Thin films of C_{60} peapods and double wall carbon nanotubes

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Abstract. Thin films of SWCNTs were prepared from toluene suspension of single wall carbon nanotubes. The material was dropped on silicon and platinum surfaces with a controlled thickness. Filling with C_{60} and DWCNT – transformation of the films was performed. Multifrequency Raman spectroscopy was used to follow the peapod formation process and double wall transformation of the tubes. An efficient filling with C_{60} and DWCNT – transformation of the films was observed on platinum surface. Silicon reacts with carbon nanotubes forming SiC at the high temperature of the DWCNT formation, 1270 °C. The studies demonstrate the possibility for DWCNT formation process on individual tubes. In addition, it enables the production of homogeneous DWCNT films for several applications such as e.g. field emission devices.

INTRODUCTION

Since their discovery in 1991, carbon nanotubes (CNT) have attracted a lot of interest in the scientific community [1] due to their unique structural and electronic properties. Recently it was discovered that the C_{60} molecules can be combined with the single wall carbon nanotubes (SWCNTs) to forme the so-called peapods (C_{60} @ SWCNT) [2]. Annealing the peapods at high temperatures for several hours, in dynamic vacuum yields double wall carbon nanotubes (DWCNTs) [3] without any additional catalyst. Also, it has been shown that inner tubes formed by the fused C_{60} molecules inside the SWCNTs are higly defect free [4].

We show in the following that thin films of SWCNTs can be produced on different surfaces such as silicon and platinum. The filling with C_{60} fullerene and the transformation to DWCNTs is characterized using Raman spectroscopy. The study of the possible reaction between carbon nanotubes and different surfaces is also of practical interest. The aim of this work is to produce double wall carbon nanotube thin films for application devices, to study individual DW tubes, and to investigate possible reactions between carbon nanotubes and different substrates which is important for nanoreactor devices. A simple shema of a possible nanoreactor which uses the interior of a CNT as a "nanoclean room" to produce defect free, C_{60} based inner tubes is depicted below, in Fig 1.

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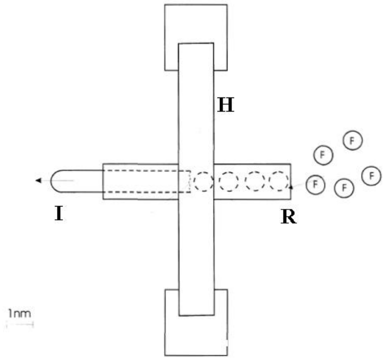

Figure 1. Simple schema of a nanoreactor. The heating zone is located at the crossover between the reactor tube (R) and the heating tube (H). F: fullerenes, I: inner tube, grown by fullerene fusion, ← : direction of growth or pulling.

EXPERIMENTAL

Comercial SWCNT (NCL-SWCNT from Nanocarblab, Moscow,Russia) suspended in toluene were used for the thin films preparation. Two different substrates, silicon and platinum, were used in this study. Likewise two different thickness of the films were studied.

One film was prepared by suspending 5 mg SWCNT in 10 mL toluene.The mixture was sonicated for 1 hour. 50 µL from the suspension was dropped on silicon and platinum platelets with 30 mm^2. The thickness of the film is approximately 1 µm.

The second film was prepared with 2 mg SWCNT in 10 mL toluene, sonicated for 1 hour and 10 µL dropped on platinum platelet. The calculated thickness was about 0.2 µm.

C_{60} fullerene filling of the SWCNT-films was performed according to the method of Kataura et al. [5] which involves sealing the material with C_{60} in a quartz ampoule and baking it at 650 °C for 2 hours.

Dynamic vacuum treatment at 800 °C was used to remove residual fullerene from the samples. DWCNT-transformation was performed by heating the peapods at 1270 °C under dynamic vacuum for 1 hour.

Multi frequency Raman spectroscopy was performed on a Dilor *xy* triple spectrometer using an Ar-Kr mixed-gas laser. All spectra were recorded for normal resolution and at ambient conditions.

RESULTS AND DISCUSSION

C_{60} peapods and DWCNT on Si surface:.The effect of the filling with C60 molecules and the following heat treatements of the SWCNT- film on silicon is clearly demonstrated by the Raman spectra shown below in Fig. 2. and Fig. 3.

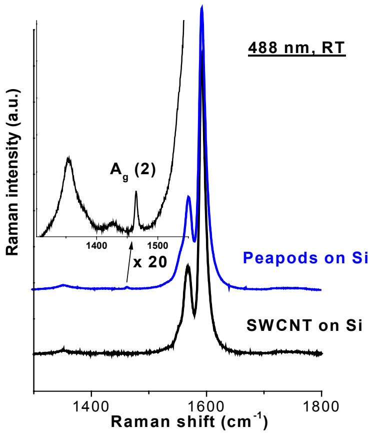

Figure 2. Raman spectra of a SWCNT film on Si (bottom) and of a C_{60} peapod film (top).

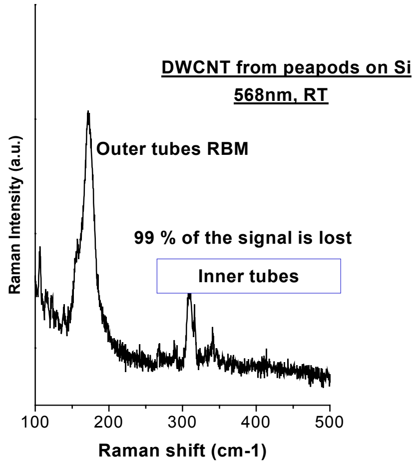

Figure 3. Raman spectra of C_{60} based DWCNT film grown on Si substrate.

