

FC250 Nano- and microtechnologies

chapter 2. Carbon Nanotubes

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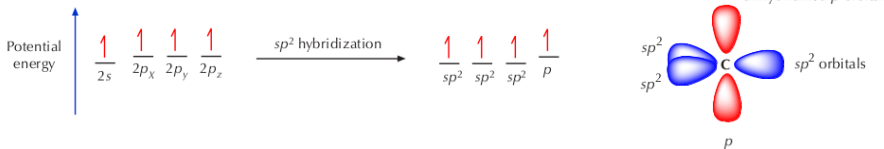
Outline - chapter 2. Carbon Nanotubes

- 2.1 Structure of Carbon Nanotubes
- 2.2 Synthesis of Carbon Nanotubes
- 2.3 Growth Mechanism of Carbon Nanotubes
- 2.4 Properties of CNTs
- 2.5 Carbon Nanotube-Based Nano-Objects
- 2.6 Potential and Current Applications

2.1 Structure of Carbon Nanotubes

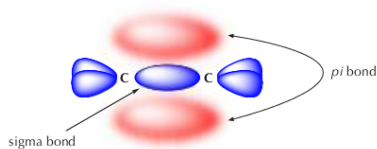
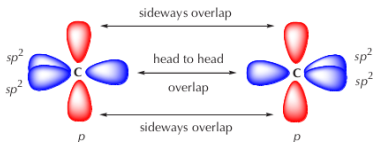
Bonds using sp^2 C hybrid orbitals

sp^2 -C valence orbitals:

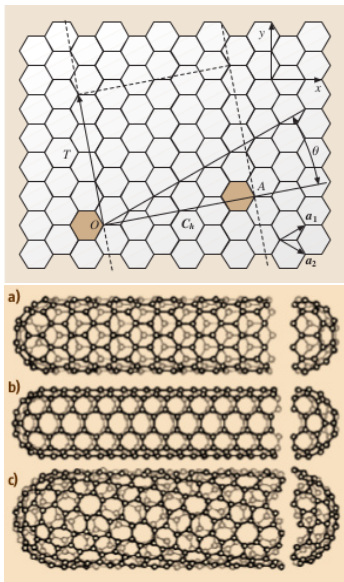


Bonds:

- ▶ one valence electron in pure p state creates π -bond by sideways overlap of atomic orbitals
- ▶ other three electrons in sp^2 hybrid orbitals (combination of $1/3s$ and $2/3p$) create σ -bonds by head-to-head overlaps
 - trigonal planar bonding directions with angles of 120°



Single-wall nanotubes - chirality



Various ways to roll graphene into tubes are mathematically defined by the vector of helicity (**chirality vector**) \vec{C}_h , \perp to the tube axis, and the angle of helicity (**chiral angle**) θ

$$\vec{OA} = \vec{C}_h = n\vec{a}_1 + m\vec{a}_2$$

$$\vec{a}_1 = \frac{a\sqrt{3}}{2}\vec{x} + \frac{a}{2}\vec{y}$$

$$\vec{a}_2 = \frac{a\sqrt{3}}{2}\vec{x} - \frac{a}{2}\vec{y}$$

where $a = 2.46 \text{ \AA}$ and

$$\cos \theta = \frac{2n + m}{2\sqrt{n^2 + m^2 + nm}}$$

- (a) **armchair** $m = n$, i. e. $\vec{C}_h \parallel$ to any C=C bonds - here (5,5)
- (b) **zigzag** $m = 0$, i. e. $\vec{C}_h \perp$ to any C=C bonds - here (9,0)
- (c) $m \neq n$ chiral (n,m) - here (10,5)

Nanotube tips contain C atoms also in pentagonal rings (hemi-fullerene) - $6 \times 5 = 30$ atoms \Rightarrow (for ideal SWCNTs) chemical reactivity will be highly favored at the tube tips (at pentagonal rings)

Single-wall nanotubes - diameter, sp^2 C bond deformation

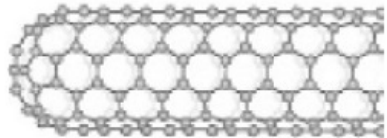
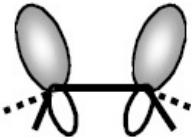
Diameter D is related to the vector of chirality \vec{C}_h

$$D = \frac{|\vec{C}_h|}{\pi} = \frac{a_{CC} \sqrt{3(n^2 + m^2 + nm)}}{\pi}$$

where the C=C bond length is elongated by the curvature imposed

$$1.41 \text{ \AA} \text{ (graphite)} \leq a_{C=C} \leq 1.44 \text{ \AA} \text{ (C}_{60}\text{)}$$

The C=C bond angles are not planar \Rightarrow hybridization is not pure sp^2 (some degree of sp^3) - same effect as in fullerene C_{60} molecule (radius 0.35 nm, bonds have 10% sp^3 character).



Bond deformation induces variable overlapping of energy bands (unique and versatile electronic behaviour), perhaps also a bit more reactive than planar graphene?

Single-wall nanotubes - ropes

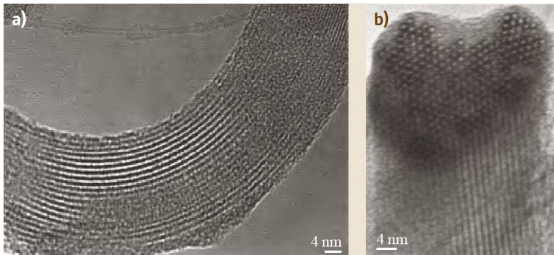


Fig. High-resolution transmission electron microscopy images of a SWNT rope. (a) Longitudinal view. An isolated single SWNT also appears at the top of the image. (b) Cross-sectional view



Fig. Image of two neighboring chiral SWNTs within a SWNT bundle as seen using high-resolution scanning tunneling microscopy

Multi-wall nanotubes



Fig. 3.5 High-resolution transmission electron microscopy image (longitudinal view) of a concentric multiwall carbon nanotube (c-MWNT) prepared using an electric arc. The *insert* shows a sketch of the Russian doll-like arrangement of graphenes

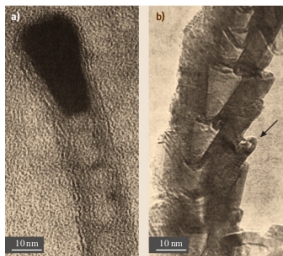


Fig. 3.6a,b Some of the earliest high-resolution transmission electron microscopy images of a herringbone (and bamboo) multiwall nanotube (bh-MWNT, longitudinal view) prepared by CO disproportionation on Fe-Co catalyst. (a) As-grown. The nanotube surface is made of free graphene edges. (b) After 2900 °C heat treatment. Both the herringbone and the bamboo textures have become obvious. Graphene edges from the surface have buckled with their neighbors (*arrow*), closing off access to the intergraphene space

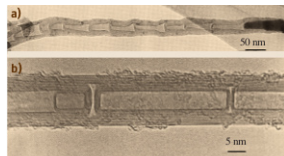


Fig. 3.7a,b Transmission electron microscopy images from bamboo multiwall nanotubes (longitudinal views). (a) Low magnification of a bamboo-herringbone multiwall nanotube (bh-MWNT) showing the nearly periodic nature of the texture, which occurs very frequently, (from [3.18]); (b) High-resolution image of a bamboo-concentric multiwall nanotube (bc-MWNT) (modified from [3.19])

