

Chapter 7

CNT and Graphene Growth: Growing, Quality Control, Thermal Expansion and Chiral Dispersion

The production of carbon nanotubes (CNTs) and graphene sheets is related to simple manipulation actions similar to production of fullerenes, different carbon allotropes and so on. The arc discharge method can be evaluated as an innovative technique for producing CNTs using graphite evaporation. Unfortunately, this technique requires significant purification and fraction separation routines which are necessary after evaporation.

An alternative CNT production method such as chemical vapour deposition (CVD) allows controlling the quality of production yield on demand. Arc discharge, laser ablation and chemical vapour deposition are three techniques useful for industrial development of CNTs in order to produce a significant amount and the required purity. Depending on the conditions of preparation, single-walled carbon nanotubes (SWCNT) or multiwalled (MWCNT) can be manufactured [1]. High vacuum technologies and magnetic field technologies are also used for purification.

7.1 The Iijima Method for Growing CNTs and Graphene

7.1.1 Arc Discharge

Iijima et al. [2] in 1992 reported a novel carbon structure synthesized by arc discharge methods. Iijima characterized it as a carbon derivative which shows complete ‘turnaround growth’, involving pentagon–heptagon pairs. The main idea was expressed as follows: tubular assemblies are producing MW–CNTs with different morphologies.

In 1994, Iijima and Ichihashi [3] and Bethune [4] synthesized SWCNTs using the same route as producing MWCNTs but adding some metal particles to the carbon electrodes (using transition-metal catalysed arc discharge).

Figure 7.1 represents schematic chart of equipment for producing CNTs in He, Ar or CH₄ gas environment (pressure 20 ÷ 200 Torr). The vacuumed arc discharge

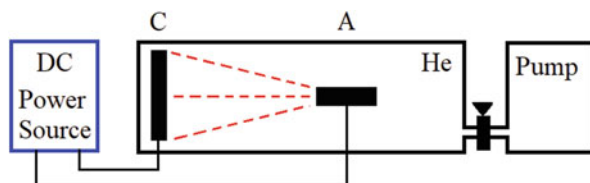


Fig. 7.1 Schematic diagram of arc discharge chamber for producing of CNT in He surrounding. Closed electric circuit includes two graphite electrodes: cathode (C) and anode (A) – both stabile. Face-to-face orientation of electrodes, traces of plasma particles are depicted in red (Adapted according to Ref. [5])

chamber contains two graphite electrodes: cathode (C) and anode (A). Direct current up to 100 A is the reason for a high discharge temperature and the following carbon evaporation. In this case, cathode sublimation occurs.

To carry out the described experiment, several conditions must be fulfilled:

1. The distance between cathode and anode – up to 2 mm
2. The orientation of surfaces of electrodes – from face-to-face up to a sharp angle
3. The voltage between cathode and anode – up to 25 V
4. The current – up to $50 \div 100$ A
5. The density of the current – up to 100 A cm^{-2}

MWCNTs were grown in the cathode deposits of soot. Ando et al. [5] reviewed different arc techniques. For SWCNTs synthesis, incorporation of metallic particles in the graphite anode is necessary. Using another technique, the so-called *arc plasma jet* method, two electrodes are placed at a sharp angle. In this case, the amount of cathode deposits decreases, the amount of soot including SWCNT increases. Ando et al. [6] described the usage of the mentioned technique to get three kinds of allotropes of carbon: CNTs, disordered polyhedra and graphene sheets. The length of CNTs exceeds $50 \mu\text{m}$, diameter up to 30 nm. Somu et al. [7] reviewed some of the important developments in the processing of CNT.

In addition to the well-known classical techniques by Iijima et al. [2–6] where direct current (DC) operates the CNT yielding, additional technique was invented in order to solve the problems of purity, homogeneity, quality, etc. Alternating current (AC) arc discharge method was reported as more effective than DC one for synthesis of SWCNT [8, 9].

Sugai et al. [10] reported the possibility of synthesis of high-quality double-walled carbon nanotubes (DWCNT). High-temperature pulsed arc discharge method was used with Y/Ni alloy catalysts at 1250°C . Using described technique, inner and outer diameter of DWCNTs was obtained as $0.8 \div 1.2$ and $1.6 \div 2.0$ nm, respectively.

