SiC formation in carbon nanotubes grown from permalloy catalyst particles

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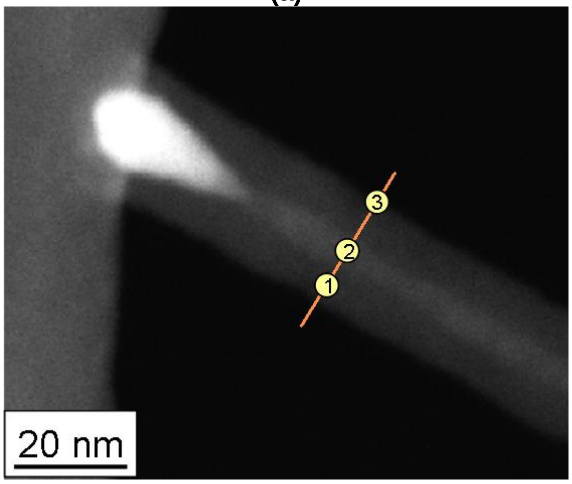
We present the formation of SiC nanowires within carbon nanotubes (CNT) that are grown from $Ni_{80}Fe_{20}$ ("permalloy") catalyst particles using plasma-enhanced chemical vapour deposition (PE-CVD). The as-produced CNT were characterized by means of aberration-corrected high resolution transmission electron microscopy (using a FEI TITAN³ 80-300 microscope operated at 80kV).
Fig. 1a shows a representative scanning electron transmission microscopy (STEM) image of a likewise grown CNT that is attached to an amorphous carbon carrier film. The image reveals a clear contrast difference between the particle, the concentric graphene layers of the CNT and its core, respectively. For a chemical analysis of this nanotube, Electron Energy Loss (EEL) spectra are collected from different positions across the CNT. Whereas these spectra allow us clearly identify the catalyst particle as $Ni_{80}Fe_{20}$ with no detectable amounts of impurities, the "filling" of the CNT (as already apparent from the enhanced Z contrast in the STEM image) does not show any signs of Ni nor Fe. Instead, local EEL spectroscopy (EELS) reveals the existence of Si from the occurrence of a Si-L absorption edge at around ΔE = 100 eV followed by a broad double-peak type of feature (figure 1b [2]). These spectral features of the "filling" carry the fingerprint structure of SiC which apparently forms during the CNT growth process. The details of the SiC formation remain to be unveiled, although it is clear that the required Si and C ingredients are largely available through the gaseous carbon feedstock utilized for the CNT growth and the plasma-induced chemical etching of the Si substrate, respectively. The observation of sp^3-hybridized carbon in the core of the tubes (which is consistent with the formation of SiC) through cross-sectional EELS lines scans further confirms that the core material is SiC. Moreover, the CNT were found to be coated with a thin layer of amorphous silicon oxide (cf. EELS line scan in figure 1b [3]) which supports the aforementioned assumption that Si is present in the gas phase during (and after) the CNT growth process. This Si vapor apparently forms a thin coating through heterogeneous nucleation and growth on the freshly prepared CNT, and this primarily formed Si layer then oxidizes during the exposure to ambient air upon removal of the sample. As a result, the CNT exhibit a complex core-shell structure with a SiC core and an amorphous SiO_2 overcoat, respectively.
Fig. 2 shows a HRTEM picture of a CNT grown from a permalloy catalyst particle. Here, the SiC filling is clearly visible. In addition, the graphene layers of the CNT are bent towards the core which indicates a strong correlation between the graphene and the SiC core which is found to form a sharp interface to the permalloy catalyst particle. The amorphous SiO_2 overcoat of the CNT is also visible in the HRTEM micrograph. These findings clearly point to a complex mutual interplay between the catalyst particle, the substrate and the carbon feed stock during the CNT growth via PE-CVD.
To the best of our knowledge, it is for the first time that such a simultaneous formation of SiC nanowires in the cores of CNT is shown. Previous work in the field is rather dedicated to the production of SiC nanowires, e.g., through the conversion of CNT to carbide rods [1], reactive laser ablation [2] and/or hot filament chemical vapor deposition [3].
Thus, the here reported experimental route renders a novel approach for producing SiC re-inforced CNT or – after a subsequent removal of the carbon "shell" – SiC nanowires.

