high density magnetic storage, chemical separation and sensing, or composites.

The aerosol-CVD method is based on the catalytic decomposition of liquid hydrocarbons from pyrolysis of mixed aerosols containing both the hydrocarbon source (toluene) and the metallic precursor (ferrocene) as catalytic source [3,10]. Sample of well aligned MWNTs arranged as in a "carpet" and almost free of any by-products are obtained (Fig. 1).
Growth mechanisms of CNTs involved during CVD of aerosols are debated [5]. While some growth models were suggested, no experimental study of the first stages of nucleation and growth of nanotubes has been reported.

The aim of the work reported here is the study of growth mechanisms during the initial stages by different techniques. Electron microscopy (SEM and HRTEM), X-Ray scattering and X-ray photoelectron spectroscopy (XPS) analyses have been performed because most of the models are often proposed without sufficient and systematic supporting experimental evidence. Therefore, we developed a special experimental procedure in order to study the initial stages of nanotube growth involved in the aerosol CVD process. This work allows us to complete our first results [9] by underlining the progression in the formation of nanotubes during the early stages of their growth regarding the nature of the particles formed and their size, the length and the organisation of the nanotubes

The experimental set-up used to synthesise the aligned MWNT has been reported elsewhere [10]. A mixed toluene/ferrocene (5 wt %) aerosol is carried by an argon flow through a quartz reactor heated in a furnace. Syntheses are performed for short durations in the [0.5-2] min range at two different temperatures (800 and 850°C).

Our observations suggest that the first stage is the formation of a catalyst particle layer on the substrate. For synthesis duration of 30s and 1 min, the substrate is mainly covered by a high-density layer of catalyst particles which are the origin of the growth of few nanotubes (Fig. 2). The MWNT roots are always attached to the catalytic particles and never directly in contact with the substrate. Only one MWNT is growing on each catalyst particle but most of the catalytic particles are not leading to the growth of one nanotube (inset fig. 2). For short-time experiments, the MWNT carpets have a randomly oriented morphology. Exploring the beginning of the growth, below 2mn duration, we found by XPS and XRD, that the silicon wafers were covered by oxidized nanoparticles of iron.

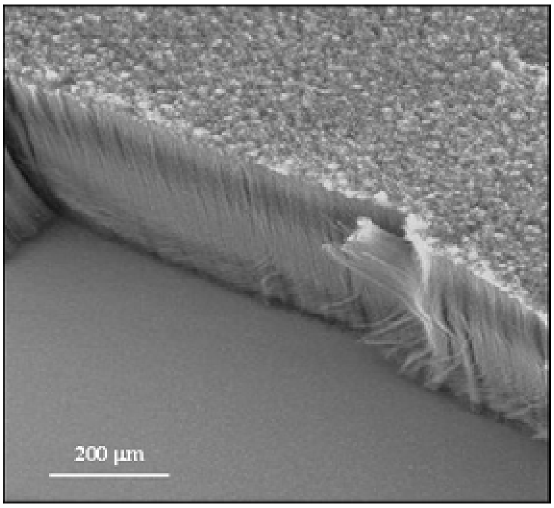
Then with prolonging growth time, the continuously aggregating carbon atoms supply feedstock for the formation and extension of MWNTs. Therefore the number of nanotubes is increasing with synthesis duration inducing the formation of a dense carpet of 20 µm long aligned MWNT for 2 min duration. Chemical analysis (performed by energy dispersive X-ray spectroscopy (EDX) coupled with transmission electron microscopy (TEM)) of catalytic nanoparticles at the root of the carbon nanotubes shows that Fe, O and C can be detected. In addition, almost no particle can be found at the MWNT tips. All these preliminary observations lend further support for the root growth mechanism in early stages of the growth.

In summary, this work demonstrates that the aerosol CVD process generates first the formation of Fe-based particles in an oxidized form and second the growth of one nanotube on one particle. According to all the observations, we believe that a base growth mechanism is controlling the first stages of the nanotubes formation.

References:

[1] Iijima S. Nature 1991, **354**(6348), 56-8.
[2] C. Singh, Chem. Phys. Lett. **372**, 860 (2003)
[3] M. Mayne, Chem. Phys. Lett. **338**, 101 (2001)
[4] R. Andrews, Chem. Phys. Lett. **303**, 467 (1999)
[5] R. Kamalakaran, Appl. Phys. Lett. **77** (2000) 3385
[6] A.Y. Cao, Carbon **39** 1 (2001), pp. 152–155.
[7] Z.J. Zhang, Appl Phys Lett **77** 23 (2000), pp. 3764–3766.
[8] H. Zhang, Physica B **337** (2003) 10-16
[9] M. Pinault, to appear in Diamond and related materials **13/4-8** pp. 1266-1269
[10] M. Mayne-L'Hermitte, Proceeding of the Chemical Vapor Deposition-XVI and EUROCVD-14, edited by M. Allendorf, F. Maury, F. Teyssandier, 2003-08, 549-556.

Figures:



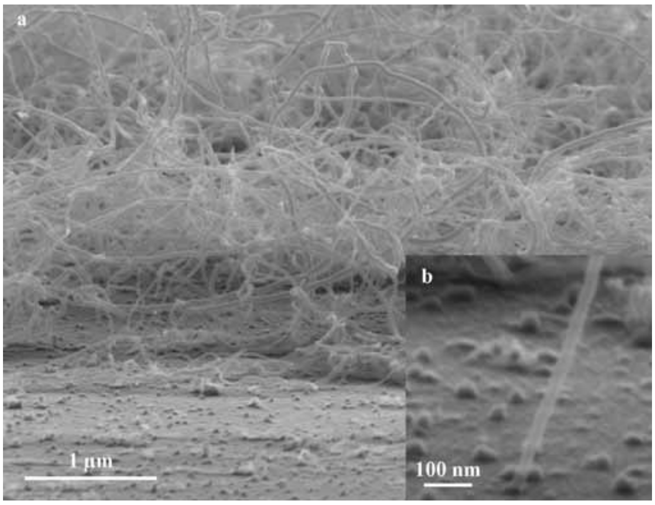


Fig. 1. SEM image showing a large area of a carpet composed of aligned nanotubes perpendicular to the silicon substrate (5 wt % ferrocene in toluene at 800°C, 15 min). The lower area of the image has been "scratched" in order to observe the cross-section of the NT carpet.

Fig. 2. (a) SEM images of the early stages of the nanotube growth with the initial layer of catalyst particles (5 wt % ferrocene in toluene at 800°C, 80 s). (b) High magnification SEM image on the root of a nanotube.