Investigation of the Formation of Fe-filled Carbon Nanotubes

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Abstract. The formation of Fe-filled carbon nanotubes by thermal decomposition of ferrocene combined with a Fe-catalyst-nanos tructuring on an oxidized Si substrate is investigated in the temperature range of 1015 – 1200 K. The optimal growth conditions for aligned and homogeneous carbon nanotubes are found at 1103 K. Mössbauer spectroscopy (both in transmis sion geometry and CEMS) was used to analyze and quantify the different formed Fe-phases. In general, \( \alpha \)-Fe, \( \gamma \)-Fe and Fe₃C are found to form within the carbon nanotubes. Depending on the growth conditions their fractions vary strongly. Moreover, an alignment of the \( \alpha \)-Fe in the tubes could be detected.

1. Introduction
The nanostructured magnetic nanowires are promising candidates for many applications ranging from magnetic data storage and sensors for scanning for ce microscopy to ferromagnetic nanocontainers for biomedical applications.

In order to protect the nanowires from oxidation, mechanical damage, and magnetic shortcuts between each other, the nanowires are encapsulated inside carbon nanotubes (CNTs).

Chemical vapor deposition (CVD) has established itself over the last years as the synthesis method for filled CNTs, because it provides material of good quality and can be easily scaled up. Most CVD procedures use metals as the process catalysts (usually Fe, Co, Ni) to produce CNTs. The catalysts can be placed on substrates and/or directly produced via a precursor compound (e.g., ferrocene). The properties of CNTs are strongly influenced by the growth conditions [1, 2].

In the past, Mössbauer spectroscopy was used several times to characterize the phases formed in iron containing CNTs. Depending on the preparation conditions, iron oxides, Fe₃C, \( \alpha \)- and \( \gamma \)-Fe were detected [3-6].

In the following, we report about the preparation of CNTs prepared by CVD and their characterization by scanning electron microscopy and Mössbauer spectroscopy.
2. Experimental

The synthesis of Fe-filled multiwalled CNTs was carried out by catalytic decomposition of ferrocene (Fe(C5H5)2) in a quartz tube reactor inside a dual-zone electrical furnace. The ferrocene acts as the carbon source for the CNTs and the Fe filler.

The following parameters were used: Sublimation temperature of the ferrocene in the first furnace ($T = 423$ K), deposition temperature in the second furnace ($T = 1015-1200$ K), Ar flow rate (120 cm$^3$/min). For the ferrocene supply rates between 3 and 6.5 mg/min were used. The experiments were performed at atmospheric pressure. Oxidized (100) oriented Si substrates (10 × 10 mm$^2$, 1 μm SiO$_x$) coated with a thin Fe layers (2 nm, sputtered) were used for the deposition. One set of samples was prepared by inserting a 10 nm Al buffer layer between the silicon oxide and the iron. The deposition time was set to 10 min. At the end of each experiment the reactor was slowly cooled down to room temperature (25 K/min). The schematic setup of the quartz tube reactor is displayed in figure 1.

![Schematic setup of the quartz tube reactor](image)

Figure 1. Schematic setup of the quartz tube reactor

The morphology of the nanotubes was monitored by scanning electron microscopy (SEM) (Gemini Leo 1530 and Hitachi S 4800, both operated at 10 kV).

The fractions of iron phases formed inside the CNTs were determined by Mössbauer spectroscopy. The CNTs were studied both in transmission geometry (TM) and by conversion electron Mössbauer spectroscopy (CEMS). Measurements were performed at room temperature with a conventional spectrometer with constant acceleration driving system with a Co-57(Rh) source of nominally 3.7 GBq. The TM spectra were taken first directly from the aligned CNTs on substrates. The absorption due to the thick Si substrate (some 100 μm) was very strong and it was difficult to obtain spectra of reasonable quality. Therefore, the CNTs were mechanical removed from the substrate and inserted as powder samples. CEMS was performed with a proportional gas flow detector with a He/CH$_4$ mixture as counting gas. Spectra were evaluated with the NORMOS program package. To improve the quality of the Mössbauer spectra some of the samples were implanted with Fe-57 ions. With an energy of 40 keV and an implantation dose of 1x10$^{16}$ cm$^{-2}$ the concentration of Fe-57 was increased to up to 10 at. % within the first some 10 nm. There was no general difference between CEM spectra taken from non-implanted and from implanted samples. Thus it can be assumed that the implanted Fe-57 ions act as probes only and do not change the phase composition or create new phases in the tubes.

3. Results and discussion

Length, homogeneity and alignment of the CNTs depend strongly on the formation temperature. The best values are achieved at 1103 K. Scanning electron micrographs of the CNTs are displayed in
figure 2. Scanning electron micrographs of the CNTs

It can be seen that the grown tubes have a length of up to 10 µm and a thickness of some 10 nm. The Fe cores have diameters of less than 20 nm.

In figure 3 some selected Mössbauer spectra are displayed. Figure 3a shows TM and CEM spectra of the same sample which was grown at 1103 K. It is obvious that the fractions of the iron phases are very different. Moreover, from the CEM spectrum a strong texture in the tubes can be assumed. In figure 3b CEM spectra of nanotubes deposited at different rates are shown. At higher rates the formation of α-Fe is preferred while at lower rates the formation of Fe₃C dominates. Due to different process temperatures and different ferrocene supply rates the fractions of the formed iron containing phases can strongly be varied. No iron oxides, silicides or aluminides could be detected. The fractions of the formed phases are given in table 1. For the fit the following hyperfine parameters are used: α-Fe: a sextet with isomer shift $\delta = 0.0$ mm/s, magnetic hyperfine field $B_{hf} = 33.0$ T; γ-Fe: a singlet line $\delta = -0.1$ mm/s; Fe₃C: a sextet $\delta = 0.2$ mm/s, $B_{hf} = 20.8$ T.

Figure 3. Mössbauer spectra from CNTs. Left: (a) TM (upper) and CEM (lower) spectra of nanotubes grown at 1103 K. Right (b): CEM spectra of nanotubes deposited at different supply rates (upper: 6.5 mg/min, lower: 3.0 mg/min).
Table 1. Fractions of the phases formed in the nanotubes

| Experimental conditions | α-Fe | γ-Fe | Fe₃C | Fig.  |
|-------------------------|------|------|------|-------|
| 1103 K, 6.5 mg/min      | 79   | 6    | 15   | 3 a top (TM) |
| 1103 K, 6.5 mg/min, Al buffer layer | 69  | 28   | 3    | 3 a bottom (CEMS) |
| 1103 K, 6.5 mg/min, Al buffer layer | 62  | 16   | 22   | 3 b top (CEMS) |
| 1103 K, 3.0 mg/min, Al buffer layer | 12  | 10   | 78   | 3 b bottom (CEMS) |

3. Conclusions

Mössbauer spectroscopy is very suitable to investigate the formation of the different iron phases. Besides metallic iron as α-Fe or γ-Fe iron carbide was formed but no iron oxide or other iron compounds. This is in agreement with the findings of [3] and [4] while in [5] only Fe₃C was detected and in [6] α-Fe and small fractions of iron oxides were found. Contrary to [3], within the tubes a strong alignment of the crystalline ranges took place. This is confirmed by transmission electron microscopy too [7]. However, the results presented here show that the formation of the different phases is strongly influenced by the kind of preparation.

The optimal growth conditions for aligned and homogeneous Fe-filled carbon nanotubes (maximum content metallic iron, minimum content iron carbide) are found at 1103 K and a high supply rate.

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