Catalyst Free Growth of Single-Wall Carbon Nanotubes (SWCNTs)

M. Holzweber[1], Ch. Kramberger[1], F. Simon[1], A. Kukovecz[1], H. Kuzmany[1], H. Kataura[2]

[1]*Institut für Materialphysik,Universität Wien, Strudlhofgasse 4, A–1090 Wien, Austria*
[2]*Department of Physics, Metropolitan University of Tokyo, Tokyo, Japan*

Abstract. We report on the growth process of single wall carbon nanotubes from a catalyst free carbon source. The carbon for the growth process is provided from C_{60} fullerenes encapsulated into the cage of the tubes (peapods). The growth process is studied by Raman scattering at various stages for the transformation of the C_{60} peas to a new SWCNT inside the primary tube. The growth process was found to start for tubes with the smallest geometrically allowed diameters. At the same time the response from the C_{60} molecules started to disappear. Eventually the signal from the latter was gone while only the thin inner tubes have reached their final concentration.

INTRODUCTION

Since their discovery in 1991, carbon nanotubes (CNT) have raised a growing interest in the scientific community [1,2]. This interest is mainly based on their unique quasi one-dimensional structure and on their high application potential. A disadvantage of the material originates from the rather large concentration of impurities present after the growth process. A great part of these impurities are encapsulated particles of the catalyst needed for the growth process. A few years ago, it became possible to combine fullerenes and single wall carbon nanotubes (SWCNTs) to form so called peapods [3]. Recently, it was discovered that the C_{60} molecules inside the tubes can be transformed into new SWCNTs accommodated inside and concentric to the primary tubes [4]. This transformation was established by annealing the system at high temperatures in dynamic vacuum. The growth process of the inner tubes is unusual as it proceeds without any additional catalysts.

Raman spectroscopy has been used extensively to study SWCNTs. This holds in particular for the tubes grown inside the primary tubes. Three main signatures are important in the Raman spectra. At low frequencies, between 150 and 450 cm^{-1}, one observes the response from the radial breathing mode (RBM), at high frequencies, between 1450 and 1600 cm^{-1} the graphitic lines (G-lines) appear and at medium high frequencies, between 1300 and 1400 cm^{-1}, a defect induced line (D-line) is seen.

For standard diameter tubes the RBM exhibits a broad structure of overlapping lines. The interest of the inner tubes is based on their small diameter in the range 0.5 – 1.0 nm. For inner tubes sharp RBM lines are observed in spectra for all geometrically allowed chiralities [5,6]. The concentric system of the two grown nanotubes is now

CP685, *Molecular Nanostructures: XVII Int'l. Winterschool/Euroconference on Electronic Properties of Novel Materials,* edited by H. Kuzmany, J. Fink, M. Mehring, and S. Roth

conveniently assigned as double wall carbon nanotubes (DWCNTs). There is also interest in the system since it combines the stiffness of MWCNTs with the small diameters of SCWNTs.

To study the growth process of the inner tubes in detail, we analyzed various components of the transformation process. The following factors are expected to have a significant influence: the annealing temperature, duration of annealing, and the details of the heating and cooling phase. In the following we concentrate on the annealing time. This was done in order to see intermediate states of the transformation process. The Raman response from these states was compared with the response from fully transformed samples.

EXPERIMENTAL

For the heat treatment we used a horizontal tube furnace with a tube diameter of 38 mm. The samples were placed in a quartz tube and pumped to a dynamic vacuum better than 10^{-7} mbar during the heat treatment. For each treatment peapods from the same charge were used as starting material. Two types of experiments were performed.

In a first type of experiment (type 1), the furnace was preheated to 1280 °C before the samples were put in. After 30 minutes of heat treatment the samples were removed from the furnace and then cooled down to room temperature rapidly.

In the second experiment (type 2) the samples were put into the furnace at room temperature. The furnace was then heated slowly up to 1280 °C. After 1 hour at the maximum temperature the furnace cooled down to room temperature in 3 hours.

TABLE 1 Summary of treatments and characterizations for four samples.

Sample	Heat Treatment	Normal Dispersion	High Dispersion
D	Peapods	RBM & G-line 488	
C	1 x Type 1	RBM & G-line 488,568,647,676	RBM 568, 647, 676
B	2 x Type 1	RBM & G-line 488,568,647,676	RBM 568, 647, 676
A	Type 2	RBM & G-line 488,568,647,676	RBM 568, 647, 676

For our Raman measurement we use a Dilor xy triple monochromator spectrometer. Specta were excited at 90 K with 4 different laser lines as litsted in Table 1. The RBM was measured with high dispersion and normal dispersion mode. The G-line was measured with normal dispersion mode with all 4 laser lines. We used the blue laser line, 488 nm, to check the pea signal from the $A_g(2)$ line.

RESULTS AND DISCUSSION

The duration of the annealing process had a significant influence on the resulting Raman spectra. In all experiments where a second tube was grown inside the primary tube very narrow lines were observed in the spectral range of the RBM as demonstrated in Fig.1 (left).

After the first annealing step the signatures of the inner tubes already appeared.

