The Growth Process of Nanotubes in Nanotubes

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Abstract. We have investigated the growth process of carbon nanotubes in carbon nanotubes as a function of anihilation temperature and duration. Raman spectroscopy is applied to characterize the produced DWCNTs. The RBM scales as 1/d and renders the very narrow new inner CNTs easily detectable. We found a dramatic decrease of the fullerene concentration in the samples before the inner CNTs start to emerge. The growth of the new inner CNTs starts with the smallest diameter nanotubes, before it is uniformly extended to all possible diameters.

INTRODUCTION

Since their discovery in 1991, carbon nanotubes (CNTs) 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. Various ways of producing CNTs have been established since then. One of them is based on annealing C_{60} peapods [3] at high temperatures in dynamic vacuum. During this procedure the one dimensional chain of fullerenes is turned into a secondary inner SWCNT [4]. The outer SWCNT, that was filled with the fullerenes formerly, acts as a nano-reactor. It enables the coalescence of the fullerenes into a very narrow inner CNT. Moreover it acts as a physical barrier and guarantees cleanroom conditions for the growth process. As the reaction is effectively shielded the new inner CNT is made from chemically pure carbon.

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. 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 conveniently assigned as doublewall carbon nanotubes (DWCNTs).

To study the growth process of the inner tubes in detail, we analyzed various steps 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

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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 sample was placed in a quartz tube and pumped to a dynamic vacuum better than 10^{-7} mbar. Then it was put into the hot furnace. After the treatment the sample was cooling down to room temperature by removing it from the furnace.

For our Raman measurement we use a Dilor xy triple monochromator spectrometer. After the sample was put into the cryostat it was tempered at 600 K to get rid of disturbing impurities. Spectra were excited at 90 K with 4 different laser lines as litsted in Table 1. The RBM was measured in normal dispersion mode with all 4 laser lines. Since the C_{60}-Molecules are best observed for blue laser excitation, we measured the high frequency region between D-line and G-line with 488 nm

TABLE 1 Summary of treatments and characterizations for four samples.

Steps	Treatment Time	Recorded spectra
A	Peapods (0 min)	RBM at 488 D-line, G-line at 488
B	30 min	RBM at 488,568,647,676, D-line, G-line at 488
C	60 min	RBM at 488,568,647,676, D-line, G-line at 488
D	90 min	RBM at 488,568,647,676, D-line, G-line at 488
E	120 min	RBM at 488,568,647,676, D-line, G-line at 488
F	180 min	RBM at 488,568,647,676, D-line, G-line at 488
G	360 min	RBM at 488,568,647,676, D-line, G-line at 488
H	540 min	RBM at 488,568,647,676, D-line, G-line at 488

RESULTS AND DISCUSSION

The duration of the annealing process has a significant influence on the resulting Raman spectra. In all experiments where a second tube has been grown inside the primary tube very narrow lines are 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 are already present. They increase with the following annealing steps. Simultaneously with the growth of the inner tubes the signals from the peas inside the tubes located at 1425 and 1465 cm^{-1} decreased considerably after the first step as demonstrated in Fig. 1(right). This behavior continues with the following steps of the annealing process.

The decrease of the C_{60} signature with increasing annealing time is depicted in Fig. 2. At 1280 °C almost the whole signal is lost after the first 30 min of annealing. There are no traces of the signal left after 1 hour. At 1100 °C the signal drops to 20 % and is then gently reduced with succeeding steps. After 9 hours the lines match again at less than 1%.

