Preparation of catalytic nano-particles and growth of aligned CNTs with HF-CVD

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Abstract. Carbon nanotubes (CNTs) - rolled up sheets of graphite - appear in various forms. One way to produce CNTs is chemical vapour deposition (CVD) using carbon containing gases in the presence of catalysts like Fe. For the so-called substrate supported catalyst (SSC) method the catalyst is provided in form of particles at the substrate surface and is thus directly accessible for the carbon containing CVD gas flux to induce CNT growth. In this work we studied five different approaches to create and use catalytic nano-particles for CNT growth. The results of the CVD deposition experiments were analyzed with SEM and TEM. For all five approaches a set of CVD-parameters could be found that led to the formation of dense films of CNTs with different degrees of alignment. HR-TEM analysis showed either fishbone arrangement or multi-walled CNTs depending on the catalyst type.

1. Introduction

Carbon nanotubes (CNTs) [1] are rolled up sheets of graphite and appear in various forms depending on their chirality and shell-structure. One way to produce CNTs is chemical vapour deposition (CVD) using carbon containing gases like CH₄ in the presence of catalysts like Fe, Co or Ni [2]. The goal of this work was to develop and study various methods to produce and homogeneously distribute catalytic particles on a substrate surface and to use these particles for the growth of CNTs with hot filament chemical vapour deposition (HF-CVD). The following approaches were studied:

- type 1: Iron based nano-particles from a ferric nitrate solution.
- type 2: Cobalt based nano-particles from a cobalt-acetate solution.
- type 3: Sol-gel supported formation of iron nano-particles.
- type 4: Deposition of size and shape controlled iron-oxide nano-particles.
- type 5: Dispersion of commercially available iron-oxide nano-particles in PEG.

The samples were processed in a hot filament CVD (HF-CVD) reactor. The results of the CVD deposition experiments were analyzed with SEM to determine the density and degree of alignment of the grown CNTs and HR-TEM to characterize the inner structure of the CNTs. For all approaches a set
of CVD-parameters could be found that led to the formation of CNTs with different degrees of alignment and zoning. HR-TEM analysis showed either fishbone arrangement of the CNTs or multi-walled CNTs depending on the catalyst type.

2. Experiment

The catalyst containing chemistry was applied on 10x10mm² quartz-glass substrates (HSQ300) using spin-coating with a Laurell WS-400A or adsorption (for type 4).

2.1. Type 1 - Iron based nano-particle from ferric nitrate solution

Samples of type 1 were prepared according to Mauron et.al. [3]. 500mmol of Fe(NO₃)₃·9H₂O (ferric nitrate) were dissolved in 100ml of C₂H₅OH (ethanol) and spin-coated on the quartz substrates at 2000rpm for 30s. Iron oxide particles formed during annealing at 650°C for 60 min in air. An AFM-image showing the typical size distribution is given in figure 1a. The filament temperature (Tᶠ) in HF-CVD reactor was around 2500°C and the substrate was held at Tsub = 700°C during CNT growth. As carbon source a gas mixture of H₂ (φH₂ = 250sccm) and CH₄ (φCH₄ = 25sccm) at a pressure of p = 30mbar was used. A dense layer of CNTs (figure 1b) grew during 60min of gas flow. In total 0.5mg of carbon in form of CNTs were deposited.

2.2. Type 2 - Cobalt based nano-particles from cobalt-acetate solution

100mmol of cobalt acetate Co(C₂H₃O₂)₂ were dissolved in 100ml ethanol and spin-coated at 2000rpm for 30s. Evaporation of the solvent during 30s at 104°C on a hot-plate resulted in the formation of sub-μm particles as shown in the AFM image of figure 2a. An approximately 20μm thick dense layer of entangled CNTs formed (figure 2b) during the following CVD process: Tᶠ = 2400°C, Tsub = 670°C, φH₂ = 250sccm, φCH₄ = 25sccm at p = 100mbar for 60min.

2.3. Type 3 - Sol-gel supported formation of iron nano-particles

Samples of this type were produced using a sol-gel process involving tetra-buthyl titanate, 2-propanol as solvent and ferric nitrite as catalyst (1:10:0.7 mol) under acid conditions. The sol was spin-coated at 4000rpm for 30s and annealed at 750°C for 60min in air to form iron oxide nanoparticles as shown in figure 3a. The filament temperature during the CVD process was 2400°C with a substrate temperature of 650°C. The gas flux consisted of 250sccm H₂ and 25sccm CH₄ at a pressure of 30mbar. The CVD result can be seen in figure 3b. Over 20μm long multi-walled CNTs (which can be seen from the FFT in inset of figure 3c) formed during 60min of carbon deposition.

