Wondrous World of Carbon Nanotubes

2. Synthesis

2.1 Introduction

In this section, different techniques for nanotube synthesis and their current status are briefly explained. First, the growth mechanism is explained, as it is almost general for all techniques. However, typical conditions are stated at the sections of all the different techniques. The largest interest is in the newest methods for each technique and the possibilities of scaling up.

Carbon nanotubes are generally produced by three main techniques, arc discharge, laser ablation and chemical vapour deposition. Though scientists are researching more economic ways to produce these structures. In arc discharge, a vapour is created by an arc discharge between two carbon electrodes with or without catalyst. Nanotubes self-assemble from the resulting carbon vapour. In the laser ablation technique, a high-power laser beam impinges on a volume of carbon -containing feedstock gas (methane or carbon monoxide). At the moment, laser ablation produces a small amount of clean nanotubes, whereas arc discharge methods generally produce large quantities of impure material. In general, chemical vapour deposition (CVD) results in MWNTs or poor quality SWNTs. The SWNTs produced with CVD have a large diameter range, which can be poorly controlled. But on the other hand, this method is very easy to scale up, what favours commercial production.

2.2 Growth mechanism

The way in which nanotubes are formed is not exactly known. The growth mechanism is still a subject of controversy, and more than one mechanism might be operative during the formation of CNTs. One of the mechanisms consists out of three steps. First a precursor to the formation of nanotubes and fullerenes, C_2, is formed on the surface of the metal catalyst particle. From this metastable carbide particle, a rodlike carbon is formed rapidly. Secondly there is a slow graphitisation of its wall. This mechanism is based on in-situ TEM observations[12].

The exact atmospheric conditions depend on the technique used, later on, these will be explained for each technique as they are specific for a technique. The actual growth of the nanotube seems to be the same for all techniques mentioned.
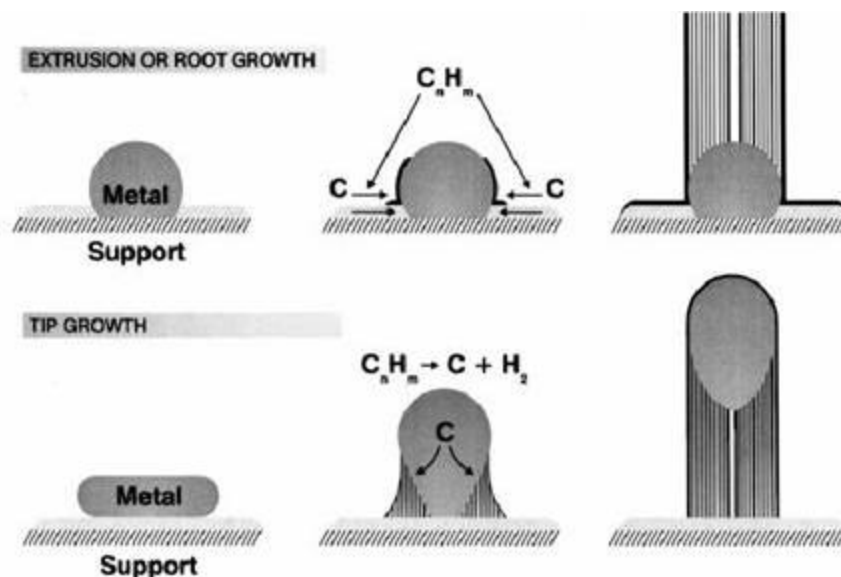
Figure 2-1: Visualisation of a possible carbon nanotube growth mechanism.

There are several theories on the exact growth mechanism for nanotubes. One theory[13] postulates that metal catalyst particles are floating or are supported on graphite or another substrate. It presumes that the catalyst particles are spherical or pear-shaped, in which case the deposition will take place on only one half of the surface (this is the lower curvature side for the pear shaped particles). The carbon diffuses along the concentration gradient and precipitates on the opposite half, around and below the bisecting diameter. However, it does not precipitate from the apex of the hemisphere, which accounts for the hollow core that is characteristic of these filaments. For supported metals, filaments can form either by "extrusion (also known as base growth)" in which the nanotube grows upwards from the metal particles that remain attached to the substrate, or the particles detach and move at the head of the growing nanotube, labelled "tip-growth". Depending on the size of the catalyst particles, SWNT or MWNT are grown. In arc discharge, if no catalyst is present in the graphite, MWNT will be grown on the C_2-particles that are formed in the plasma.

2.3 Arc discharge

The carbon arc discharge method, initially used for producing C_{60} fullerenes, is the most common and perhaps easiest way to produce carbon nanotubes as it is rather simple to undertake. However, it is a technique that produces a mixture of components and requires separating nanotubes from the soot and the catalytic metals present in the crude product.

This method creates nanotubes through arc-vaporisation of two carbon rods placed end to end, separated by approximately 1mm, in an enclosure that is

usually filled with inert gas (helium, argon) at low pressure (between 50 and 700 mbar). Recent investigations have shown that it is also possible to create nanotubes with the arc method in liquid nitrogen[14]. A direct current of 50 to 100 A driven by approximately 20 V creates a high temperature discharge between the two electrodes. The discharge vaporises one of the carbon rods and forms a small rod shaped deposit on the other rod. Producing nanotubes in high yield depends on the uniformity of the plasma arc and the temperature of the deposit form on the carbon electrode[15].

Insight in the growth mechanism is increasing and measurements have shown that different diameter distributions have been found depending on the mixture of helium and argon. These mixtures have different diffusions coefficients and thermal conductivities. These properties affect the speed with which the carbon and catalyst molecules diffuse and cool., affecting nanotube diameter in the arc process. This implies that single-layer tubules nucleate and grow on metal particles in different sizes depending on the quenching rate in the plasma and it suggests that temperature and carbon and metal catalyst densities affect the diameter distribution of nanotubes[15].