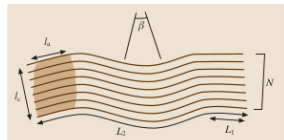


Fig. 3.8 Sketch explaining the various parameters obtained from high-resolution (lattice fringe mode) transmission electron microscopy, used to quantify nanotexture: L_1 is the average length of perfect (distortion-free) graphenes of coherent areas; N is the number of piled-up graphenes in coherent (distortion-free) areas; L_2 is the average length of continuous though distorted graphenes within graphene stacks; β is the average distortion angle. L_1 and N are related to the L_a and L_c values obtained from X-ray diffraction

2.2 Synthesis of Carbon Nanotubes

- ▶ Various methods - need of controlling purity, structural quality and chirality (for SWCNTs)
 - ▶ How to understand the mechanism of nanotube nucleation and growth? - still controversial subject
 - ▶ Not only carbon involved: aside from c-MWCNTs derived from electric arc (catalyst-free), nanotubes are frequently found to be associated with the catalyst crystals from which they are formed
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- ▶ 2.2.1 Solid Carbon Source - Based Synthesis of CNTs
 - ▶ 2.2.2 Gaseous Carbon Source-Based Production Techniques

2.2.1 Solid carbon source - based synthesis of CNTs

four solid carbon source - based techniques

- ▶ laser ablation
- ▶ dc electric arc
- ▶ three-phase ac arc plasma
- ▶ solar energy

⇒ high temperature ($1000 \text{ K} < T < 6000 \text{ K}$) is common feature but morphologies of carbon nanostructures and the SWCNTs yields can differ notably

Before CNTs, production of fullerenes:

- ▶ laser vaporization of graphite - 1st method for C_{60}
- ▶ electric arc - 1st method for production of fullerenes in relatively large quantities

Methods that helped to discover CNTs:

- ▶ 1991, Iijima, catalyst-free formation of c-MWCNTs by electric arc
- ▶ 1993, Iijima+Ichihashi and independently Bethune, attempts to fill MWCNTs with metal
⇒ transition metals introduced as part of electrode ⇒ accidentally discovered SWCNTs

Laser ablation - experimental devices

During the interaction between the laser beam and the material, numerous phenomena occur at the same time and/or follow each other within the certain time period. It is sensitive to

- ▶ characteristics of laser beam,
- ▶ incoming power density (fluence),
- ▶ nature of target,
- ▶ surrounding environment.

Two types are currently used

- ▶ pulsed laser
- ▶ laser operating in continuous mode (generally smaller fluence)

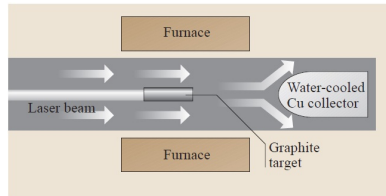


Fig. 3.9 Sketch of an early laser vaporization apparatus

Graphite pellet with catalyst is placed in the middle of a quartz tube filled with inert gas and placed in oven (1200 °C).

Pellet is vaporized, carbon species swept by a flow and deposited as **soot** in different regions (conical water-cooled copper collector, tube walls, backside of the pellet)

Laser ablation - improvements

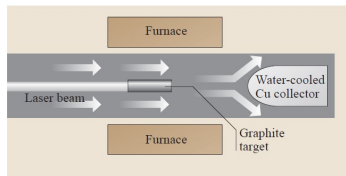
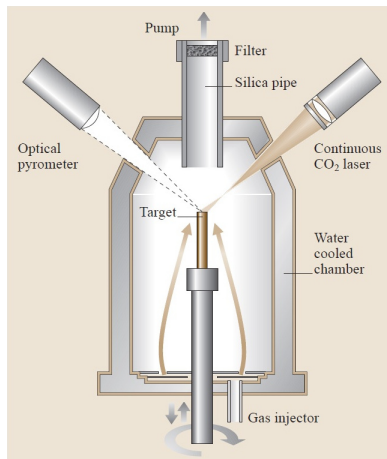


Fig. 3.9 Sketch of an early laser vaporization apparatus

some improvements:

- ▶ second pulsed laser - evaporation of coarse aggregates
- ▶ peller on revolving system for uniform heating
- ▶ two pellets (graphite and catalyst separately)



continuous CO₂ laser (10.6 μm), power 100-1600 W, control of pellet T - pyrometer, gas is heated by contact with pellet - external furnace unnecessary, products taken by gas flow and collected on filter

Laser ablation - results

- ▶ without catalyst: soot contains mainly c-MWCNTs, length up to 300 nm, quantity and quality depend on oven T (best at 1200 °C, lower T yields defective MWCNTs).
- ▶ with catalyst (transition metal like Ni, Co), a few percent or less: SWCNTs, yield depends on catalyst and increases with T , uniform diameter, rope-like crystals with diameter 5-20nm (see fig)

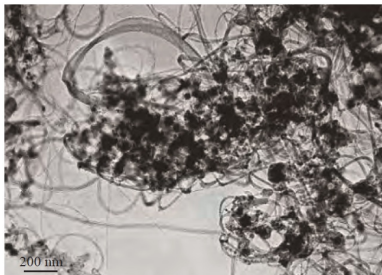


Fig. 3.11 Low-magnification TEM images of a typical raw SWNT material obtained using the laser vaporization technique. The fibrous structures are SWNT bundles, and the dark particles are remnants of the catalyst. Raw SWNT materials obtained from an electric arc exhibit similar features

Electric arc - experimental devices

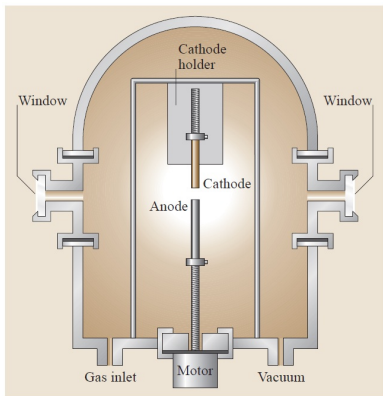


Fig. 3.12 Sketch of an electric arc reactor

- ▶ two graphite rods (few mm in diameter) are the electrodes between which the potential is applied
- ▶ anode - graphite with catalyst (Fe, Ni, Co, Y etc.) for SWCNTs growth
- ▶ inert atmosphere (Ar, He)
- ▶ plasma in carbon and catalyst vapors mixed with inert gas

Two types of anode

- ▶ graphite anode with a coaxial hole, several cm in length, into which mixture of catalyst and graphite powder is placed (more popular)
- ▶ graphite anode within which catalysts are homogeneously dispersed

Electric arc - experimental devices

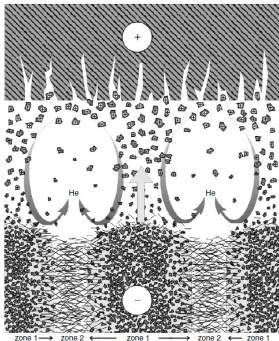


FIGURE. Schematic of MWNT growth in a DC arc. Positively charged graphitic splinters spallated from the anode partially vaporize on the way to the tops of the columns (zone 1). Intense carbon flux above the columns is due to enhanced thermionic emission from zone 1, which produces a high degree of carbon vapor ionization. Carbon density above the columns is further increased by circular convection of helium. Nanotubes grow in dense gas near the cathode surface from low-molecular carbon species and precipitate in zone 1 and zone 2 with their axes oriented preferentially parallel to the surface. This orientation is held constant in as-produced deposit core in both zone 2 and the nanotube braid of the column [1].

