Selective growth of vertically aligned Fe-filled carbon nanotubes on oxidized silicon substrates

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Abstract. Vertically aligned Fe-filled multi-wall carbon nanotubes (MWNTs) have been grown selectively on the SiO2 surfaces of patterned amorphous carbon (a-C)/SiO2/Si substrates. Their morphology, structure and magnetic properties have been studied. The a-C patterns were prepared using conventional lithography processes combined with a sputter-deposition of a-C (thickness of 100 nm). The aligned Fe-filled MWNTs were produced by pyrolysis of ferrocene in a CVD reactor with a two zone furnace system and have high filling yield. The encapsulated Fe nanowires grown on the SiO2 structures of the patterned a-C/SiO2/Si substrates have diameters of 10-20 nm and can reach a few micrometers in length. The described method enables the preparation of complex architectures of Fe-filled MWNTs and may be used for future applications based on filled nanotubes.

1. Introduction
In the past few years, ferromagnetic filled multi-wall carbon nanotubes (MWNTs) have attracted much attention due to their distinct magnetic properties compared to the bulk ferromagnetic material [1,2]. Several studies have been reported on MWNTs filled with Fe, Co, Ni or their alloys [1-11]. Fe-filled MWNTs are of particular interest, because they are likely to be used as tips for magnetic force microscopy (MFM) sensors [6] as well as in biomedicine as a nanocarrier for different human medical treatments in anti-tumour therapy [7,8]. The carbon shells provide an effective barrier against oxidation ensuring the long-term stability of the ferromagnetic filling.

Fe-filled MWNTs with high filling yield are produced by pyrolysis of ferrocene [1-8,11]. They are obtained as bundles grown on the CVD (chemical vapor deposition) reactor walls or vertically aligned on SiO2/Si substrates. In a previous study, we reported on arrays of vertically aligned Fe-filled MWNTs grown on SiO2/Si substrates[1,4,5]. The aligned Fe-filled MWNTs have shown interesting structural and magnetic properties compared to the bulk ferromagnetic material. However, for future applications – such as Fe-filled MWNTs as MFM sensors, in biomedicine and especially for their implementation in nanoelectronic devices, the achievement of selective growth of Fe-filled MWNTs on specific substrates is highly necessary. Hence, controlled CVD growth strategies on patterned substrates must be developed.

Here we report on the selective growth of vertically aligned Fe-filled MWNTs. The filled carbon nanotubes (CNTs) are grown selectively on the SiO2 surfaces of patterned amorphous carbon (a-C)/SiO2/Si substrates.
2. Experimental

The vertically aligned Fe-filled MWNTs are produced via the pyrolysis of ferrocene in a CVD reactor with a two zone furnace system [4]. The a-C patterns on the thermally oxidized Si (100) wafers (1 µm SiO₂) are prepared using conventional lithography processes combined with a sputter-deposition of an a-C (thickness of 100 nm).

For the growth of the vertically aligned Fe-filled MWNTs, Ar gas is used as a carrier gas and ferrocene (Fe(C₅H₅)₂) is employed as the precursor. This material supplies both, the Fe for the filling inside the CNTs, and the carbon for growing the nanotube shells. A quartz boat with ferrocene is positioned in the first temperature zone of the reactor and the a-C-patterned silicon substrates are placed in the second zone. As a first step, the ferrocene is sublimated at temperature of 150 °C. The ferrocene vapor is transferred by a controlled Ar flow (100 standard cubic centimeter per minute) into the second zone, the reaction zone, heated at 900 °C where the decomposition of the ferrocene and the growth of the filled nanotubes took place. The growth period was set to 10 min. Finally, the reactor is slowly cooled down to room temperature in the Ar flow gas atmosphere. Aligned CNTs are grown only on the SiO₂ surfaces. On the a-C-precovered surfaces, however, no deposition could be observed.

The morphology of the samples is studied by scanning electron microscopy (SEM, Leo 1530), transmission electron microscopy (TEM, Tecnai F30 with GIF200) and element specific imaging (ESI) analysis. The crystalline structure and the chemical composition of the filled nanotubes are investigated by energy dispersive X-ray (EDX) and high resolution TEM (HRTEM) methods. The magnetic behavior of the obtained samples is investigated by alternating gradient magnetometry (AGM) measurements.

3. Results and discussion

3.1. Morphology of the samples

Figure 1(a) displays a typical SEM image of the selective growth of vertically aligned Fe-filled MWNTs on a-C-prepatterned silicon substrates. It can be clearly seen that the CNTs formed only on the uncovered SiO₂ surfaces, but not on the patterned a-C structures. The reason of this can be attributed to the different behavior of the Fe catalyst particles, which deposited by the pyrolysis of the ferrocene [11], on both surfaces (a-C and SiO₂).

The nanotubes have high packing density and are aligned vertical to the substrate surface (see inset of figure 1(a)). They have a length of about 3 µm and an outer diameter of 20-55 nm. For the TEM studies the nanotubes are separated from the substrate and dispersed onto a copper grid. The studies revealed MWNTs with a high filling yield (see figure 1(b)). The encapsulated Fe nanowires have diameters of 10-20 nm and can reach a few micrometers in length.