Depending on the exact technique, it is possible to selectively grow SWNTs or MWNTs, which is shown in Figure 2-2. Two distinct methods of synthesis can be performed with the arc discharge apparatus.
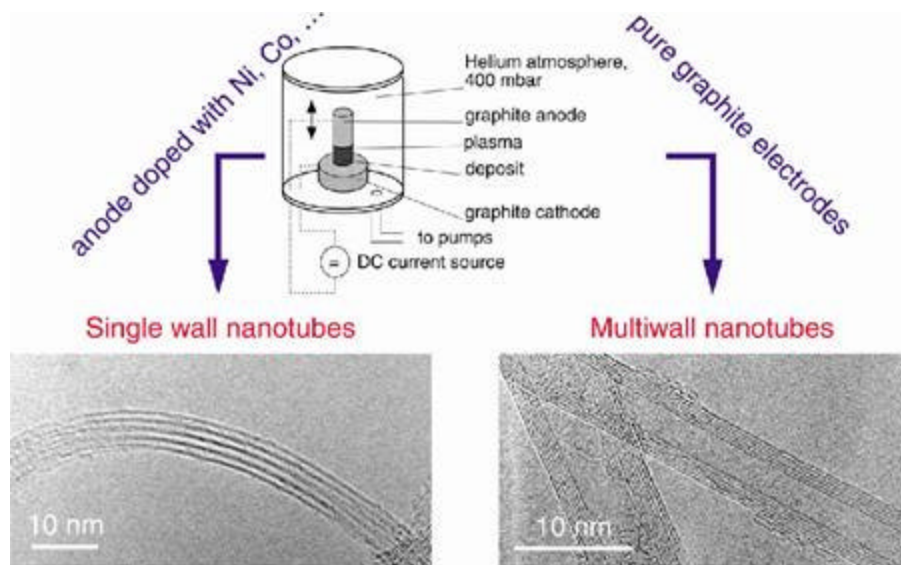

Figure 2-2: Experimental setup of an arc discharge apparatus

2.3.1 Synthesis of SWNT

If SWNTs are preferable, the anode has to be doped with metal catalyst, such as Fe, Co, Ni, Y or Mo. A lot of elements and mixtures of elements have been tested by various authors[16] and it is noted that the results vary a lot, even

though they use the same elements. This is not surprising as experimental conditions differ. The quantity and quality of the nanotubes obtained depend on various parameters such as the metal concentration, inert gas pressure, kind of gas, the current and system geometry. Usually the diameter is in the range of 1.2 to 1.4 nm. A couple of ways to improve the process of arc discharge are stated below.

a) Inert gas

The most common problems with SWNT synthesis are that the product contains a lot of metal catalyst, SWNTs have defects and purification is hard to perform. On the other hand, an advantage is that the diameter can slightly be controlled by changing thermal transfer and diffusion, and hence condensation of atomic carbon and metals between the plasma and the vicinity of the cathode can control nanotube diameter in the arc process. This was shown in an experiment in which different mixtures of inert gases were used[17].

It appeared that argon, with a lower thermal conductivity and diffusion coefficient, gave SWNTs with a smaller diameter of approximately 1.2 nm. A linear fit of the average nanotube diameter showed a 0.2 nm diameter decrease per 10 % increase in argon helium ratio, when nickel/yttrium was used (C/Ni/Y was 94.8:4.2:1) as catalyst.

b) Optical plasma control

A second way of control is plasma control by changing the anode to cathode distance (ACD). The ACD is adjusted in order to obtain strong visible vortices around the cathode. This enhances anode vaporisation, which improves nanotubes formation. Combined with controlling the argon-helium mixture, one can simultaneously control the macroscopic and microscopic parameters of the nanotubes formed[18].

With a nickel and yttrium catalyst (C/Ni/Y is 94.8:4.2:1) the optimum nanotube yield was found at a pressure of 660 mbar for pure helium and 100 mbar for pure argon. The nanotube diameter ranges from 1.27 to 1.37 nanometre.

c) Catalyst

Knowing that chemical vapour deposition (CVD) could give SWNTs with a diameter of 0.6-1.2 nm, researchers tried the same catalyst as used in CVD on arc discharge. Not all of the catalysts used appeared to result in nanotubes for both methods. But there seemed to be a correlation of diameter of SWNTs synthesised by CVD and arc discharge

As a result, the diameter can be controllably lowered to a range of 0.6-1.2 nm with arc-discharge. Using a mixture of Co and Mo in high concentrations as

catalyst resulted in this result. These diameters are considerably smaller than 1.2-1.4 nm[16], which is the usual size gained from arc-discharge.[19]

d) Improvement of oxidation resistance

There is also progress in developing methods to improve the oxidation resistance of the SWNTs, which is a consequence of the defects present in nanotubes. A strong oxidation resistance is needed for the nanotubes if they have to be used for applications such as field emission displays. Recent research has indicated that a modified arc-discharge method using a bowl-like cathode (see Figure 2-3), decreases the defects and gives cleaner nanotubes, and thus improves the oxidation resistance[20].
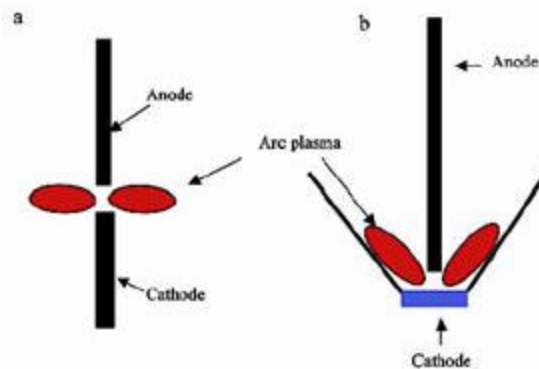

Figure 2-3: Schematic drawings of the electrode set-ups for (a) the conventional and (b) the new arc discharge electrodes.