SWCNTs deposited in different regions

- ▶ collaret (formed around cathode)
- ▶ weblike deposit above the cathode
- ▶ soot all around reactor walls and the bottom

MWCNTs are formed in a hard cathode deposit under the cathode whether catalysts are used or not

The formation of collaret and web is not systematic and depends on exp. conditions. Cathode deposit and soot are obtained consistently.

Products do not consist solely of CNTs (see table on next page): carbon NPs, fullerene-like structures, poorly organized polyaromatic carbons, nearly amorphous carbon nanofibers, multiwall shells, single-wall nanocapsules, amorphous carbon ...

Table 3.1 Different carbon morphologies obtained by changing the type of anode, the type of catalyst and the pressure in a series of arc discharge experiments (electrode gap = 1 mm)

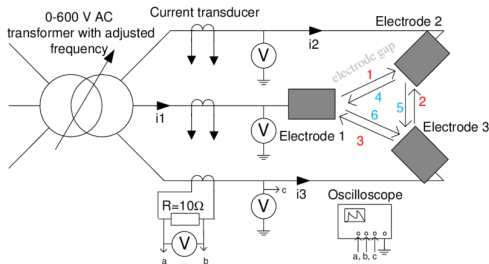
Catalyst (atom%) Arc conditions	0.6Ni + 0.6Co (homogeneous anode) $P \sim 60$ kPa $I \sim 80$ A	0.6Ni + 0.6Co (homogeneous anode) $P \sim 40$ kPa $I \sim 80$ A	0.5Ni + 0.5Co $P \sim 60$ kPa $I \sim 80$ A	4.2Ni + 1Y $P \sim 60$ kPa $I \sim 80$ A
Soot	<ul style="list-style-type: none"> MWNT + MWS + POPAC or Cn \pm catalysts $\phi \sim 3-35$ nm NANF + catalysts AC particles + catalysts [DWNT], [SWNT], ropes or isolated, + POPAC 	<ul style="list-style-type: none"> POPAC and AC particles + catalysts $\phi \sim 2-20$ nm NANF + catalysts $\phi \sim 5-20$ nm + MWS [SWNT] $\phi \sim 1-1.4$ nm, distorted or damaged, isolated or ropes + Cn 	<ul style="list-style-type: none"> AC and POPAC particles + catalysts $\phi \sim 3-35$ nm NANF + catalysts $\phi \sim 4-15$ nm [SWNT] $\phi \sim 1.2$ nm, isolated or ropes 	<ul style="list-style-type: none"> POPAC and AC + particles + catalysts $\phi \leq 30$ nm SWNT $\phi \sim 1.4$ nm, clean + Cn, short with tips, [damaged], isolated or ropes $\phi \leq 25$ nm [SWNC] particles
Web	<ul style="list-style-type: none"> [MWNT], DWNT, $\phi 2.7-4-5.7$ nm SWNT $\phi 1.2-1.8$ nm, isolated or ropes $\phi < 15$ nm, + POPAC \pm Cn AC particles + catalysts $\phi \sim 3-40$ nm + MWS [NANF] 	None	None	<ul style="list-style-type: none"> SWNT, $\phi \sim 1.4$ nm, isolated or ropes $\phi \leq 20$ nm, + AC POPAC and AC particles + catalysts $\phi \sim 3-10-40$ nm + MWS
Collaret	<ul style="list-style-type: none"> POPAC and SWNC particles Catalysts $\phi \sim 3-250$ nm, < 50 nm + MWS SWNT $\phi 1-1.2$ nm, [opened], distorted, isolated or ropes $\phi < 15$ nm, + Cn [AC] particles 	<ul style="list-style-type: none"> AC and POPAC particles + catalysts $\phi \sim 3-25$ nm SWNT $\phi \sim 1-1.4$ nm clean + Cn, [isolated] or ropes $\phi < 25$ nm Catalysts $\phi \sim 5-50$ nm + MWS, [SWNC] 	<ul style="list-style-type: none"> Catalysts $\phi \sim 3-170$ nm + MWS AC or POPAC particles + catalysts $\phi \sim 3-50$ nm SWNT $\phi \sim 1.4$ nm clean + Cn isolated or ropes $\phi < 20$ nm 	<ul style="list-style-type: none"> SWNT $\phi \sim 1.4-2.5$ nm, clean + Cn, [damaged], isolated or ropes $\phi < 30$ nm POPAC or AC particles + catalysts $\phi \sim 3-30$ nm [MWS] + catalysts or catalyst-free.
Cathode deposit	<ul style="list-style-type: none"> POPAC and SWNC particles Catalysts $\phi \sim 5-300$ nm MWS MWNT $\phi < 50$ nm [SWNT] $\phi \sim 1.6$ nm clean + Cn, isolated or ropes 	<ul style="list-style-type: none"> POPAC and SWNC particles + Cn Catalysts $\phi \sim 20-100$ nm + MWS 	<ul style="list-style-type: none"> MWS, catalyst-free MWNT $\phi < 35$ nm POPAC and PSWNC particles [SWNT], isolated or ropes [Catalysts] $\phi \sim 3-30$ nm 	<ul style="list-style-type: none"> SWNT $\phi \sim 1.4-4.1$ nm, clean + Cn, short with tips, isolated or ropes $\phi \leq 20$ nm. POPAC or AC particles + catalysts $\phi \sim 3-30$ nm MWS + catalysts $\phi < 40$ nm or catalyst-free [MWNT]

Abundant – Present – [Rare]

Glossary: AC: amorphous carbon; POPAC: poorly organized polyaromatic carbon; Cn: fullerene-like structure, including C₆₀; NANF: nearly amorphous nanofiber; MWS: multiwall shell; SWNT: single-wall nanotube; DWNT: double-wall nanotube. MWNT: multiwall nanotube; SWNC: single-wall nanocapsule.

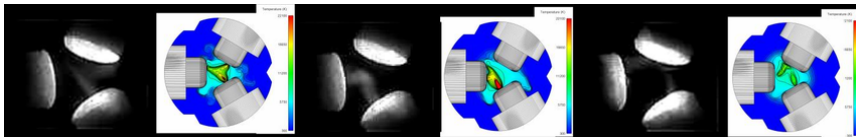
SWCNTs favoring conditions:
He 600 mbar, arc current 80 A,,
electrode gap 1 mm, Ni/Y
50-70% SWCNTs in collaret,
50% in web and soot
MWCNTs in cathode deposit

Three-phase AC arc plasma



Semi-industrial technology: electric arc is established between three graphite electrodes, three-phase AC power supply operating at 600 Hz, current 250-400 A.

Carbon precursors, gaseous, liquid or solid, are injected at the desired (variable) position into the plasma zone.