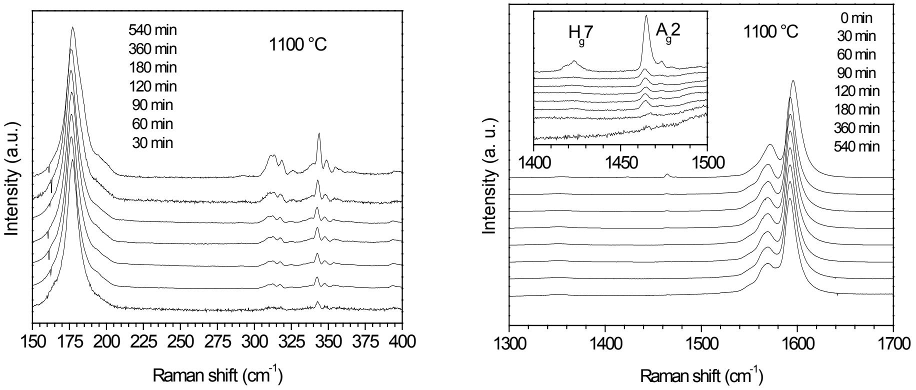

FIGURE 1. Left: RBM of DWCNTs excited with 568 nm. The duration of heat treatment increases from bottom to top. Right: Ag(2) and Hg(7) lines of C_{60} excited with 488 nm. The duration of the heat treatment increases from top to bottom. All spectra are normalized to the response of the RBM from the outer tubes.

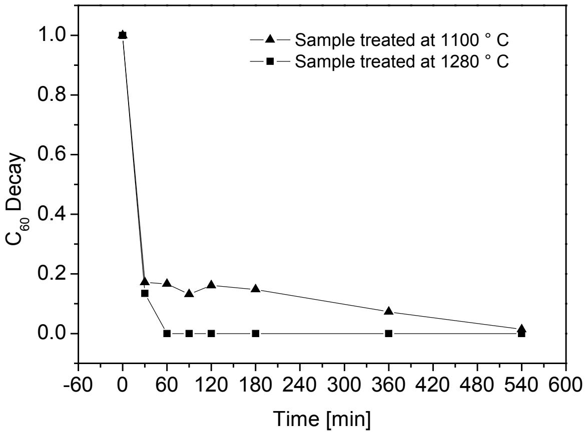

FIGURE 2. C_{60} signal decay after the different treatment steps is plotted against time. Both samples were measured with 488 nm at 90 K.

At the same time the peapod signal decreases the nanotube lines of the inner tubes formed out during the annealing start to emerge which is shown in Fig 3. In contrary to the rapidly dropping peapod signal this signal increases slowly. After 30 min annealing at 1100 °C already 82% of the C_{60} signal is lost but anly 10% of the DWCNT signal is obtained. Furthermore the signal growth is not the same for all the different inner tubes. Figure 3 shows the signal evolution of two different peaks which correspond to two different tube diameters, 364 cm $^{-1}$, for the smaller tubes and 302 cm $^{-1}$, the larger tubes. The small tube growth shows a steep slope in the beginning and a smaller slope to the end. On the contrary the bigger one start to grow slower and shows a steeper slope at the final steps. This diamater dependence of the signal evolution is observed for all the laserlines.

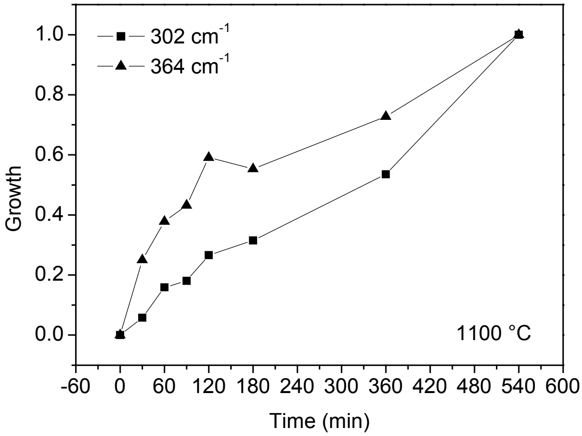

FIGURE 3. The evolution of the signal of two different inner tubes is plotted against time. The The spectra are recorded with 676 nm at 90 K.

In summary, we have produced singlewall 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 but is delayed with respect to the loss of the peapod signal. 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.

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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.*, *Phys. Rev. Lett.* **90**, 225501 (2003).
6. Kramberger, Ch. *et al.*, *Phys. Rev. B* **68**, 235404 (2003).