The task to increase the reaction yield by producing SWCNTs and DWCNTs was partially solved by means of plasma rotating in arc discharge technique. Cassel et al. [11] reported plasma rotating arc discharge technique. Figure 7.2 represents arc discharge chamber where anode (A) is rotating at a high velocity along the long axis. Cathode stays stabile. The rotation of the anode stabilizes the plasma. Due to

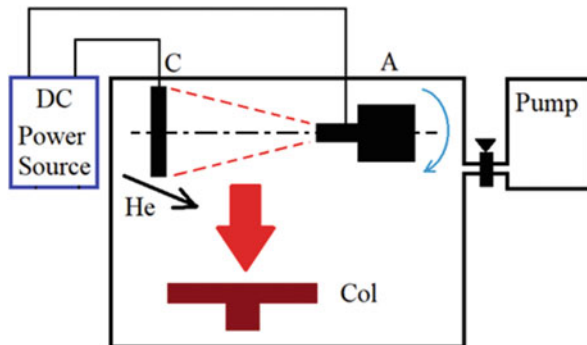


Fig. 7.2 Schematic diagram of arc discharge chamber for producing of CNT in He surrounding. Closed electric circuit includes two graphite electrodes: stable cathode (C) and anode (A), which are rotating at a high velocity along the long axis. Deposition of carbon particles occurs on graphite collector (Col) (Adapted according to [11])

centrifugal rotation forces, turbulence accelerates the particles of carbon vapour perpendicular to the anode.

Carbon vapour is collected on the collector at the periphery of the plasma. CNT increases with the increasing of rotational speed.

7.1.2 Purification

Using the arc discharge method, CNT yield exceeds 50%. The deposit on cathode also contains additional amount of fullerenes, graphene sheets, disordered polyhedra, etc.

Three operations are necessary for the cleaning purposes:

1. The mixture of deposit and methanol must be dispersed by ultrasound until some suspension occurs.
2. The dispersed suspension must be diluted by water. Centrifuging separates diluted suspension into large agglomerates (deposited on the wall of centrifuge) and CNT (in suspension).
3. The suspension including CNT must be influenced by pure nitric acid (HNO_3) and afterward must be dried by gaseous mixture containing 20% O_2 and 80% H_2 at temperature $\approx 750^\circ\text{C}$.

The mentioned purification technique allows getting a mixture of CNT of diameter in average 20 nm. The use of nitric acid HNO_3 is related to the structure of impurities. The reactivity of hexagonal layer is much lower in comparison to pentagonal one. Pentagonal rings are involved in fullerenes, etc. Oxidizer reacts with spherical derivatives. CNTs, as ordered hexagonal structures, are inert in reaction path. The purification of DWCNTs can be achieved by oxidation in air at 500°C [10].

7.2 Arc Discharge and Induced Non-regularities

The arc discharge technique initially was invented for the synthesis of fullerenes. Direct current up to 100 A generates a high discharge temperature. The arc discharge is a rather unstable process. The current flow contains certain discontinuities, which is related to the inhomogeneity of the electric field. The spatial density of current is determined by the rapid processes of graphite particle evaporation from electrode surface. Actually, it is a time-dependent and gradient-dependent process which is impossible to control by current stabilization.

CNTs and graphene sheets were obtained in product soot as the additional product to fullerenes. As Ando et al. [5] claimed this method represents the easiest way to synthesize the CNT. Several disadvantages of the arc method occur in practice:

- (a) The pure quality of CNTs (quality is strongly dependent on the uniformity of the plasma arc).
- (b) The selection of filling gases (He, Ar, etc.) influences the growth of CNTs.
- (c) The reaction product always contains a mixture of different types of CNTs.
- (d) To remove fullerenes and amorphous carbon, several purification processes are necessary.

Eftekhari et al. [12] probed to estimate different aspects of damages in graphene structure. They told that in a sense, ideal defect less flat graphene is an analogy to diamond. The chemical reactivity decreases for an ideally ordered hexagonal structure in comparison with the damaged one. Practical interest in applications increases with increasing reactivity due to certain damages so-called crystallographic defects.

The Stone–Wales defect is related to the change of connectivity between two π -bonded carbon atoms with changing orientation [13]. Stone and Wales described these phenomena in 1986 on the isomerization of fullerenes [14]. Figure 7.3 represents conversion from naphthalene to fulvene with following redistribution of carbon atoms in the centrum part when two hexagons are converted into two pentagons. The previous central [$\text{C} = \text{C}$] junction changes orientation by 90° with respect to the midpoint of their bond. Reaction of this type is typical for CNT,

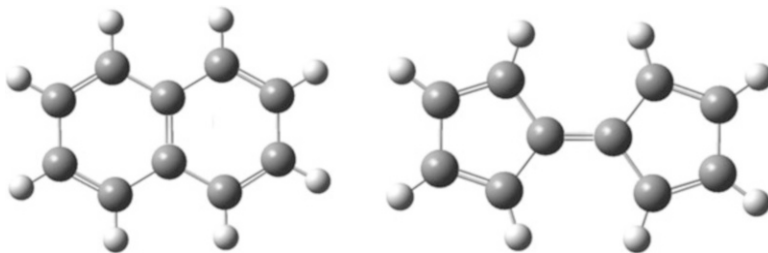


Fig. 7.3 The Stone–Wales defect. Conversion from naphthalene to fulvene. Two hexagons are converted into two pentagons. [$\text{C} = \text{C}$] junction changes orientation by 90°