Free parameters: arc current, flow rate and nature of plasma gas (N_2 , Ar, H_2 , He etc.), carbon precursor, injection and extraction positions

T. M. Gruenberger et al., Fullerenes, Nanotubes and Carbon Nanostructures 12 (3), 571 (2004)

Solar furnace

- ▶ based on the sublimation of a mixture of graphite powder and catalysts placed in a crucible in an inert gas
- ▶ high temperature of about 4000K causes both the carbon and the catalysts to vaporize; the vapors are then dragged by the neutral gas and condense onto the cold walls of the thermal screen
- ▶ target is a graphite rod that includes pellets containing the catalysts, which is surrounded by a graphite tube

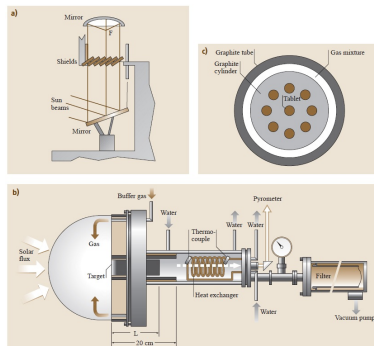


Fig. 3.14a–c Sketch of a solar energy reactor in use in the PROMES-CNRS Laboratory, Odeillo (France). (a) Gathering of sun rays, focused at F; (b) Side view of the experimental set-up at the focus of the 1 MW solar furnace; (c) top view of the target graphite rod.

- ▶ with Ni/Co, and at low pressure, the sample collected contains mainly MWNTs with bamboo texture, carbon shells, and some bundles of SWNTs
- ▶ at higher pressures, only bundles of SWNTs are obtained, with fewer carbon shells; relatively long bundles of SWNTs are observed with Ni/Y and at a high pressure; the diameters of the SWNTs range from 1 to 2 nm
- ▶ can be scaled up from 0.1–0.2g/h to 10 g/h and then to 100 g/h productivity using existing solar furnaces; experiments performed on a medium scale produced about 10 g/h of SWNT-rich material using various mixtures of catalysts (Ni/Co, Ni/Y, Ni/Ce)

2.2.2 Gaseous Carbon Source-Based Production Techniques

Catalytic decomposition of a carbon-containing source on small metallic particles or clusters - **catalytic CVD** involves

- ▶ either an **heterogeneous process** if a solid substrate is involved (**supported catalyst**)
- ▶ or an **homogeneous process** if everything takes place in the gas phase (**floating catalyst**)

Both, homogeneous and heterogeneous, processes appear very sensitive to the nature and the structure of the catalyst used, as well as to the operating conditions:

- ▶ metals generally used for these reactions are transition metals, such as Fe, Co and Ni
- ▶ rather low-temperature process compared to arc discharge and laser ablation methods, with the formation of carbon nanotubes typically occurring between 600 °C and 1000 °C

Quality of CNTs:

- ▶ CNTs prepared by CCVD methods are generally much longer (a few tens to hundreds of micrometers) than those obtained by arc discharge (a few micrometers); depending on the experimental conditions, it is possible to grow dense arrays of nanotubes
- ▶ MWNTs from CCVD contain more structural defects than MWNTs from arc discharge, due to the lower temperature of the reaction, which does not allow any structural rearrangements
- ▶ CCVD SWNTs generally gather into bundles of smaller diameter (a few tens of nm) than their arc discharge and laser ablation counterparts. Specifically, when using fluidized bed reactor, CCVD provides reasonable good perspectives on large-scale and low-cost processes.

CCVD heterogeneous process - supported catalyst

Although **CCVD formation mechanisms for SWNTs and MWNTs can be quite different** it is agreed that CNTs form on very small metal particles, typically nm range size

⇒ **two steps for CCVD heterogenous process:**

- ▶ preparation of catalytic particles - reduction of transition metal compounds (salts, oxides) by H_2 prior to the CNTs growth (important parameters: temperature, treatment duration, gas composition and flow rate, catalyst nature and size)
- ▶ at a given temperature, depending mainly on the nature of the catalyst and the carbon-containing gas, the catalytic decomposition will take place at the surfaces of the metal particles, followed by mass transport of the freshly produced carbon by surface or volume diffusion until the carbon concentration reaches the solubility limit, and the precipitation starts.

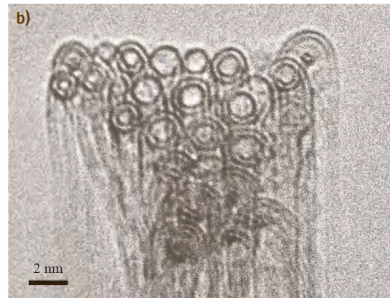
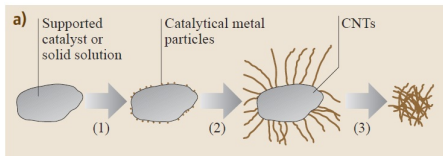


Fig. 3.15 (a) Formation of nanotubes via the CCVD-based impregnation technique. (1) Formation of catalytic metal particles by reduction of a precursor; (2) Catalytic decomposition of a carbon-containing gas, leading to the growth of carbon nanotubes; (3) Removal of the catalyst to recover the nanotubes
(b) Example of a bundle of double-wall nanotubes (DWNTs) prepared this way

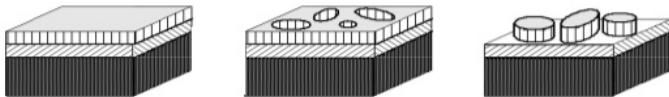
Preparation of Catalysts

Floating catalyst method uses organometallic volatile compounds such as ferrocene $\text{Fe}(\text{C}_5\text{H}_5)_2$ or iron pentacarbonyl $\text{Fe}(\text{CO})_5$.

Supported catalyst method uses Fe, Ni, Co, . . . and their alloys in the form of

- ▶ **thin film** (vacuum evaporation, magnetron sputtering):

The key factor is to perform restructuring into active catalyst nanoparticles (NPs): heating in N_2 , H_2 , NH_3 or plasma treatment.



Process depends on time, gas, thickness of the film and its morphology. Importance of material under the catalyst. Particles can coalesce during continuous heating, other material phases can be formed . . .

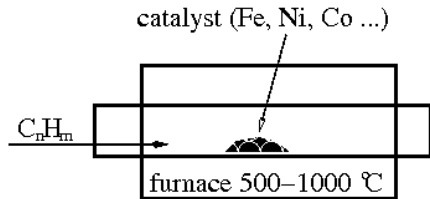
- ▶ **wet chemistry impregnation of substrate** - impregnation of a substrate with a solution of salt (nitrate, chloride, acetate) of desired transition metal catalyst
- ▶ **solid solution-based catalysts** - preparation of solid solution of an oxide of the chosen catalytic metal in a chemically inert and thermally stable host oxide
- ▶ **direct deposition of NPs** - electrochemical deposition, PECVD

Controlling metal particle size is key issue, coalescence has to be avoided (various supports like Al_2O_3 , SiO_2 , zeolites, MgO).