The Raman spectrum of the newly synthesised nanotubes shows that the nanotubes formed are cleaner and less defective compared with those synthesised by conventional methods. The anode rod contained Ni and Y catalyst (C /Ni/Y is 94.8:4.2:1). No information is given about the diameter size.

e) Open air synthesis with welding arc torch

Only a couple of years ago, researchers discovered that it was possible to form MWNTs in open air [21]. A welding arc torch was operated in open air and the process was shielded with an argon gas flow. The anode and cathode were made of graphite containing Ni and Y (Ni/Y is 4.2:1 at. %).
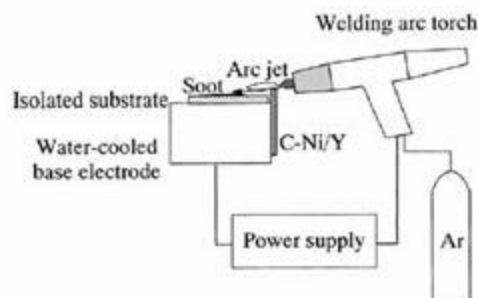
Figure 2-4: Experimental set-up of the torch arc method in open air.

This method was modified for preparing SWNTs[22]. A plate target made of graphite containing metal catalyst Ni and Y (Ni/Y is 3.6:0.8 at. per cent), was fixed at the sidewall of a water-cooled, steel based electrode. The torch arc aimed at the edge of the target and the soot was deposited on the substrate behind the target (see Figure 2-4). The arc was operated at a direct current of 100 A. and shielding argon gas flowed through the torch, enhancing the arc jet formation beyond the target.

In the soot, carbon nanohorns (CNHs) and bundles of SWNT with an average diameter of 1.32 nm were found. However, the yield was much lower than for the conventional low-pressure arc discharge method. There are two reasons for this fact. At first, because of the open air, the lighter soot will escape into the atmosphere. Secondly, the carbon vapour might be oxidised and emitted as carbon dioxide gas. In order to improve the yield in this method, contrivances for collecting soot and development of an appropriate target are required.

This method promises to be convenient and inexpensive once the conditions for higher yield are optimised. With a Ni/Y catalyst (Ni/Y is 3.6:0.8), SWNT bundles and CNHs are formed. In this case the SWNTs have a diameter of approximately 1.32 nm [22].

2.3.2 Synthesis of MWNT

If both electrodes are graphite, the main product will be MWNTs. But next to MWNTs a lot of side products are formed such as fullerenes, amorphous carbon, and some graphite sheets. Purifying the MWNTs, means loss of structure and disorders the walls. However scientist are developing ways to gain pure MWNTs in a large-scale process without purification.

Typical sizes for MWNTs are an inner diameter of 1-3 nm and an outer diameter of approximately 10 nm. Because no catalyst is involved in this process, there is no need for a heavy acidic purification step. This means, the MWNT, can be synthesised with a low amount of defects.

a) Synthesis in liquid nitrogen

A first, possibly economical route to highly crystalline MWNTs is the arc-discharge method in liquid nitrogen[14], with this route mass production is also possible. For this option low pressures and expensive inert gasses are not needed.
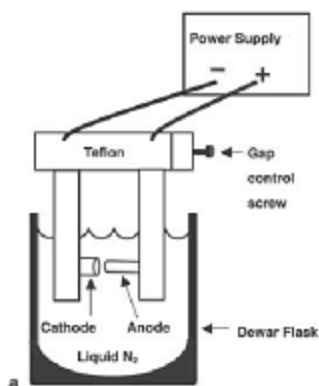

Figure 2-5: Schematic drawings of the arc discharge apparatus in liquid nitrogen.

The content of the MWNTs can be as high as 70 % of the reaction product. Analysis with Auger-spectroscopy revealed that no nitrogen was incorporated in the MWNTs. There is a strong possibility that SWNTs can be produced with the same apparatus under different conditions.

b) Magnetic field synthesis

Synthesis of MWNTs in a magnetic field[23] gives defect-free and high purity MWNTs that can be applied as nanosized electric wires for device fabrication. In this case, the arc discharge synthesis was controlled by a magnetic field around the arc plasma.
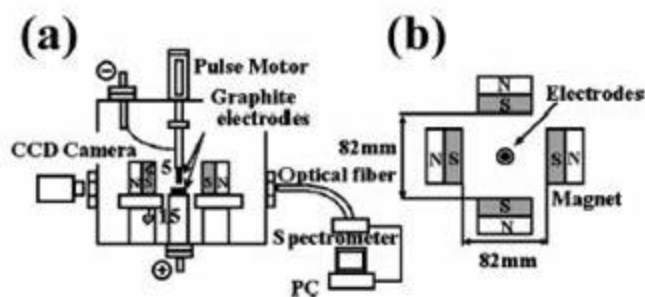

Figure 2-6: Schematic diagram of the synthesis system for MWNTs in a magnetic field.

Extremely pure graphite rods (purity > 99.999 %) were used as electrodes. Highly pure MWNTs (purity > 95 %) were obtained without further purification, which disorders walls of MWNTs.
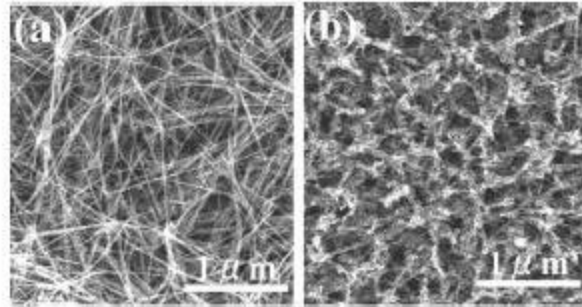

Figure 2-7: SEM images of MWNTs synthesised with (a) and without (b) the magnetic field.

