

Parametric study of nanotube growth from C_2H_2 and C_{60} on supported iron catalyst particles

R.-E Morjan, O.A. Nerushev, M.Sveningsson, L.K.L.Falk, F.Rohmund,
E.E.B Campbell

*School of Physics and Engineering Physics, Gothenburg University and
Chalmers University of Technology, SE-41296, Sweden*

Abstract. CVD growth of nanotubes from two carbon feedstock gases C_2H_2 and C_{60} , is facilitated by correlating two important parameters: size distribution of catalytic iron particles and temperature. The thickness of catalytic iron films deposited on Si substrates was controlled between 0.5 and 20nm. The annealed iron films were imaged with atomic force microscopy showing the distribution of iron particles. It was found that with increasing film thickness, both the particle diameter and height increase. After this treatment of the Si substrates, nanotube growth was performed at various temperatures between 550° – 1100° C. The mean nanotube diameters remain constant while the nanotube growth rate depends on temperature. The density of CNT formation is temperature dependent. The presence of SWNT was observed at high temperatures (850° - 950° C). SEM, TEM and Raman spectroscopy were used for sample analysis.

INTRODUCTION

MWNT, SWNT and AMWNT were synthesized systematically by Chemical Vapor Deposition using two different molecules: C_2H_2 and C_{60} as carbon feedstock gases. The method used for our CNT production, CVD, is used for a wide range of applications from the fabrication of microelectronic devices to the deposition of protective coatings. CVD is a very useful (practical) tool because it is versatile, simple, reproducible, productive and cheap. The technique employs the catalytic activity of transition metal particles at elevated temperatures. We investigated the behavior of CNT growth from the two molecules mention it above at different temperature and different flow-rates. We start our study looking at catalytic particles by varying the iron layer thickness. Various studies on the catalyst size dependence have been carried out, leading to different relations between surface thickness and particle size [1,2]. Varying growth temperature and carbon feedstock flux, we continued our parametrical study. Sample analyses were performed using the following methods: SEM, TEM and Raman spectroscopy.

EXPERIMENTAL

All the experiments were performed in a horizontal tube furnace described in detail elsewhere [3,4]. For these experiments we used catalytic iron films ranging in thickness from 0.5 to 20nm deposited by electron beam sputtering on clean Si substrates. For the synthesis of nanotubes a gas mixture of C_2H_2 (C_{60}), H_2 and Ar was used, in which the latter served both as a diluter and carrier gas. Typical flow rates are

600sccmAr, (2-16sccm) C_2H_2 and 100sccm H_2 through the cold injector and a back flow of 100sccm Ar. The operating pressure in the furnace is slightly larger than 1atm.

RESULTS AND DISCUSSION

The films were introduced into the furnace and heated up in flowing Ar (600sccm) and H_2 (100sccm) at different temperatures, where they were held for 15 minutes. The surface morphology of the annealed iron films was examined with AFM (fig.1a). The analysis of AFM images results in the mean particle diameters and particle heights are as plotted in fig.1b.

From very thin Fe films, flat particles with diameter of 26 nm are formed. With increasing film thickness, both particle diameter and height increase and reach values of 475 and 85 nm for $d=20\text{nm}$, respectively. The catalyst particle distribution is not affected at all, by changing the annealing temperature range from 500-800 $^{\circ}\text{C}$.