Supported catalyst - hydrocarbons

methane or other hydrocarbon CVD

- ▶ passing a gaseous flow containing a given proportion of a hydrocarbon (mainly CH_4 , C_2H_2 , C_2H_4 , or C_6H_6 , usually as a mixture with either H_2 or an inert gas such as Ar) over small transition metal particles (Fe, Co, Ni) in a furnace
- ▶ reaction is chemically defined as catalysis-enhanced thermal cracking
- ▶ $\text{C}_x\text{H}_y \rightarrow x\text{C} + y/2\text{H}_2$



- ▶ Synthesis of carbon nanofibres (< 10 nm) in 70-80ties.
Galuszka et al. Carbon 22 (1984), Tibbetts et al. Carbon 25 (1987)
Synthesis of MWCNTs mostly with C_2H_2 and C_2H_4 from 90ties .
Synthesis of bulk amount of single-walled nanotubes (SWNTs) using methane CVD.
Dai's group: Kong et al. Nature 395 (1998), Kong et al. Chem. Phys. Lett 292 (1998)

Supported catalyst - other gases

carbon monoxide CVD

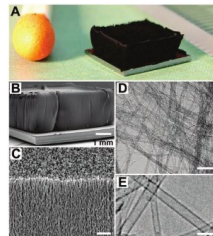
- ▶ Mass production of SWCNTs by high-pressure decomposition of CO (HiPCO) on metal NPs. Smalley's group: Dai et al. Chem. Phys. Lett. (1996) 471, Hafner et al. Chem. Phys. Lett. (1998) 195

alcohol CVD

- ▶ CO can be used instead of hydrocarbons; the reaction is then chemically defined as catalysis-enhanced disproportionation (the so-called the Boudouard equilibrium)
- ▶ $2\text{CO} \rightarrow \text{C} + \text{CO}_2$
- ▶ High-purity long SWCNTs using alcohols (CH_3OH , $\text{C}_2\text{H}_5\text{OH}$) – OH radical formed at high temperature from alcohol can remove amorphous carbon. Maruyama et al. Chem. Phys. Lett. (2002) 229

supergrowth – water-assisted CVD

- ▶ CVD often limited by low activity and short life time of catalyst. Dramatic improvement obtained by addition of water vapor – root growth of SWCNTs forest. Although aligned, the SWCNTs occupy only 3.6 % of the total volume, i.e. growth is not diffusion limited. Hata et al. Science (2004) 1362: 10 min growth using C_2H_4



CCVD Involving Thin Film Catalysts

Example of the CCVD involving thin film catalysts from *M. Jung et al. Diamond and Related Materials 10 (2001) 1235*

- ▶ Substrate: Si with SiO₂ film (1 μm)
- ▶ Catalyst: Ni film prepared by DC magnetron sputtering (2–7 nm)
- ▶ NPs preparation: annealing at 800 °C for 15 min in H₂ ⇒ size and number density depending on film thickness

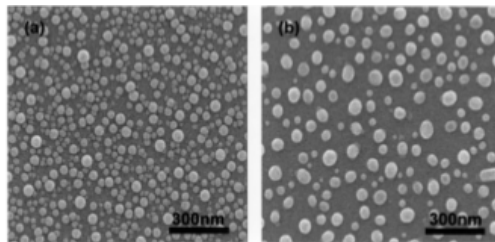


Fig. 1. SEM microstructure of Ni particles on SiO₂/Si substrate formed by annealing of sputter deposited Ni film of (a) 3.4 nm and (b) 6.8 nm in thickness.

CCVD Involving Thin Film Catalysts

M. Jung et al. Diamond and Related Materials 10 (2001) 1235

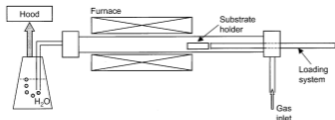


Fig. 2. Schematic of horizontal flow reactor for carbon nanotube growth.

- ▶ NPs preparation (contin.): pre-treatment directly in quartz tube, 700–1000 °C heating for 1 hour in various gas environments such as H_2 , N_2 , H_2/N_2 , H_2/Ar , H_2/NH_3
- ▶ CNTs growth: C_2H_2 added to previous gases (concentration varied from 2.4 to 20 vol.%), 20 min deposition

studies of $H_2/N_2/C_2H_2$ mixtures:

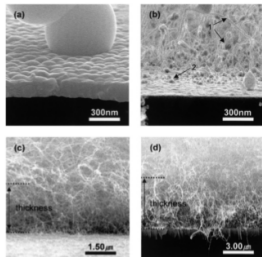


Fig. 3. SEM microstructures of the carbon deposits for 20 min with 2.4 vol.% C_2H_2 at 850°C after pretreatment for 1 h in the environments of various $H_2/(N_2 + H_2)$ fractions: (a) $H_2/(N_2 + H_2) = 0$; (b) $H_2/(N_2 + H_2) = 0.6$; (c) $H_2/(N_2 + H_2) = 0.85$; and (d) $H_2/(N_2 + H_2) = 1.0$.

H_2 prevents passivation of catalyst mixture influences decomposition kinetics of C_2H_2 (no growth for 850 °C for $H_2/(N_2+H_2)=0.35$ but ok for pure H_2)

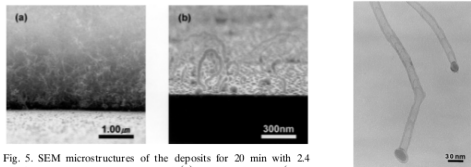


Fig. 5. SEM microstructures of the deposits for 20 min with 2.4 vol.% C_2H_2 after pretreatment for 1 h (a) at 750°C when $H_2/(N_2 + H_2) = 0.35$ and (b) at 950°C when $H_2/(N_2 + H_2) = 1.0$.

Fig. 6. TEM microstructure of CNT synthesized with 2.4 vol.% C_2H_2 after pretreatment for 1 h at 850°C when $H_2/(N_2 + H_2) = 1.0$.

CCVD Involving Thin Film Catalysts

M. Jung et al. Diamond and Related Materials 10 (2001) 1235

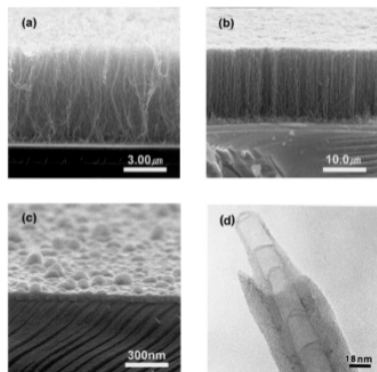


Fig. 7. (a) SEM microstructures of the CNTs synthesized for 20 min with 9.1 vol.% C₂H₂ after pretreatment for 1 h in NH₃ environment. (b) SEM microstructures of the CNTs synthesized for 20 min with 13.0 vol.% C₂H₂ after pretreatment for 1 h in NH₃ environment. (c) SEM microstructures of the deposits synthesized for 20 min with 7.0 vol.% C₂H₂ after pretreatment for 1 h in the environment of a mixture of N₂ and H₂ environment [H₂/(N₂ + H₂) = 0.75]. (d) TEM microstructure of the CNT of Fig. 7b.

