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Nucleation and aligned growth of multi-wall carbon nanotube films during thermal CVD

Y. Yao [a], L.K.L. Falk [a,*], R.E. Morjan [b], O.A. Nerushev [b], E.E.B. Campbell [b]

[a] *Department of Applied Physics, Chalmers University of Technology, SE-412 96 Göteborg, Sweden*
[b] *Department of Physics, Göteborg University, SE-412 96 Göteborg, Sweden*

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Abstract

The development during early growth of a multi-wall carbon nanotube film by thermal CVD with acetylene (C_2H_2) and hydrogen at 750 °C has been characterized in detail by cross-section transmission electron microscopy. The studies provide information on the nanotube growth mechanisms and the complex catalyst transformations that are essential for the onset of different growth stages. An initial random growth catalysed by supported particles is followed by aerosol growth of aligned tubes. This results in a two-layered film structure, where a film of aligned nanotubes is lifting up an initially formed nanotube network from the substrate.

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1. Introduction

Films of multi-wall carbon nanotubes and carbon nanowires may be fabricated by different chemical vapour deposition (CVD) techniques in the presence of a supported catalyst. CVD experimental procedures for film growth have been established in a number of systems [1–9].

The mechanisms behind the development of an aligned film of carbon nanotubes are, however, not fully understood. Proposed models for aligned nanotube growth include van der Waals interaction [5], steric hindrance [6], an over-crowding effect [10] and mechanical leaning [7]. A high nucleation density is, in general, believed to be important for the alignment [8,9,11]. This would require a sufficiently high density of catalyst particles with diameters suitable for nanotube growth.

Detailed analyses of carbon nanotube films, grown by thermal CVD with acetylene (C_2H_2) and hydrogen on silicon wafers supporting $(Fe,Si)_3O_4$ particles, have been described in previous publications [1,2]. The analyses were carried out on thin-foil cross-section specimens in a transmission electron microscope (TEM). This technique allows the direct observation and analysis of the carbon nanotube film and the interface between the film and the substrate. The technique also makes it possible to image the interaction between the supported catalyst particles and the nanotubes [1,2,4]. It was found that the pre-formed $(Fe,Si)_3O_4$ particles were reduced to catalytic iron silicides (α-(Fe,Si), α_1- and α_2-Fe_2Si) during the CVD process. In addition, there was an obvious particle refinement during CVD at 750 °C. It was suggested that this refinement played a key role in the development of the aligned film of multi-wall carbon nanotubes [2].

The present paper is focussed on the development of supported catalyst particles and carbon nanotubes during the CVD process at 750 °C. TEM cross-sections were prepared from samples subjected to different times of CVD. The purpose of this investigation was to characterise the particle refinement process, and to clarify its effect on nanotube nucleation and growth.

2. Experimental

2.1. Carbon nanotube film growth

An iron film with a thickness of around 1 nm was deposited on polished and sonicated silicon (002) wafers by electron beam evaporation at room temperature. The coated substrates were transferred to the

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[*] Corresponding author. Fax: +46 0 31 772 3224.
E-mail address: lklfalk@fy.chalmers.se (L.K.L. Falk).

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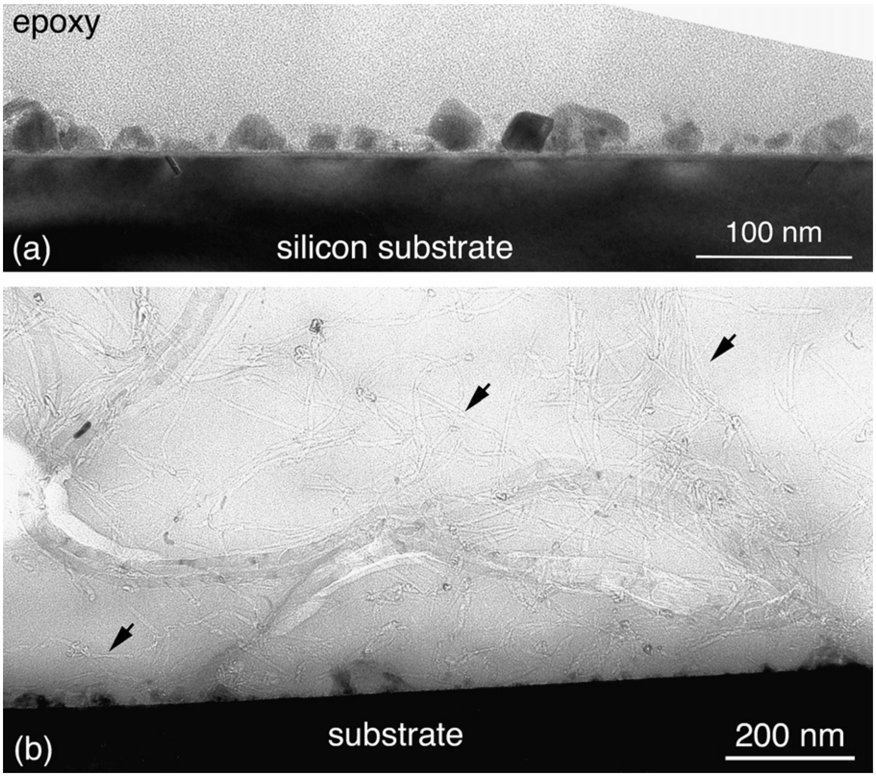