c) Plasma rotating arc discharge

A second possibly economical route to mass production of MWNTs is synthesis by plasma rotating arc discharge technique[24]. The centrifugal force caused by the rotation generates turbulence and accelerates the carbon vapour perpendicular to the anode. In addition, the rotation distributes the micro discharges uniformly and generates a stable plasma. Consequently, it increases the plasma volume and raises the plasma temperature.
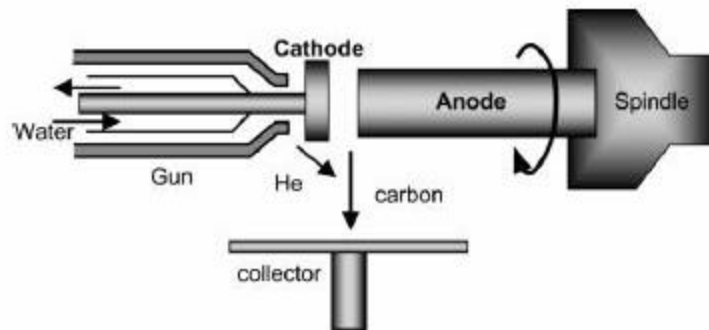

Figure 2-8: Schematic diagram of plasma rotating electrode system.

At a rotation speed of 5000 rpm a yield of 60 % was found at a formation temperature of 1025 °C without the use of a catalyst. The yield increases up to 90% after purification if the rotation speed is increased and the temperature is enlarged to 1150 °C. The diameter size was not mentioned in this publication.

2.4 Laser ablation

In 1995, Smalley's group[25] at Rice University reported the synthesis of carbon nanotubes by laser vaporisation. The laser vaporisation apparatus used by Smalley's group is shown in Figure 2-9. A pulsed[26;27], or continuous[28;29] laser is used to vaporise a graphite target in an oven at 1200 °C. The main difference between continuous and pulsed laser, is that the pulsed laser demands a much higher light intensity (100 kW/cm^2 compared with 12 kW/cm^2). The oven is filled with helium or argon gas in order to keep the pressure at 500 Torr. A very hot vapour plume forms, then expands and cools rapidly. As the vaporised species cool, small carbon molecules and atoms quickly condense to form larger clusters, possibly including fullerenes. The catalysts also begin to condense, but more slowly at first, and attach to carbon clusters and prevent their closing into cage structures.[30] Catalysts may even open cage structures when they attach to them. From these initial clusters, tubular molecules grow into single-wall carbon nanotubes until the catalyst particles become too large, or until conditions have cooled sufficiently that carbon no longer can diffuse through or over the surface of the catalyst particles. It is also possible that the particles become that much coated with a carbon layer that they cannot absorb more and the nanotube stops growing. The SWNTs formed in this case are bundled together by van der Waals forces[30].
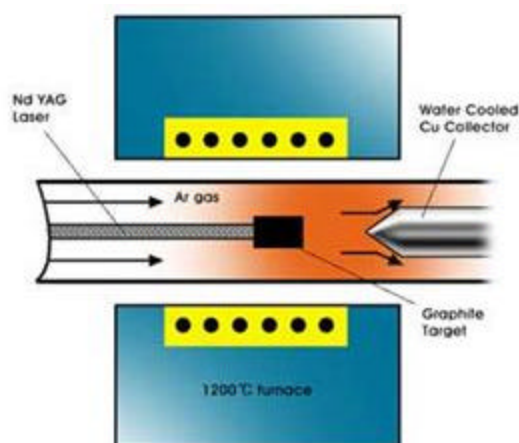

Figure 2-9: Schematic drawing of a laser ablation apparatus.

There are some striking, but not exact similarities, in the comparison of the spectral emission of excited species in laser ablation of a composite graphite target with that of laser-irradiated C_{60} vapour. This suggests that fullerenes are also produced by laser ablation of catalyst-filled graphite, as is the case when no catalysts are included in the target. However, subsequent laser pulses excite fullerenes to emit C_2 that adsorbs on catalyst particles and feeds SWNT growth. However, there is insufficient evidence to conclude this with certainty[30]

Laser ablation is almost similar to arc discharge, since the optimum background gas and catalyst mix is the same as in the arc discharge process. This might be due to very similar reaction conditions needed, and the reactions probably occur with the same mechanism.

2.4.1 SWNT versus MWNT

The condensates obtained by laser ablation are contaminated with carbon nanotubes and carbon nanoparticles. In the case of pure graphite electrodes, MWNTs would be synthesised, but uniform SWNTs could be synthesised if a mixture of graphite with Co, Ni, Fe or Y was used instead of pure graphite. SWNTs synthesised this way exist as 'ropes', see Figure 2-10 [28;30]. Laser vaporisation results in a higher yield for SWNT synthesis and the nanotubes have better properties and a narrower size distribution than SWNTs produced by arc-discharge.

Nanotubes produced by laser ablation are purer (up to about 90 % purity) than those produced in the arc discharge process. The Ni/Y mixture catalyst (Ni/Y is 4.2/1) gave the best yield.

Figure 2-10: TEM images of a bundle of SWNTs catalysed by Ni/Y (2:0.5 at. %) mixture, produced with a continuous laser.

The size of the SWNTs ranges from 1-2 nm, for example the Ni/Co catalyst with a pulsed laser at 1470 °C gives SWNTs with a diameter of 1.3-1.4 nm[26]. In case of a continuous laser at 1200 °C and Ni/Y catalyst (Ni/Y is 2:0.5 at. %), SWNTs with an average diameter of 1.4 nm were formed with 20-30 % yield, see Figure 2-10.[28]

2.4.2 Large scale synthesis of SWNT

Because of the good quality of nanotubes produced by this method, scientists are trying to scale up laser ablation. However the results are not yet as good as for the arc-discharge method, but they are still promising. In the next two sections, two of the newest developments on large-scale synthesis of SWNTs will be discussed. The first is the "ultra fast Pulses from a free electron laser[27]" method, the second is "continuous wave laser-powder" method[29]. Scaling up is possible, but the technique is rather expensive due to the laser and the large amount of power required.