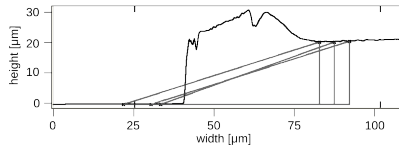
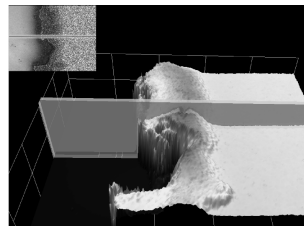
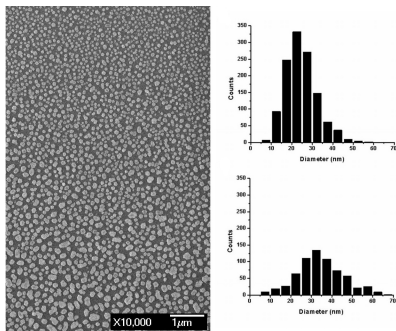
- ▶ improvements of CNTs growth for admixed NH₃
- ▶ size and density of catalytic NPs did not change but nitrogen is incorporated in Ni particles

CCVD Involving Thin Film Catalysts

pre-heating of the substrate in Ar/H₂ plasma, average $T = 700\text{ }^{\circ}\text{C}$

Ar/H₂ - 1500/570 sccm, $t = 30\text{ s}$,
Fe 10 nm

Ar/H₂ - 1500/430 sccm, $t = 30\text{ s}$
Ar/H₂/CH₄ - 1500/430/42 sccm, $t = 30\text{ s}$
Fe 15 nm



non-uniformity caused by thinner Fe film at the edges

CCVD Involving Impregnated Catalysts

Process generally involves four different and successive steps:

1. impregnation of the support by a solution of a salt (nitrate, chloride) of the chosen metal catalyst;
2. drying and calcination of the supported catalyst to get the oxide of the catalytic metal;
3. reduction in a H_2 containing atmosphere to make the catalytic metal particles,
4. the decomposition of a carbon-containing gas over the freshly prepared metal particles that leads to nanotube growth

CCVD Involving Impregnated Catalysts

Example of CCVD involving impregnated catalysts from *Ph. Mauron et al. Carbon 40 (2002) 1339*

- ▶ **Step 1 - deposition of iron(III) nitrate, $\text{Fe}(\text{NO}_3)_3$, film:** $\text{Fe}(\text{NO}_3)_3$ /ethanol solutions of different concentrations (7.5–60 mmol/l) spin-coated on Si substrate. The film thickness can be changed by varying the concentrations of $\text{Fe}(\text{NO}_3)_3$ solution.
- ▶ **Step 2 - heating prior to CNTs growth:** quartz glass tube evacuated to 10^{-4} Pa, temperature increased to 650–750 °C (8 min to reach the temperature, kept constant for 10 min), constant flux of N_2 (98 sccm) introduced to get $p = 5 \times 10^4$ Pa. Iron oxide clusters were formed by heating the $\text{Fe}(\text{NO}_3)_3$ -coated substrate according to the reaction:

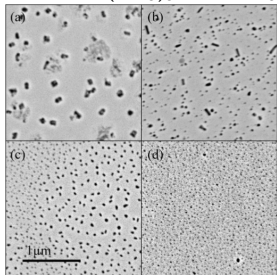
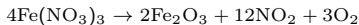


Fig. 2. SEM images (back scattered electrons) of Fe_2O_3 clusters formed on silicon substrates. The substrates were coated with iron(III)

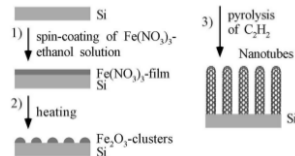


Fig. 1. Deposition of nanotubes in three steps: (1) spin-coating of iron(III) nitrate solution on the silicon substrate; (2) formation of Fe_2O_3 clusters by heating to 650–750 °C; (3) pyrolysis of acetylene at 650–750 °C.

CCVD Involving Impregnated Catalysts

Ph. Mauron et al. Carbon 40 (2002) 1339

- **Step 3** - synthesis of CNTs by adding a constant flux of acetylene (2 sccm) to the N₂ carrier gas during 30 min.

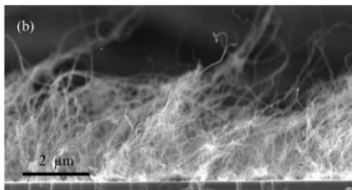
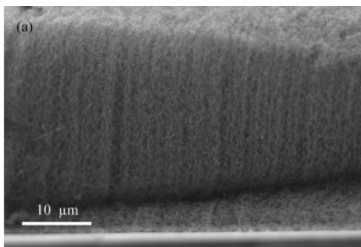


Fig. 3. SEM images (secondary electrons) of nanotube films on a silicon substrate. The samples were cut and are shown from the side. The nanotubes were synthesized by pyrolysis of acetylene over an iron(III) nitrate coated silicon substrate. (a) Film thickness $d=33\ \mu\text{m}$, diameter of the nanotubes 23–28 nm, concentration of the $\text{Fe}(\text{NO}_3)_3$ solution $c=7.5\ \text{mmol/l}$, synthesis temperature $T=700\ ^\circ\text{C}$. (b) Film thickness $d=5\ \mu\text{m}$, diameter of the nanotubes 20–25 nm, concentration of the $\text{Fe}(\text{NO}_3)_3$ solution $c=15\ \text{mmol/l}$, synthesis temperature $T=700\ ^\circ\text{C}$.

CCVD Involving Solid Solution-Based Catalysts

... uses solid solution of an oxide of the chosen catalytic metal in a chemically inert and thermally stable host oxide

- ▶ solid solution of two metal oxides is formed when ions of one metal mix with ions of the other metal, e.g. Fe_2O_3 can be prepared in solid solution in $\text{Al}_2\text{O}_3 \rightarrow \text{Al}_{2-2x}\text{Fe}_{2x}\text{O}_3$
- ▶ use of a solid solution allows a perfectly homogeneous dispersion of one oxide in the other to be obtained

Preparation methods:

- ▶ coprecipitation of mixed oxalates
- ▶ combustion synthesis

Homogeneous dispersion of catalytic oxide \Rightarrow very small catalytic metal NPs

- ▶ heating of solid solution from room to 850–1050 °C in H_2/CH_4 (18 mol% of CH_4)
- ▶ the product depends upon nature of both, the transition metal (or alloy) and inert oxide (matrix)
- ▶ nanotubes obtained are typically gathered into small-diameter bundles (less than 15 nm) with lengths of up to 100 μm ; nanotubes are mainly SWNTs and DWNTs, with diameters of between 1 and 3 nm
- ▶ to remove host oxides aggressive treatments (KOH, NaOH for Al_2O_3 ; HF for SiO_2) are required; these treatments have no effect, however, on other impurities such as other forms of carbon (a-C, graphitized carbon particles and shells . . .).
- ▶ oxidizing treatments (air oxidation, use of strong oxidants such as HNO_3 , KMnO_4 , H_2O_2) are thus required to remove most unwanted forms of carbon, but they result in a low final yield

CCVD with Floating Catalyst - Homogeneous Processes

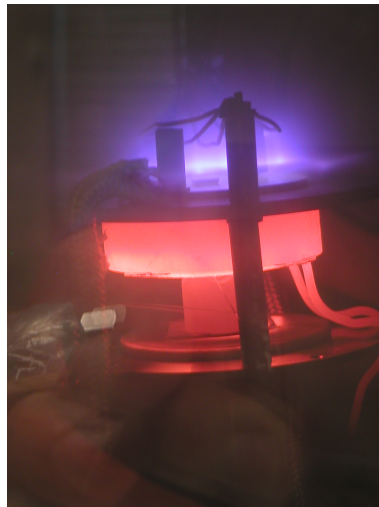
Supported catalyst - reactors are using static phase placed within the gas flow or fine powder suspended by gas phase, so called fluidised bed process