References

[1] Dai et al., Nature, **375** (1995) 769-772.
[2] Zhang et al., Science, **281** (1998) 973-975.
[3] Zhou et al., APL, **74** (1999) 3942-3944.

Figures

(a)



(b)

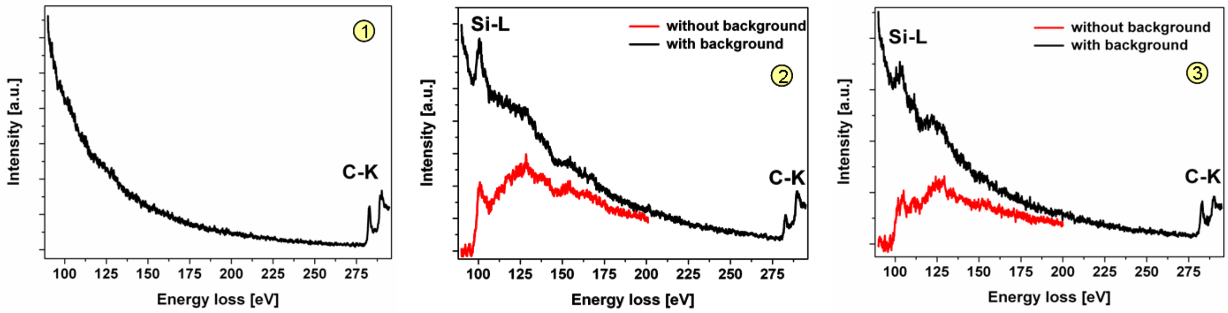


Figure 1. (a) The STEM image of a carbon nanotube gown from a permalloy catalyst particle reveals a clear difference in Z contrast between the CNT, the SiC core and the catalyst. (b) EEL spectra of the positions marked by numbers in figure 1a. Both the Si-L and the C-K absorption edges are indicated. There is no indication of Si “contaminations” within the graphene layers of the CNT[1]. The fine structure of the Si-L absorption edge provides evidence for the formation of SiC [2] and SiO_2 [3].

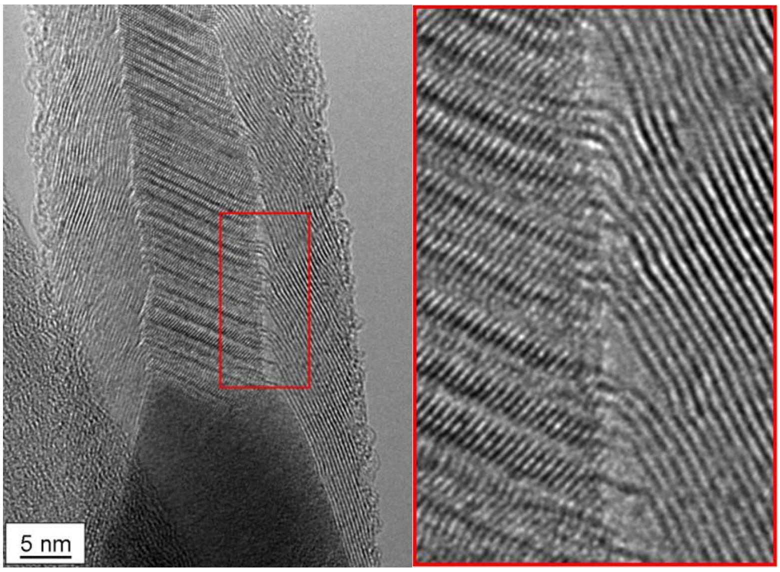


Figure 2. The HRTEM image of the CNT clearly shows the occurrence of a crystalline “filling” within the nanotube identified as SiC. A close-up of the interface region between the CNT and the SiC core implies local termination of the grapheme layer of the CNT through covalent bonding. The outer amorphous SiO_2 coating of the CNT can also be seen in the (left) HRTEM image.