Clear information on the interaction of the metal catalyst particles with the substrate material (a-C and SiO₂) by the filled nanotube growth could be obtained by cross-sectional TEM observations of the patterned a-C/SiO₂/Si substrate. TEM images of the cross section of the substrate after CVD growth of filled nanotubes are shown in figure 2. On the SiO₂ area, filled nanotubes can be easily identified (see figures 2(a) and (b)). While on the a-C surface no trace of nanotubes is found, but precipitates of particles are observed beneath the surface (see figures 2(a) and (c)). ESI analysis in TEM indicated that these particles are Fe-containing particles.

The obtained results point out that during the pyrolysis of ferrocene catalytic active Fe particles formed on the SiO₂ substrate surface [11]. Due to the high activity of carbon in the gas phase, carbon dissolved into the Fe particles. Thus, the metal particles became supersaturated with carbon atoms, and the precipitation of carbon from the surface of the Fe particles led to the formation of tubular carbon structure. However, the metal catalyst particles, which deposited on the a-C surface during the pyrolysis process, diffused through the amorphous carbon layer and therefore, they can not catalyze the carbon nanotube growth.
3.1.2. Structure and magnetic properties

High resolution transmission electron microscopy studies reveal that the Fe-filled MWNTs are well graphitized and consist of concentric carbon shells with a spacing of about 0.34 nm wrapping the metal core, which appears to be crystalline. A typical HRTEM image is shown in Fig. 3(a). The graphitic layers are stacked parallel to the tube axis and to the outside surface of the metallic core. All

Figure 1. (a) SEM image of the selective growth of aligned Fe-filled MWNTs on the SiO$_2$ structures. The inset shows that the nanotubes are perpendicular to the substrate surface; (b) TEM image of Fe-filled MWNTs grown on the SiO$_2$ surfaces.

Figure 2. TEM images of a cross section of the patterned a-C/SiO$_2$/Si substrate after CVD growth (a); (b) SiO$_2$ area in (a) showing the growth of filled nanotubes; (c) a-C area from (a) showing the formation of Fe-containing particles inside the amorphous carbon layer. The Pt layer is used for the cross section preparation.
the Fe nanowires are tightly wrapped by the nanotubes wall, i.e., no gap between the filling and the inner carbon shell is found, indicating that carbon and metal are intimately related in the growth process.

Global and local energy dispersive X-ray investigations of the aligned nanotubes confirm that the encapsulated filling is Fe (see figure 3(b)). The other features in the EDX spectrum arise from the nanotube (C) shells, the oxidized silicon substrate (Si) and the TEM grid supporting the sample (Cu).

Figure 3. (a) HRTEM image of an Fe-filled MWNT, showing the metal core and the carbon shells; (b) Local EDX spectrum of a cross section through an Fe-filled MWNT (scanning TEM-modus, the diameter of the electron beam is 2 nm; the probe was moved across the filled nanotube). The copper signals result from the TEM grid supporting the sample.

Magnetometry measurements with a maximum applied field of 1 T are done on the studied samples at room temperature. Figure 4 shows the hysteresis loops for the field applied parallel and
perpendicular to the substrate surface. Compared with the coercivity value of \( \mu_0 H_C \approx 0.09 \text{ mT} \) for bulk Fe, a strongly enhanced value of \( \mu_0 H_C \approx 40 \text{ mT} \) is obtained, showing this material is a promising aspect for magnetic stability considerations. In addition, a weak uniaxial magnetic anisotropy associated with an easy axis perpendicular to the substrate plane is found, which, however, is less pronounced than is observed for aligned Fe-filled MWNTs grown on non-patterned SiO\(_2\)/Si substrates [1]. Actually, the uniaxial magnetic anisotropy phenomenon is often seen in arrays of magnets, whose shapes can be approximated as thin cylinders [12]. Therefore, the peculiar magnetic behavior of the sample of Fe-filled MWNTs grown on patterned a-C/SiO\(_2\)/Si substrate may be attributed to the Fe-containing particles embedded in the a-C layer.

4. Conclusions
This work showed a method for the selective growth of vertically aligned Fe-filled MWNTs with high filling yield on patterned a-C/SiO\(_2\)/Si substrates. The filled nanotubes grew preferentially on the SiO\(_2\) surfaces, but not on the patterned a-C structures. During the filled nanotube growth process the metal catalyst particles formed on the a-C surface diffused through the amorphous carbon layer, and hence no nanotube growth is found. Active metal catalyst particles are formed on the silicon oxide surface resulting in the formation of aligned Fe-filled CNTs on this substrate surface. The carbon nanotube encapsulated Fe nanowires grown on the SiO\(_2\) surface are crystalline. They have diameters of 10-20 nm and can reach a few micrometers in length. This method enables the production of complex architectures of Fe-filled MWNTs, which may be promising for the use in sensors as well as functional elements.

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