Floating catalyst - differs because it uses only gaseous species and does not require the presence of any solid phase in the reactor

- ▶ basic principle of this technique, similar to the other CCVD processes, is to decompose a carbon source (ethylene, xylene, benzene, carbon monoxide, and so on) on nanosized transition metal (generally Fe, Co, or Ni) particles in order to obtain carbon nanotubes
- ▶ catalytic particles are formed directly in the reactor, however, and are not introduced before the reaction, as occurs in supported CCVD for instance

CCVD with Floating Catalyst II

- ▶ typical reactor used in this technique is a quartz tube placed in an oven into which the gaseous feedstock, containing the metal precursor, the carbon source, some hydrogen and a vector gas (N_2 , Ar, or He)
- ▶ first zone of the reactor is kept at a lower temperature, and the second zone, where the formation of tubes occurs, is heated to 700-1200 °C
- ▶ metal precursor is generally a metal-organic compound, such as a zerovalent carbonyl compound like $Fe(CO)_5$, or a metallocene such as ferrocene, nickelocene or cobaltocene



CCVD with Floating Catalyst III

- ▶ metal-organic compound decomposes in the first zone of the reactor, generating nanosized metallic particles that can catalyze nanotube formation; in the second part of the reactor, the carbon source is decomposed to atomic carbon, which is then responsible for the formation of nanotubes
- ▶ quite flexible and SWNTs, DWNTs and MWNTs have been obtained, in proportions depending on the carbon feedstock gas
- ▶ main drawback of this type of process is again that it is difficult to control the size of the metal NPs, and thus nanotube formation is often accompanied by the production of undesired carbon forms (amorphous carbon or polyaromatic carbon phases found as various phases or as coatings)
- ▶ same kind of parameters have to be controlled as for heterogeneous processes in order to finely tune this process and selectively obtain the desired morphology and structure of the nanotubes formed, such as: the choice of the carbon source; the reaction temperature; the residence time; the composition of the incoming gaseous feedstock, with particular attention paid to the role played by the proportion of hydrogen, and the ratio of the metallorganic precursor to the carbon source

Plasma Enhanced CVD

PECVD in hard competition with CVD:

Mostly MWNTs because of plentiful supply of carbon (presence of reactive radicals and unsaturated hydrocarbons), ion damage and non-optimized catalyst preparation

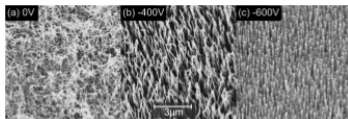
Deposition of SWNTs



- ▶ low pressure PECVD: Kato et al. Chem. Phys. Lett. (2003) 422, Kato et al. Nanotechnology (2006), 2223, Iwasaki et al., J. Phys. Chem. B. Lett. (2005), 19556
- ▶ atmospheric pressure PECVD: Nozaki et al. Carbon (2007) 364

What PECVD can offer over CVD?

- ▶ Presence of inherent electric field influencing the growth orientation of CNTs: widely accepted argument for PECVD

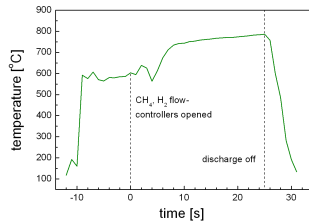
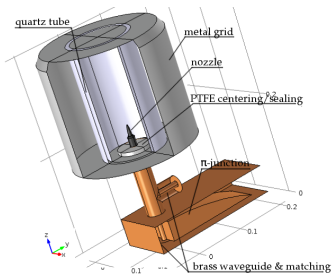
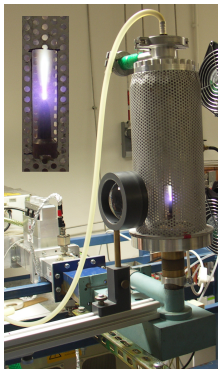
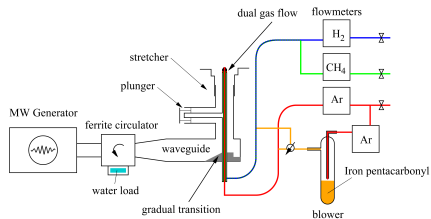


Chhowalla et al., J.
Appl. Phys. 90, (2001), 5308

- ▶ Lower process temperature: conventional argument for PECVD over CVD but CNT growth does not require pyrolysis of precursor
Hoffman et al., Appl. Phys. Lett. (2003), 135 – carbon nanofibres at 120 °C by dc-PECVD
- ▶ Preferential growth of semiconducting SWNTs. Li et al., Nano Lett. (2004), 317

PECVD in Microwave Torch

- ▶ $f = 2.45 \text{ GHz}$
- ▶ $P = 100\text{--}400 \text{ W}$
- ▶ dual gas flow:
 - ▶ central channel: Ar (500–1500 sccm)
 - ▶ side channel: CH_4 , H_2 , Ar + $\text{Fe}(\text{CO})_5$



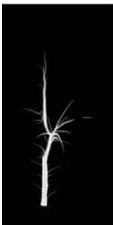
Visualization of Torch Dynamics

MW power 210 W, Ar 660 sccm

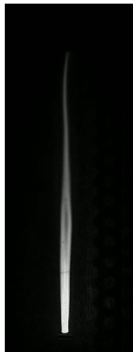
side view



front view



1st appearance of visible
plasma channel



after 29 s
(front view)



Ar/Fe(CO)₅
670/1 sccm

Ar/H₂

430sccm



145sccm

Ar/H₂/CH₄

total video time 30s,
camera resolution 1000 frames/s,
video resolution 10 frames/s

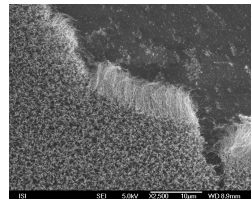
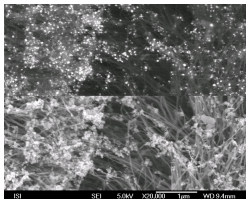
Deposition on Si/SiO₂/Fe Facing MW Torch



- ▶ Ar/H₂/CH₄ gas feed - 1500/430/42 sccm,
- ▶ catalytic film - Fe 5 nm, average $T = 700^\circ\text{C}$
- ▶ non-uniform deposition because of gradients of substrate T

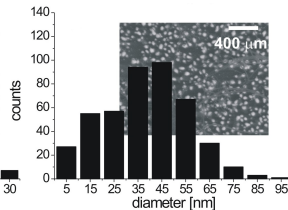
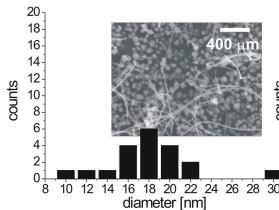
center

average diameter
38 nm



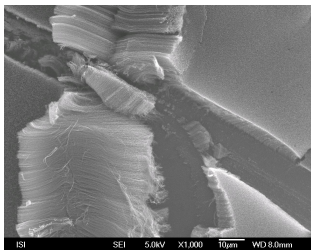
edge

average diameter
18 nm



CNTs on Si/Fe

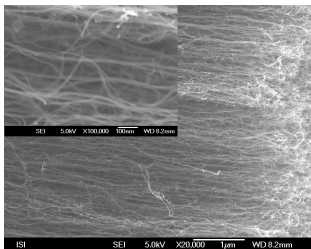
growth on Si without barrier layer - some applications require electrical contact to CNTs