Fig. 1. TEM thin-foil cross-sections showing (a) pre-formed magnetite particles on top of the silicon substrate prior to CVD, and (b) disintegrated supported particles and carbon nanotubes (arrowed) just above the substrate after CVD for 60 s.

CVD chamber and annealed at 750 °C for 15 min in flowing argon and hydrogen. This heat treatment results in a transformation of the iron film into fcc $(Fe,Si)_3O_4$ magnetite particles separated from the silicon by the inherent surface silica layer, see Fig. 1a [1,2]. The peak of the particle size distribution is ~15–20 nm, and the particle surface density on the substrate is around $4.5 \times 10^{14}\ m^{-2}$ [1]. Locally, this heat treatment also results in an enrichment of iron at the interface between the silicon substrate and the surface silica film.

Thermal CVD was carried out at 750 °C by introducing a gas mixture of acetylene (C_2H_2, 99.9%), hydrogen (H_2, 99.99%) and argon. The flow rates of C_2H_2/H_2/argon were 12/100/600 sccm, respectively. The total gas pressure was 1 atm. The growth time was varied from 30 s to 15 min (30, 60, 300, 600, 900 s). The samples were furnace cooled under flowing argon and hydrogen after the completion of deposition.

The general morphology of the produced carbon nanotube films was examined in a field emission scanning electron microscope (FEG-SEM; Leo Ultra 55). The SEM was operated at a low acceleration voltage between 2 and 5 kV in order to avoid sample damage.

2.2. Transmission electron microscopy

Thin-foil cross-sections for TEM were prepared from pieces composed of two film covered wafers glued face to face by M-bond 601 epoxy. Thin slices were cut perpendicular to the bond and hand polished to a 0.25 μm surface finish on both sides and a final thickness of ~15–25 μm. The polished slices were mounted on molybdenum support grids (1 mm hole), and ion-beam polished to electron transparency.

The cross-sections were examined in a field emission transmission electron microscope (FEG-TEM; Philips CM200) equipped with an energy dispersive X-ray spectroscopy system (EDX; Oxford Instrument Link ISIS) and the Gatan imaging filter (GIF). Local elemental compositions were determined by fine probe EDX analysis using an electron probe with a nominal FWHM of around 2 nm. The elemental spatial distribution was also obtained from electron spectroscopic images. Pre- and post-edge images were recorded around the Fe–L_{23} (708 eV), O–K (532 eV), Si–L (149 eV) and C–K (284 eV) edges in the electron energy loss (EEL) spectrum using a 50 eV energy selecting slit. The spatial distributions of these elements were displayed as jump ratio images computed by dividing the post-edge image by the pre-edge image. The structure of individual catalytic particles was determined by electron micro-diffraction using a 1–2 nm electron probe with a convergence angle of $2\alpha = 2.04$ mrd. The camera length was calibrated using a {1 1 1} reflection from the silicon substrate ($d_{111} = 0.3135$ nm). Identification of electron diffraction patterns was performed using the auto-indexing function of the EMS On Line software[1].

3. Results

3.1. CVD for 30 s

The supported particles did not show any obvious morphological changes after CVD for 30 s. Fine probe EDX analysis showed that the particles still contained iron, silicon and oxygen, and electron micro-diffraction patterns were consistent with the cubic magnetite structure (Fe_3O_4; $a = 0.8396$ nm; $Fm3m$). Carbon nanotube growth was not observed at this stage.

3.2. CVD for 60 s

There was an increased nucleation and growth of multiwall nanotubes in the time interval 30–60 s of the CVD

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[1] http://cimesg1.epfl.ch

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