In Figure 2., we compare Raman spectra of a SWCNT- film and C_{60} based peapods for the films on the Si substrate. The well known Raman active line of C_{60} peapods, the A_g (2) mode at 1466 cm^{-1}, is shown enlarged. This Raman line is evidence that the carbon nanotubes on the film are filled with C_{60}. The Raman spectra after transformation of the peapods to a DWCNT- film on Si is shown on Figure 3. The line around 170 cm^{-1} corresponds to radial breathing mode (RBM) of outer tubes and the group of lines between 250 and 350 cm^{-1} to the RBM of the inner tubes. The relative low Raman intensity of the inner tubes evidences a low level of DWCNT formation from the peapod film. We supose the carbon nanotubes react with silicon at the high temperature treatement, 1270 °C, forming silicon carbide composites.

C_{60} peapods and DWCNT on Pt surface: In Fig 4. and Fig 5. we show Raman spectra of SWCNT film on Pt and as-transformed DWCNTs respectively.

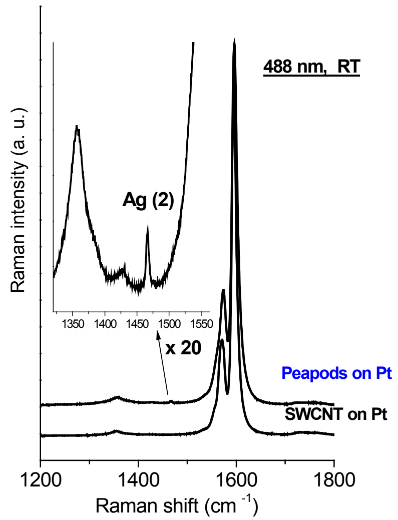

Figure 4. Raman spectra of SWCNT film on Pt (bottom), C_{60} peapods (top).

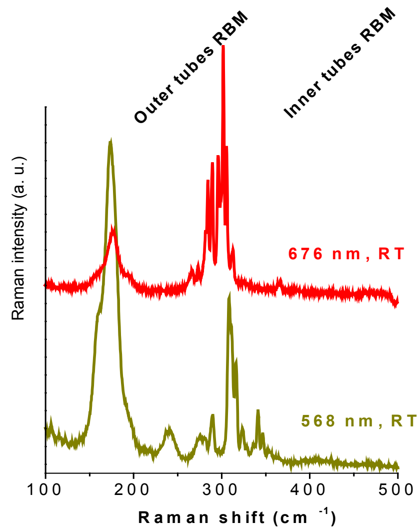

Figure 5. Raman spectra of C_{60} based DWCNT film on Pt substrate for two different laser exitation.

Raman characterization of the 1μm film was performed with a blue laser (488 nm). It clearly shows the A_g (2) mode at 1466 cm^{-1} (Fig 4., top spectra). The average integrated intensity ratio A_g (2) / G-mode = 2.6 * 10^{-3} which is consistent with the maximum attained level of filling as reported in the literature [6].

In Fig 5., we present the Raman shift of the DWCNT film obtained from annealing the peapod film at 1270 °C for 1 hour under dynamic vacuum. Yellow (568 nm) and red (676 nm) lasers were used to record the spectra. For the two excitations we see sharp and distinct lines between 230 and 350 cm^{-1} which correspond to the RBM of the inner tubes. For the red excitation (Fig 5., top spectra) the response of the inner tube RBM is even stronger than that of the outer tube RBM. This is a clear evidence that the transformation of the peapod film on platinum into DWCNTs was successful and the sharp RBM structure is a sign for defect free inner tubes.The defect free groth conditions inside the tubes makes them a perfect "nanospace". Simmilar patern were seen also for the 0.2 μm thick film on Pt, (not shown).

In summary, we have produced thin films of C_{60} peapods and DWCNT on silicon and platinum substrates. We have shown that transformation of peapod films on silicon in DWCNT films has a very low efficiency of DWCNT formation because of the reaction between carbon nanotubes and silicon substrate, forming SiC. Films of peapods on platinum substrate were transformed successfully to DWCNT films as shown by Raman investigation. This assigns a platinum substrate as a possible candidate for nanoreactor devices. Investigations on thinner films and other substrates is the ongoing work.

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REFERENCES

1. Iijima, S., *Nature*, **354**, 56 (1991).
2. Smith, B. W., Monthioux, M. and Luzzi, D. E., *Nature,* **396**, 323 (1998).
3. Bandow, S., Takizaw, M., Hirahara, K., Yudasaka, M., Ijima, S., *Chem. Phys. Lett*., 48, **337** (2001).
4. Pfeiffer, R., Kuzmany, H., Kataura, H, Pichler, T., Kürti, J. et al, *Phys. Rev. Lett*. (2003).
5. Kataura, H., Maniwa, Y., Kodama, T., Kikuchi, K., Hirahara, K., Suenaga, K., Iijima, S., Suzuki, S., Achiba, Y., Kratschmer, W., *Synth. Met*. **121,** 1195, (2001).
6. Kuzmany, H. et al., *Appl. Phys. A*, **76**, 449, (2003).