2.4.3 Ultra fast Pulses from a free electron laser (FEL) method

Usually the pulses in an Nd:YAG system have width of approximately 10 ns, in this FEL system the pulse width is ~ 400 fs. The repetition rate of the pulse is enormously increased from 10 Hz to 75 MHz. To give the beam the same amount of energy as the pulse in an Nd:YAG system, the pulse has to be focused. The intensity of the laser bundle behind the lens reaches ~5 x 10^{11} W/cm^2, which is about 1000 times greater than in Nd:YAG systems. [27]

A jet of preheated (1000 °C) argon through a nozzle tip is situated close to the rotating graphite target, which contains the catalyst. The argon gas deflects the ablation plume approximately 90° away from the incident FEL beam direction, clearing away the carbon vapour from the region in front of the target. The produced SWNT soot, is collected in a cold finger. This process can be seen in Figure 2-11. The yield at this moment is 1,5 g/h, which is at 20 % of the maximum power of the not yet upgraded FEL. If the FEL is upgraded to full power and is working at 100 % power, a yield of 45 g/h could be reached since the yield was not limited by the laser power.
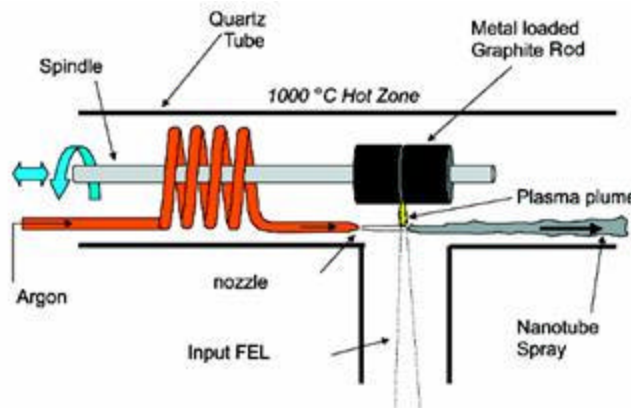

Figure 2-11: Schematic drawings of the ultra fast-pulsed laser ablation apparatus.

With this method the maximum achievable yield with the current lasers is 45 g/h, with a NiCo or NiY catalyst, in argon atmosphere at 1000 °C and a wavelength of ~3000 nm. The SWNTs produced in bundles of 8-200 nm and a length of 5-20 microns has a diameter range 1-1.4 nm.[27]

2.4.4 Continuous wave laser-powder method

This method is a novel continuous, highly productive laser-powder method of SWNT synthesis based on the laser ablation of mixed graphite and metallic catalyst powders by a 2-kW continuous wave CO_2 laser in an argon or nitrogen stream. Because of the introduction of micron-size particle powders, thermal conductivity losses are significantly decreased compared with laser heating of the bulk solid targets in known laser techniques. As a result, more effective utilisation of the absorbed laser power for material evaporation was achieved. The set-up of the laser apparatus is shown in Figure 2-12 [29].
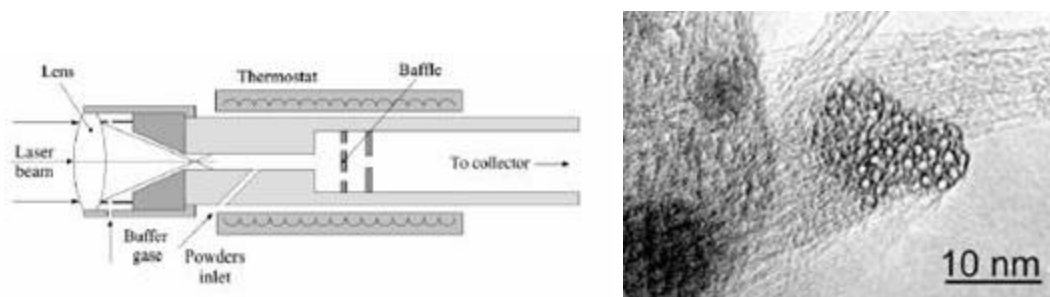

Figure 2-12: (Left) The principle scheme of the set-up for carbon SWNT production by continuous wave laser-powder method (Right) HRTEM of a SWNT-bundle cross-section.

The established yield of this technique was 5 g/h. A Ni/Co mixture (Ni/Co is 1:1) was used as catalyst, the temperature was 1100 °C. In the soot a SWNT abundance of 20-40% w

as found with a mean diameter of 1.2-1.3 nm. An HRTEM-picture of this sample is shown in Figure 2-12.

2.5 Chemical vapour deposition

Chemical vapour deposition (CVD) synthesis is achieved by putting a carbon source in the gas phase and using an energy source, such as a plasma or a resistively heated coil, to transfer energy to a gaseous carbon molecule. Commonly used gaseous carbon sources include methane, carbon monoxide and acetylene. The energy source is used to "crack" the molecule into reactive atomic carbon. Then, the carbon diffuses towards the substrate, which is

heated and coated with a catalyst (usually a first row transition metal such as Ni, Fe or Co) where it will bind. Carbon nanotubes will be formed if the proper parameters are maintained. Excellent alignment[31], as well as positional control on nanometre scale[32], can be achieved by using CVD. Control over the diameter, as well as the growth rate of the nanotubes can also be maintained. The appropriate metal catalyst can preferentially grow single rather than multi-walled nanotubes[13].

CVD carbon nanotube synthesis is essentially a two-step process consisting of a catalyst preparation step followed by the actual synthesis of the nanotube. The catalyst is generally prepared by sputtering a transition metal onto a substrate and then using either chemical etching or thermal annealing to induce catalyst particle nucleation. Thermal annealing results in cluster formation on the substrate, from which the nanotubes will grow. Ammonia may be used as the etchant[31-34]. The temperatures for the synthesis of nanotubes by CVD are generally within the 650-900 °C range[31-34]. Typical yields for CVD are approximately 30%.