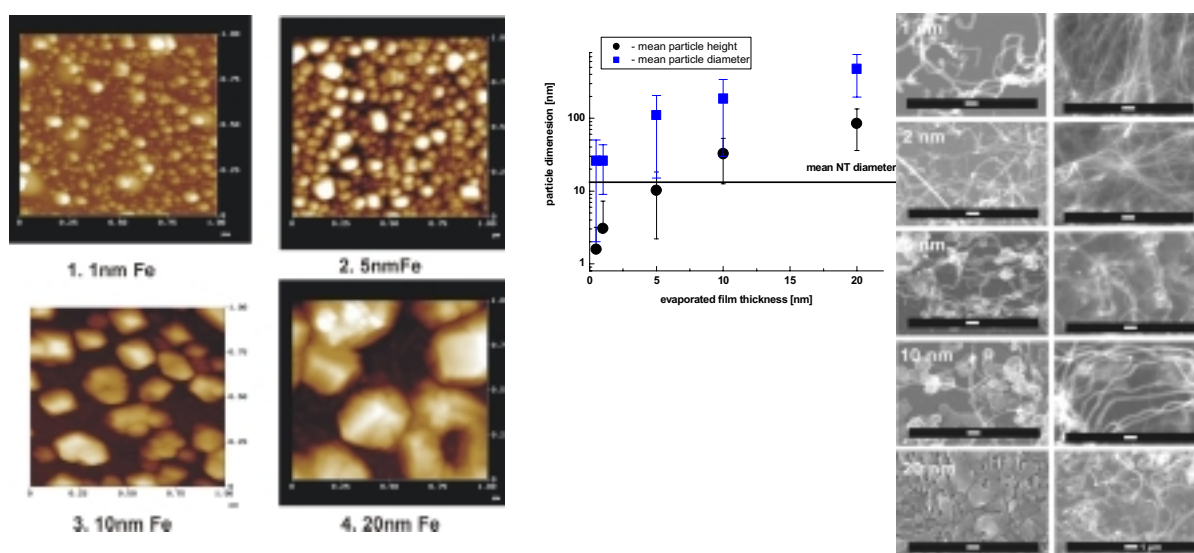


FIGURE 1. a) AFM scans of Silicon substrates where Fe with different thickness was deposited and annealed at 750 $^{\circ}\text{C}$; b) iron particle diameter and heights and nanotube diameter as function of evaporated iron film thickness d ; c) SEM images of as-grown NT films from C_{60} (left panel) and C_2H_2 (right) precursors molecules. The iron film is indicated for each row in the figure. All scale bars 100nm except where noted

After the annealing step, nanotube films were grown from C_{60} and C_2H_2 on iron films of increasing thickness d was carried out at the same temperature and atmospheric pressure by adding the corresponding carbon feedstock gas to the gas flow (C_2H_2 (8sccm) and C_{60} was evaporated at ca. 600 $^{\circ}\text{C}$). The films were imaged with SEM (fig.1c). The morphology of the deposited carbon depends sensitively on the size of the catalytic particle. In the case of sufficiently small particles pure MWNT are produced. If the particles' mean diameter exceeds approx. 100nm, non-tubular pyrolytic deposits are increasingly formed. The mean NT diameter does not depend strongly on the mean particle size which decreases strongly with decreasing iron film thickness. In

the case of the lowest film thickness the mean NT and particle diameter are very close in value.

Another important parameter for NT growth is the temperature. We studied the temperature dependence of NT growth from C_2H_2 on sputtered Fe films of 1nm thickness. We observed that the yield of tubes is decreasing drastically from temperatures below $700^{\circ}C$. Interestingly, even at a temperature as low as $550^{\circ}C$ and without any additional precursor, nanotubes are formed together with carbon fibers. Raman characterizations of NT films from C_2H_2 at different temperatures demonstrate that the disorder of sp^2 -hybridised carbon material decrease with increasing temperature, while higher order Raman signals decrease (fig3a). NT films were formed mainly from MWNT except the sample where the film was grown at $900^{\circ}C$. At this temperature, besides MWNT and amorphous carbon, SWNT were found. Because SWNT's radial breathings modes (RBM) are usually found in the lowest part of the spectrum ($100-300cm^{-1}$), the sample for $900^{\circ}C$ was analyzed in 3 different regions (fig.3b). The spectra collected within this window correspond to three different radial breathing modes. According to [4], we can say that SWNT found in our sample have diameters between 1.2-1.6nm. TEM images (fig.3c) show the clear difference in CNT films obtained for different temperatures: the $750^{\circ}C$ material consists entirely of very nice, thin-walled and straight NT, while at $550^{\circ}C$, CNT are not so well shaped, but much shorter than at high temperature.