2.4. Type 4 - Deposition of size and shape controlled iron-oxide nano-particles

Iron-oxide (FeₓOᵧ) nano-particles were produced according to Kovalenko et.al. [5] out of a colloidal solution and adsorbed to the substrate surface during 30min of dipping at a concentration of 4mg/ml. Figure 4a shows an SEM image of these particles, a very narrow size distribution. At Tsub = 820°C and Tᶠ = 2300°C the CNTs shown in figure 4b were grown at a pressure of 100mbar and the following gas flux: H₂ 250sccm, CH₄ 25sccm.

2.5. Type 5 - Dispersion of commercially available iron-oxide nano-particles in PEG

Commercial available iron metal powder (Nanostructured & Amorphous Materials, Inc, product# 0266JY) with a nominal mean size of 25nm were dispersed in polyethyleneglykol (PEG-1000) and spin-coated onto the quartz substrate at 1000rpm for 30s. At Tsub = 670°C and Tᶠ = 2400°C the CNTs given in figure 5b were grown at a pressure of 100mbar with this gas flux: H₂ 250sccm, CH₄ 25sccm.

3. Results

The results of the CVD deposition experiments were analyzed with SEM and HR-TEM (figure 1 - figure 5). HR-TEM analyses reveal either fishbone arrangement with bamboo defects for sample type 1, 2, 4 and 5 or multi-walled CNTs for sample type 3, the sol-gel method.
Figure 1. type 1: (a) AFM image of iron-oxide particles after annealing; (b) SEM image of dense film of CNTs; (c) HR-TEM image of CNT with fishbone arrangement, inset: FFT of marked area.

Figure 2. type 2: (a) AFM image of cobalt particles after annealing; (b) SEM image of dense film of grown CNTs with substrate layer; (c) HR-TEM image of CNT with fishbone arrangement.

Figure 3. type 3: (a) AFM image of iron-oxide nano particles out of sol-gel after annealing; (b) SEM image of dense film of multi-walled CNTs; (c) HR-TEM image of MW-CNT; inset shows FFT of marked area, indicating the high regularity of the layers-sequence in the MW-CNT.

Figure 4. type 4: (a) SEM image of Fe$_x$O$_y$ nano-particles; (b) SEM image of grown CNTs; (c) HR-TEM image of CNTs with fishbone arrangement with a high density of bamboo defects.
Figure 5. type 5; (a) AFM image of metallic iron particles in PEG; (b) SEM image of entangled, dense film of CNTs; (c) HR-TEM image of CNT with fishbone arrangement.

4. Discussion

For all five different catalytic systems, a set of CVD parameters could be found which led to the formation of CNTs. Iron nano-particles produced with sol-gel technique triggered the formation of well aligned multi-walled carbon nanotubes. The CNTs show different degrees of alignment. According to the SEM studies entanglement of the CNT can be related to the density of the catalyst particles - the less dense the particles are spread the higher the degree of entanglement. CNTs grown on samples with high particle density like type 3 show nice alignment, since the CNTs lack free horizontal space and thus are guided in the vertical direction by their next neighbours.

Also the quality of the CNTs regarding defects can be related to the particle density. A narrow size distribution of the catalytic particles not necessarily leads to the formation of MW-CNTs, as can be seen from sample type 4, covered with spherical Fe$_x$O$_y$ nano-particles having a diameter of 12±1nm (fwhm).

No single-walled CNTs were found during TEM studies. This might be due to the relatively large size of catalytic particles compared to the diameter of a single-walled CNT.

5. Outlook

The following work will focus on sol-gel method and the dispersion of size controlled iron-oxide nanoparticles. We think that there is still room for improvement regarding the CVD-process to control the quality of the CNTs and to increase the yield of MW-CNTs avoiding bamboo defects and fishbone arrangement. Furthermore UV-nanoimprint lithography and microcontact printing will be used for the structured deposition of the catalytic particles for the creation of patterned arrays of CNTs.

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