These are the basic principles of the CVD process. In the last decennia, different techniques for the carbon nanotubes synthesis with CVD have been developed, such as plasma enhanced CVD, thermal chemical CVD, alcohol catalytic CVD, vapour phase growth, aero gel-supported CVD and laser-assisted CVD. These different techniques will be explained more detailed in this chapter.

2.5.1 Plasma enhanced chemical vapour deposition

The plasma enhanced CVD method generates a glow discharge in a chamber or a reaction furnace by a high frequency voltage applied to both electrodes. Figure 2-13 shows a schematic diagram of a typical plasma CVD apparatus with a parallel plate electrode structure.
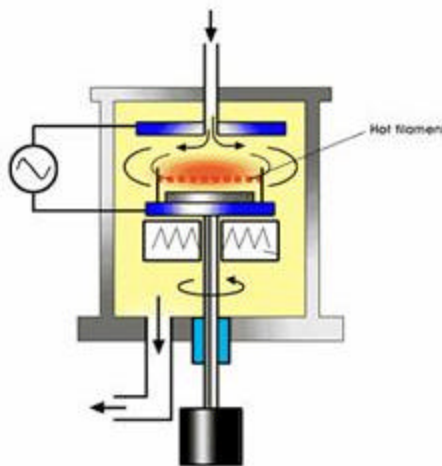

Figure 2-13: Schematic diagram of plasma CVD apparatus.

A substrate is placed on the grounded electrode. In order to form a uniform film, the reaction gas is supplied from the opposite plate. Catalytic metal, such as Fe, Ni and Co are used on for example a Si, SiO_2, or glass substrate using thermal CVD or sputtering. After nanoscopic fine metal particles are formed, carbon nanotubes will be grown on the metal particles on the substrate by glow discharge generated from high frequency power. A carbon containing reaction gas, such as C_2H_2, CH_4, C_2H_4, C_2H_6, CO is supplied to the chamber during the discharge[35].

The catalyst has a strong effect on the nanotube diameter, growth rate, wall thickness, morphology and microstructure. Ni seems to be the most suitable pure-metal catalyst for the growth of aligned multi-walled carbon nanotubes (MWNTs)[36]. The diameter of the MWNTs is approximately 15 nm. The highest yield of carbon nanotubes achieved was about 50% and was obtained at relatively low temperatures (below 330° C)[35].

2.5.2 Thermal chemical vapour deposition

In this method Fe, Ni, Co or an alloy of the three catalytic metals is initially deposited on a substrate. After the substrate is etched in a diluted HF solution with distilled water, the specimen is placed in a quartz boat. The boat is positioned in a CVD reaction furnace, and nanometre-sized catalytic metal particles are formed after an additional etching of the catalytic metal film using NH_3 gas at a temperature of 750 to 1050° C. As carbon nanotubes are grown on these fine catalytic metal particles in CVD synthesis, forming these fine catalytic metal particles is the most important process. Figure 2-14 shows a schematic diagram of thermal CVD apparatus in the synthesis of carbon nanotubes.
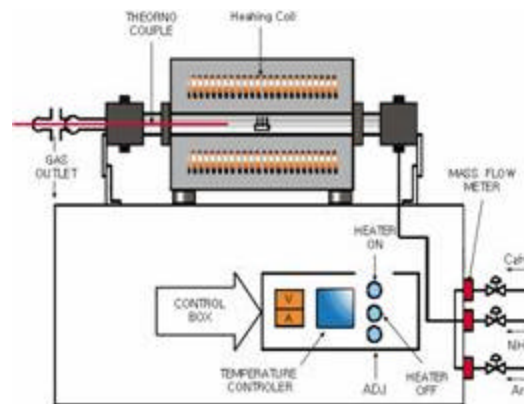

Figure 2-14: Schematic diagram of thermal CVD apparatus.

When growing carbon nanotubes on a Fe catalytic film by thermal CVD, the diameter range of the carbon nanotubes depends on the thickness of the catalytic film. By using a thickness of 13 nm, the diameter distribution lies

between 30 and 40 nm. When a thickness of 27 nm is used, the diameter range is between 100 and 200 nm. The carbon nanotubes formed are multiwalled[37].

2.5.3 Alcohol catalytic chemical vapour deposition

Alcohol catalytic CVD (ACCVD) is a technique that is being intensively developed for the possibility of large-scale production of high quality single wall nanotubes SWNTs at low cost. In this technique, evaporated alcohols, methanol and ethanol, are being utilised over iron and cobalt catalytic metal particles supported with zeolite. Generation is possible is possible at a relatively low minimum temperature of about 550 ^{o}C. It seems that hydroxyl radicals, who come from reacting alcohol on catalytic metal particles, remove carbon atoms with dangling bonds, which are obstacles in creating high-purity SWNTs. The diameter of the SWNTs is about 1 nm. *Figure 2-15* shows the ACCVD experimental apparatus.
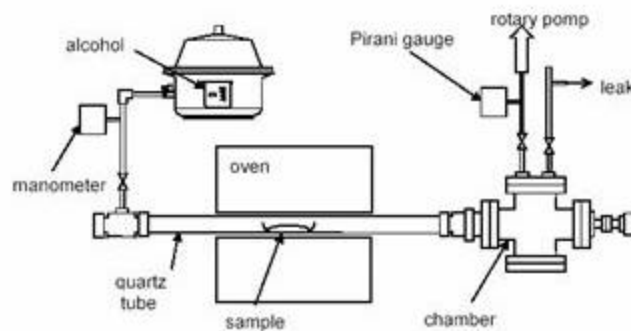

Figure 2-15: ACCVD experimental apparatus[38].

The lower reaction temperature and the high-purity features of this ACCVD technique guarantee an easy possibility to scale production up at low cost. Furthermore, the reaction temperature, which is lower than 600 ^{o}C, ensures that this technique is easily applicable for the direct growth of SWNTs on semiconductor devices already patterned with aluminium[38].