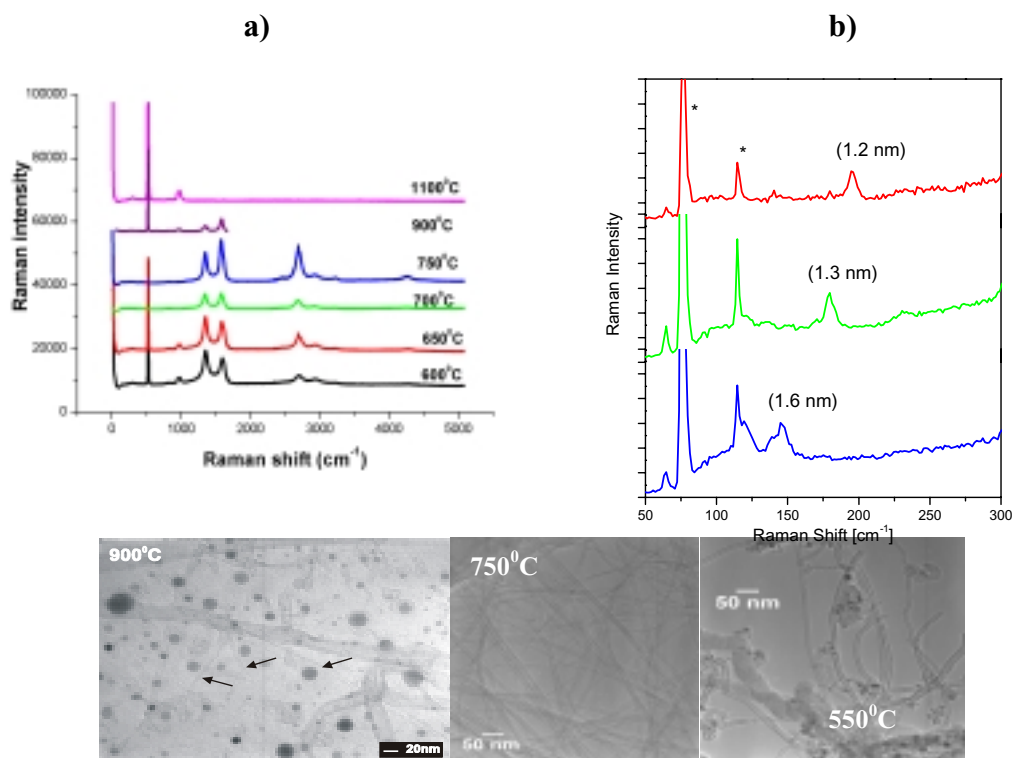


FIGURE 2: a) Raman spectra of NT films from C_2H_2 at different temperatures; b) Raman spectra for $900^{\circ}C$ sample in 3 different spots; peaks marked with stars are due to laser line used; c) TEM images of NT films growth at $900^{\circ}C$, $750^{\circ}C$ and $550^{\circ}C$

Further experiments were done by changing the carbon feedstock which was

provided in our NT synthesis by the flow rate of C_2H_2 and C_{60} , respectively. In the C_2H_2 experiments flow rate was varied between 2 and 16 sccm. C_{60} was evaporated at different temperatures ($620^{\circ}C$, $750^{\circ}C$ and $820^{\circ}C$) from a stainless steel boat which was held by a thermocouple rod close to the hot zone of the furnace (experimental details see [5]).

Film growth at different flow rates was investigated by SEM (fig.3). For the hydrocarbon molecule case, we observed that for higher flow rates (16-6 sccm), the NT film consisted in aligned MWNT, while for low flow rates (4-2 sccm) the material is not so dense, but the appearance of tubes with diameters less than 5 nm was evident. For the fullerene precursor the distribution of the NT diameter became broader by increasing the fullerene source temperature.

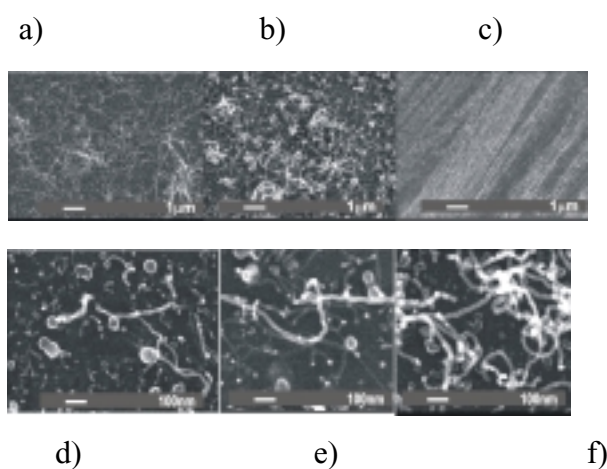


FIGURE 3. SEM images for material synthesized from C_2H_2 :
a) 2 sccm; b) 4 sccm; c) 8 sccm. All the scale bar are $1\mu m$
 C_{60} precursor: flow rate was established for 3 different source temperatures
d) $620^{\circ}C \sim 0.1 sccm$; e) $750^{\circ}C \sim 10 sccm$; f) $820^{\circ}C \sim 100 sccm$.
All the scale bar are 100 nm
CNT were grown on 1 nm Fe thickness at $750^{\circ}C$

ACKNOWLEDGMENTS

Financial support from the Swedish Program for Strategic Research (SSF) within the CAMEL consortium is gratefully acknowledged.

REFERENCES

- [1] C.J.Lee, S.C.Lyu, Y.R.Cho, J.H.Lee and K.I.Cho, Chem.Phys Lett.341, 245 (2001)
- [2] J.I.Sohn, C.-J.Choi, S.Lee and T.-Y Seong, Appl.Phys.Lett. 78, 3130 (2001)
- [3] K. Bladh, L.K.L. Falk and F.Rohmund, Appl.Phys.A 70 (3) (2000)
- [4] M.Sveningsson, R.-E Morjan, O.A.Nerushev, Y.Sato, J.Bäckström, E.E.B.Campbell, F.Rohmund, Appl.Phys.A 73, 409, (2001)
- [5] M.S. Dresselhaus, G.Dresselhaus, A.Jorio, A.G.Souza Filho and R.Saito “Raman Spectroscopy on Isolated Single Wall Carbon Nanotube”
- [6] R.-E Morjan, O.A.Nerushev, M.Sveningsson, L.K.L Falk, E.E.B.Campbell, F.Rohmund (unpublished results)