- ▶ 1500/430/42 sccm
- ▶ 700 °C, 45 s
- ▶ 15 nm Fe



alignment of CNTs (people) by crowding effect



CNTs deposited without barrier layer exhibit similar density and quality as with SiO₂ barrier

Templating

- ▶ only other method aside from the electric arc that is able to synthesize CNTs without any catalyst
- ▶ principle is to deposit the solid carbon coating obtained from the CVD method onto the walls of a porous substrate whose pores are arranged in parallel channels
- ▶ feedstock is a hydrocarbon; substrate can be alumina or zeolite for instance, while the whole system is heated to a temperature that cracks the hydrocarbon selected as the carbon source
- ▶ both MWNTs (exclusively concentric type) and SWNTs can be obtained; the smallest SWNTs have diameters ~ 0.4 nm, lengths are directly determined by the channel lengths; in other words by the thickness of the substrate plate

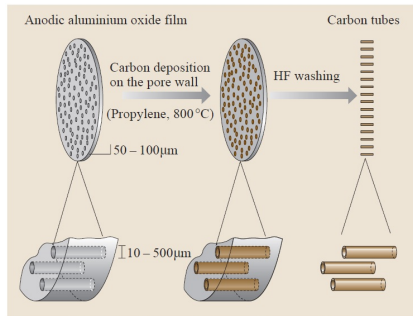


Fig. 3.16 Principle of the templating technique used in the catalyst-free formation of single-walled or concentric-type multiwalled carbon nanotubes

2.3 Growth Mechanism of Carbon Nanotubes

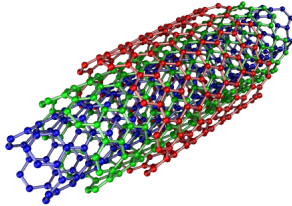
- ▶ Catalyst-free growth (templating method, electric arc - here driving force is related to electric field, precursors species C_2 as in fullerene production)
- ▶ Catalytically Activated Growth
 - ▶ **low T conditions** - typically in CCVD: VLS mechanism (1. adsorption + decomposition, 2. dissolution + diffusion 3. precipitation); catalyst as crystallized solid (texture defined by crystal) or liquid droplet (energy minimization make concentric product); c-MWCNTs, h-MWCNTs, platelet nanofibers (formed for large particles > 100 nm); tip-growth for large NPs or absence of substrate \times base growth
 - ▶ **high T conditions** - solid carbon-source: carbon source and catalyst is atomized, at some distance from atomization zone - carbon metal alloy droplets + secondary carbon species (C_2 and higher like corannulene: central pentagon surrounded by five hexagons) \Rightarrow adjacent pentagons are not stable \Rightarrow hexagons; in the zones with low T solubility threshold of C in metal decreases - combination of VLS and adatom mechanism

Mechanical Properties

- ▶ Strongest and stiffest material yet discovered (tensile strength and elastic modulus)
- ▶ In 2000 a MWNT tested to have a tensile strength of 63 GPa
- ▶ Translates into ability to hold 6500 kg on a cable with cross-section of 1 mm²
- ▶ Specific strength of up to 48,000 kN·m·kg⁻¹ (high carbon steel's is 154 kN·m·kg⁻¹)
- ▶ Not so strong under compression

Telescopic Properties

- ▶ Multi-walled coaxial nanotubes show striking telescopic properties
- ▶ Shells slide with almost no friction
- ▶ Molecular nanotechnology
- ▶ World's smallest rotational motor created already



Electric Properties

- ▶ Indices (m, n) tune the gap
- ▶ $n = m$ – nanotube is metallic
- ▶ $n = -m$ – nanotube is semiconducting with a very small gap
- ▶ otherwise – moderate semiconductor

Thermal Properties

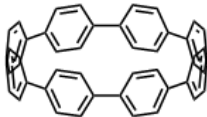
- ▶ Very good thermal conductivity along a tube
- ▶ Good insulator laterally to the tube axis
- ▶ Three orders difference
- ▶ One order better on-axis conductivity than copper

2.5 Carbon Nanotube-Based Nano-Objects

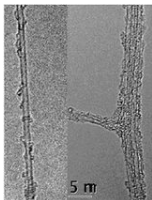
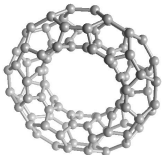
- ▶ 2.5.1 Extreme CNTs and Related Geometries
- ▶ 2.5.2 Functionalized Nanotubes
- ▶ 2.5.3 Heteronanotubes (replacement of some C atoms by other elements, e.g. N, B)
- ▶ 2.5.4 Hybrid CNTs (inner cavities filled with foreign atoms, molecules, compounds or crystals)

2.5.1 Extreme Carbon Nanotubes and Other Related Geometries

- ▶ The longest carbon nanotube (18.5 cm) reported in 2009. Grown on Si using improved CVD
- ▶ The shortest CNT is the organic compound cycloparaphenylene synthesized in early 2009
- ▶ The shortest CNT synthesized is armchair (2,2) with diameter of 3 Å
- ▶ The thinnest free-standing SWNT is about 4.3 Å in diameter

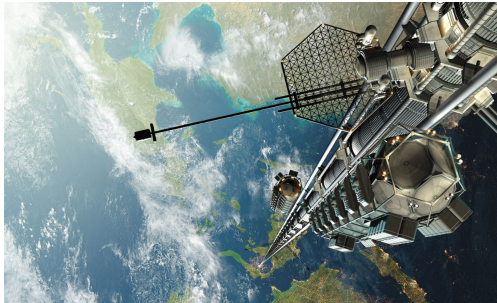


- ▶ **Nanotorus** – Theoretically described, many unique properties described
- ▶ **Nanobud** – Combination of fullerene and NT allotropes. Useful properties of both, improving mechanical properties

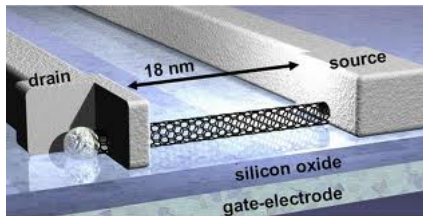


Structural Applications

- ▶ Because of superior mechanical properties, many structures have been proposed
- ▶ From clothes, sports gear, combat jackets up to space elevators



Electrical Circuits



- ▶ Nanotube-based transistors have been made
- ▶ Semiconducting nanotube required ($n \neq m$)
- ▶ Capable of digital switching using a single electron

Other Applications

- ▶ Solar Cells - Nanotubes with buckyballs containing a polymer
- ▶ As paper batteries – supercapacitors
- ▶ Nanoscale electric motors
- ▶ Radio receiver consisting of a single NT demonstrated
- ▶ Demonstrated that sheet on NTs can work like a speaker – thermoacoustically
- ▶ Nano-tips for SPM
- ▶ Emitters for electron microscopy