2.5.4 Vapour phase growth

Vapour phase growth is a synthesis method of carbon nanotubes, directly supplying reaction gas and catalytic metal in the chamber without a substrate [39].

Figure 2-16 shows a schematic diagram of a vapour phase growth apparatus. Two furnaces are placed in the reaction chamber. Ferrocene is used as catalyst. In the first furnace, vaporisation of catalytic carbon is maintained at a relatively low temperature. Fine catalytic particles are formed and when they reach the second furnace, decomposed carbons are absorbed and diffused to

the catalytic metal particles. Here, they are synthesised as carbon nanotubes. The diameter of the carbon nanotubes by using vapour phase growth are in the range of 2 - 4 nm for SWNTs[40] and between 70 and 100 nm for MWNTs. [39]
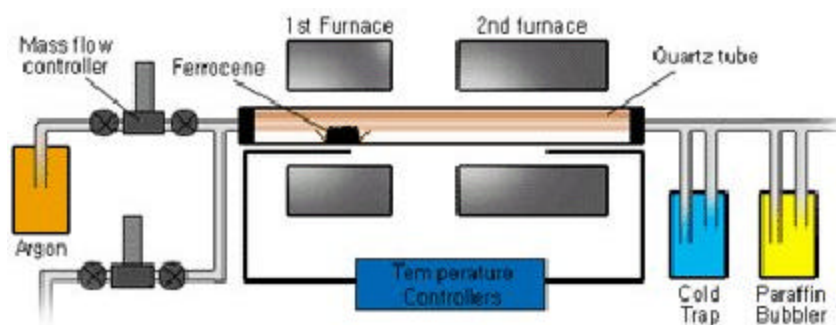

Figure 2-16: Schematic diagram of a vapour phase growth apparatus.

2.5.5 Aero gel-supported chemical vapour deposition

In this method SWNTs are synthesised by disintegration of carbon monoxide on an aero gel-supported Fe/Mo catalyst. There are many important factors that affect the yield and quality of SWNTs, including the surface area of the supporting material, reaction temperature and feeding gas. Because of the high surface area, the porosity and ultra-light density of the aero gels, the productivity of the catalyst is much higher than in other methods[41]. After a simple acidic treatment and a oxidation process high purity (>99%) SWNTs can be obtained.

When using CO as feeding gas the yield of the nanotubes is lower but the overall purity of the materials is very good. The diameter distribution of de nanotubes is between 1,0 nm and 1,5 nm. The optimal reaction temperature is approximately 860 ^{o}C [42].

2.5.6 Laser-assisted thermal chemical vapour deposition

In laser-assisted thermal CVD (LCVD) a medium power, continuous wave CO_2 laser, which was perpendicularly directed onto a substrate, pyrolyses sensitised mixtures of $Fe(CO)_5$ vapour and acetylene in a flow reactor. The carbon nanotubes are formed by the catalysing action of the very small iron particles. Figure 2-17 shows the experimental set-up for laser-assisted CVD[43].
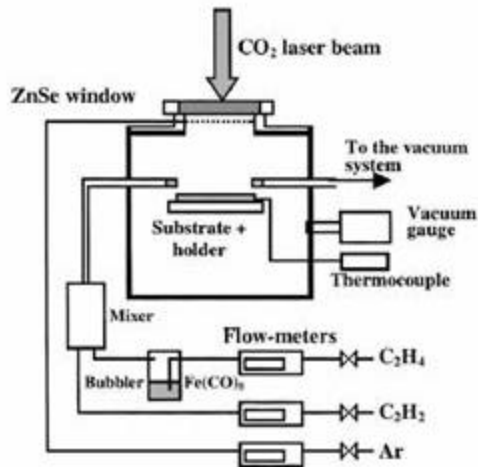
Figure 2-17: Experimental set-up for laser-assisted CVD [43].

By using a reactant gas mixture of iron pentacarbonyl vapour, ethylene and acetylene both single- and multi-walled carbon nanotubes are produced. Silica is used as substrate. The diameters of the SWNTs range from 0.7 to 2.5 nm. The diameter range of the MWNTs is 30 to 80 nm[43].

2.5.7 CoMoCat process

In this method, SWNTs are grown by CO disproportionation at 700 - 950 $^{\circ}$C. The technique is based on a unique Co-Mo catalyst formulation that inhibits the sintering of Co particles and therefore inhibits the formation of undesired forms of carbon that lower the selectivity. During the SWNT reaction, cobalt is progressively reduced from the oxidic state to the metallic form. Simultaneously Molybdenum is converted to the carbidic form (Mo_2C). Co acts as the active species in the activation of CO, while the role of the Mo is possibly dual. It would stabilise Co as a well-dispersed Co^{2+}, avoiding its reduction and would act as a carbon sink to moderate the growth of carbon inhibiting the formation of undesirable forms of carbon[44].

It is found that one of the critical conditions for an effective reactor operation is that the space velocity has to be high enough to keep the CO conversion as low as possible. Figure 2-18 shows a fluidised bed reactor for a CoMoCat process. The most important advantage of fluidised bed reactors is that they permit continuous addition and removal of solid particles from the reactor, without stopping the operation.
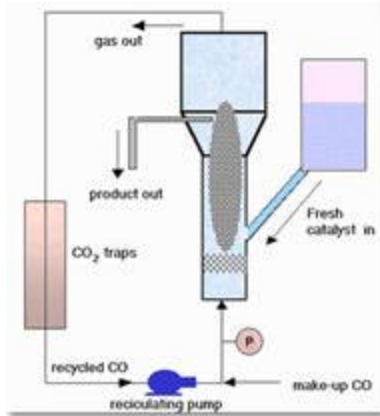
Figure 2-18: Schematic diagram of a CoMoCat apparatus

This is a method that can be scaled-up without losses in SWNT quality. By varying the operation conditions, SWNTs can be produced with different diameter ranges.