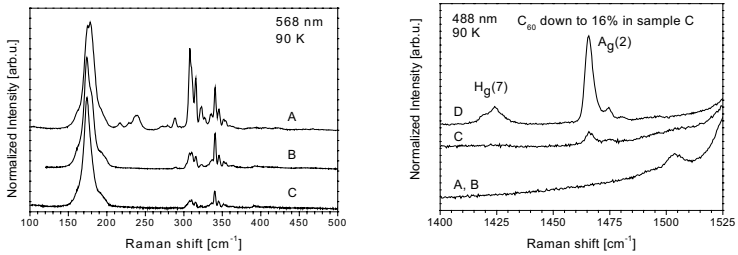

FIGURE 1. Left: RBM of sample A (annealed for 1 hour), B (annealed for 2 x 30 min), and C (annealed for 30 min), all spectra excited with a yellow laser at 568 nm; right: Ag(2) and Hg(7) lines of C_{60} excited with 488 nm. Intensities are normalized to G-Line area, D: peapod starting material

They increased with the second annealing step but do not yet reach the final height as it is observed for the sample which was continuously annealed. Simultaneously with the growth of the inner tubes the signal from the peas inside the tubes located at 1425 and 1465 cm^{-1} had considerably decreased after the first step as demonstrated in Fig. 1(right). This behavior continues with the second step of the annealing process even though a quantitative correlation between the loss of signal from the C_{60} molecules and a gain of signal from the inner tubes is not provided. This can be considered as an indication that the inner tubes are not formed out directly from the C_{60} molecules. We conclude that there exists at least one intermediate state which cannot be observed by Raman with the excitation frequencies used. The line shape of the RBM of the outer tubes changes only marginally during the transformation process.

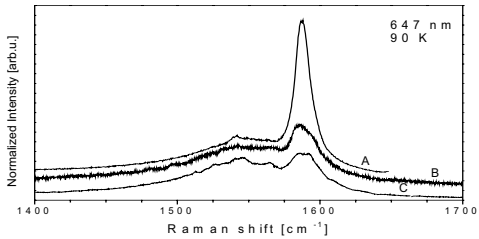

FIGURE 2. G- Line of samples A, B, and C with 647 nm at 90 K
A: treated for1 hour,
B: treated for 2 x 30 min,
C: treated for 30 min

In the spectra measured with the red laser lines we found a major change in the line shape of the G-line. The broad structure of the G-line has a Fano shape which originates from metallic primary tubes. A sharp line of semiconducting inner NTs appears in the spectra. The narrow structure shows no Fano shape and is not found in the spectra of the starting material. It is assigned to the resonance for an E_{22} transition of semiconducting inner tubes.

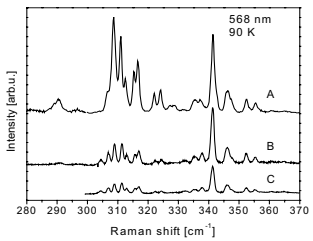

FIGURE 3. High resolution spectra of the RBM of inner tubes excited with 568 nm at 90 K,. A: treated for 1 hour, B: treated for 2 x 30 min, C: treated for 30 min

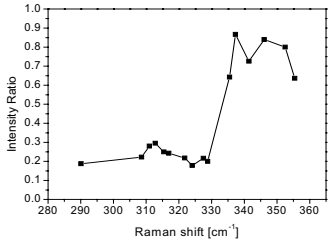

FIGURE 4. Ratio of the line intensities (relative signal heights between spectrum B and spectrum A) shown in Fig 3.

The extremely narrow lines are demonstrated by the high resolution spectra in Fig. 3. The figure exhibits the response from inner tubes for 3 different samples. Sample A heated for 1 hour at 1280 °C shows the largest signal. Sample B was heated 2 x 30 min. The peaks of this measurement do not reach the same height although the-overall treatment time and the temperature are the same. Sample C was heated for 30 min. The signal from this sample was the smallest as we expected. The signals increase as a function of time. Tubes with different diameters form out at different times starting with small diameter tubes. Large diameter tubes appear to need longer treatment to reach the maximum signal height. Fig. 4 shows the ratio of RBM intensities for two differently annealed samples. It is evident that in the stepwise annealed sample B the number of small diameter tubes is comparable to sample A but that the larger inner tubes were not formed or were destroyed during the annealing.

In summary, we have produced single wall tubes from C_{60} peas with different annealing procedures. We have shown that the duration of the thermal treatment plays an important role in the transformation process. The growth process was found to start for tubes with the smallest diameters.

ACKNOWLEDGMENTS

This work was supported by the FWF in Austria, Project 14893 and by the EU RTN FUNCARS (HPRN-CT-1999-00011)

REFERENCES

1. Iijima, S., and Ichihashi, T., *Nature*, **363**, 603–605 (1993).
2. Thess, A. *et al.*, *Science*, **273**, 483–487 (1996).
3. Smith, B. W., Monthioux, M., and Luzzi, D. E., *Nature*, **396**, 323–324 (1998).
4. Bandow, S. *et al.*, *Chem. Phys. Lett.*, **337**, 48-54 (2001).
5. Pfeiffer, R.,. *et al.*, V., submitted.
6. Kramberger, Ch. *et al.*, in this volume.