In Table 2-1 several diameter ranges at different temperatures are given. [45]

Temperature (°C)	Diameter range (nm)
750	0,9 ± 0,05
850	0,9 - 1,25
950	1,00 - 1,40

The CoMoCat catalyst has a high selectivity towards SWNTs, namely 80 - 90 %[46].

2.5.8 High pressure CO disproportionation process

The High pressure CO disproportionation process (HiPco) is a technique for catalytic production of SWNTs in a continuous-flow gas phase using CO as the carbon feedstock and $Fe(CO)_5$ as the iron-containing catalyst precursor. SWNTs are produced by flowing CO, mixed with a small amount of $Fe(CO)_5$ through a heated reactor. Figure 2-19 shows the layout of CO flow-tube reactor. Size and diameter distribution of the nanotubes can be roughly selected by controlling the pressure of CO. This process is promising for bulk production of carbon nanotubes.
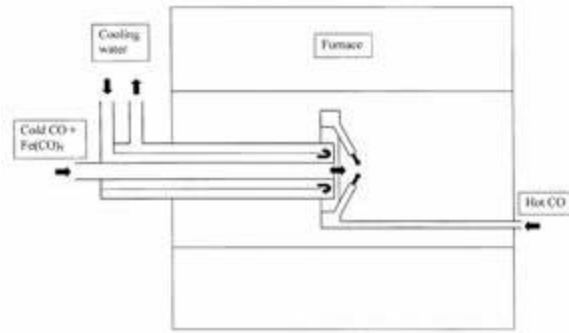
Figure 2-19: Layout of CO flow-tube reactor [47].

Nanotubes as small as 0.7 nm in diameter, which are expected to be the smallest achievable chemically stable SWNTs [48], have been produced by this method. The average diameter of HiPco SWNTs is approximately 1.1 nm. The yield that could be achieved is approximately 70%. The highest yields and narrowest tubes can be produced at the highest accessible temperature and pressure [47]. SWNT material with 97% purity can be produced at rates of up to 450 mg/h [49].

2.6 Flame synthesis

This method is based on the synthesis of SWNTs in a controlled flame environment, that produces the temperature, forms the carbon atoms from the inexpensive hydrocarbon fuels and forms small aerosol metal catalyst islands[50-52]. On these metal islands the SWNTs are grown in the same manner as in laser ablation and arc discharge.

These metal catalyst islands can be made in three ways. The metal catalyst (cobalt) can either be coated on a mesh[50], on which metal islands resembling droplets were formed by physical vapour deposition. These small islands become aerosol after being exposed to a flame. The second way[52], is to create aerosol small metal particles by burning a filter paper that is rinsed with a metal-ion (e.g. iron nitrate) solution. The third way, is the thermal evaporating technique in which metal powder (e.g. Fe or Ni) is inserted in a trough and heated[51].
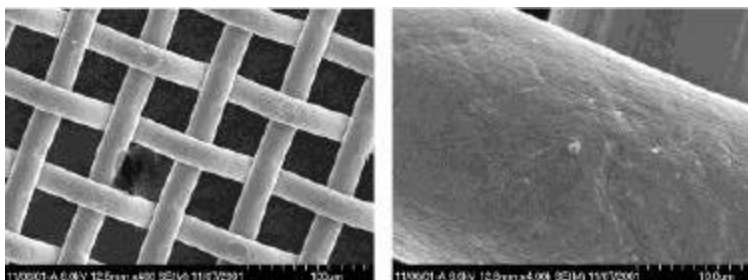
Figure 2-19 Meshes on which the metal catalyst is coated, used in flame synthesis

In a controlled way a fuel gas is partially burned to gain the right temperature of ~800 °C and the carbon atoms for SWNT production. On the small metal particles the SWNTs are than formed. As optimisation parameters the fuel gas composition, catalyst, catalyst carrier surface and temperature can be controlled[50]. In the references used the yield, typical length and diameters are not stated.

2.7 Summary

In Table 2-2, a short summary of the three most common techniques used nowadays is given.

Method	Arc discharge method	Chemical vapour deposition	Laser ablation (vaporization)
Who	Ebbesen and Ajayan, NEC, Japan 1992 [15]	Endo, Shinshu University, Nagano, Japan [53]	Smalley, Rice, 1995[14]
How	Connect two graphite rods to a power supply, place them a few millimetres apart, and throw the switch. At 100 amps, carbon vaporises and forms a hot plasma.	Place substrate in oven, heat to 600 ^{o}C, and slowly add a carbon-bearing gas such as methane. As gas decomposes it frees up carbon atoms, which recombine in the form of NTs	Blast graphite with intense laser pulses; use the laser pulses rather than electricity to generate carbon gas from which the NTs form; try various conditions until hit on one that produces prodigious amounts of SWNTs
Typical yield	30 to 90%	20 to 100 %	Up to 70%
SWNT	Short tubes with diameters of 0.6 - 1.4	Long tubes with diameters ranging	Long bundles of tubes (5-20 microns), with

Method	Arc discharge method	Chemical vapour deposition	Laser ablation (vaporization)
	nm	from 0.6-4 nm	individual diameter from 1-2 nm.
M-WNT	Short tubes with inner diameter of 1-3 nm and outer diameter of approximately 10 nm	Long tubes with diameter ranging from 10-240 nm	Not very much interest in this technique, as it is too expensive, but MWNT synthesis is possible.
Pro	Can easily produce SWNT, MWNTs. SWNTs have few structural defects; MWNTs without catalyst, not too expensive, open air synthesis possible	Easiest to scale up to industrial production; long length, simple process, SWNT diameter controllable, quite pure	Primarily SWNTs, with good diameter control and few defects. The reaction product is quite pure.
Con	Tubes tend to be short with random sizes and directions; often needs a lot of purification	NTs are usually MWNTs and often riddled with defects	Costly technique, because it requires expensive lasers and high power requirement, but is improving

Table 2-2: A summary of the major production methods and their efficiency