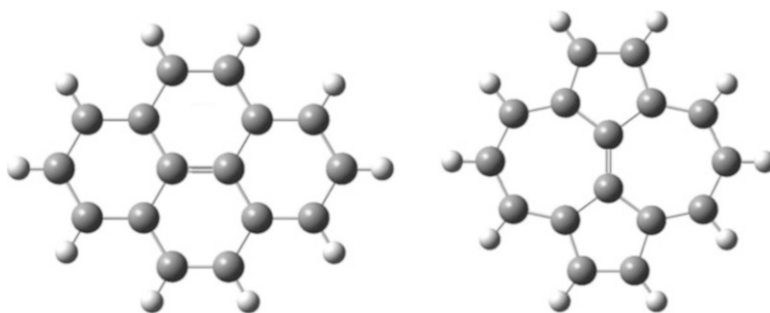
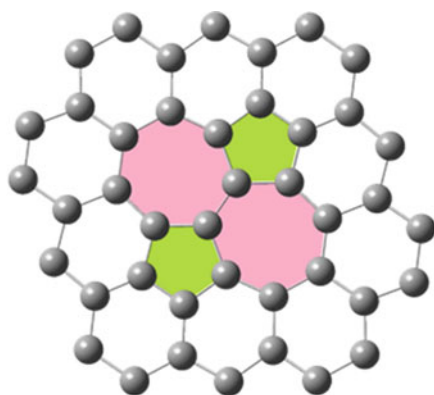


Fig. 7.4 The Stone–Wales defect in pyrene with formation of pentagon–heptagon pair

Fig. 7.5 The Stone–Wales defect in graphene sheet with the formation of pentagon–heptagon alternating pairs (green–red) (Adapted according to [16])



graphene, etc. Figure 7.4 represents Stone–Wales defect in pyrene with formation of pentagon–heptagon pair.

Figures 7.3 and 7.4 represent two structures when rearrangement structure contains a region with greater chemical reactivity. Due to large surface area, high affinity of such type defects increases the possibility of hydrogen adsorption. Letardi et al. [15] proposed to solve atomic hydrogen storing problem using graphene defects of the Stone–Wales type.

Meyer et al. [16] presented transmission electron microscopy investigation of graphene membranes. Figure 7.5 represents Stone–Wales (SW) defect with formation of pentagon–heptagon alternating pairs. Such defects, consisting of pentagon–heptagon pairs, play a key role in bonding by transformation of sp^2 hybridization. Figure 7.6 represents defects in a graphene sheet – an open vacancy is presented.

Figure 7.7 represents a set of non-aligned pentagon–heptagon pairs (four pentagons and four heptagons) in a graphene sheet. Meyer et al. [16] stated that in the study of defects, the vacancies are important for basic understanding of potential electronic and thermal applications.

Side effects described by Eftekhari et al. [12] are also important for analysing electronic properties of graphene sheets as well as CNT. Figure 7.8 represents a

Fig. 7.6 A defect in a graphene sheet (Adapted according to [16])

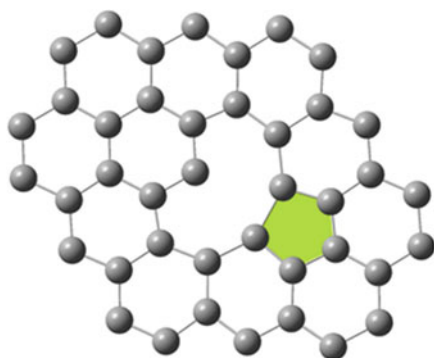
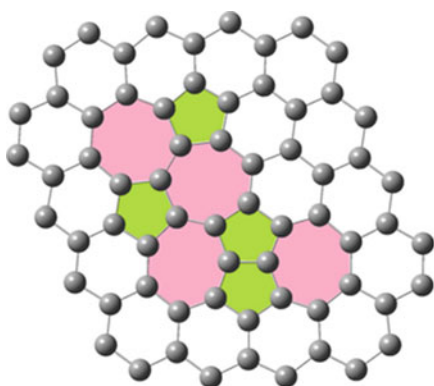


Fig. 7.7 A set of non-aligned pentagon–heptagon pairs (green–red) in a graphene sheet (Adapted according to [16])



schematic chart of graphene edge cuts. Corners (yellow), armchair (red) and zigzag (blue) arrangements are the places of interest due to increased electronic reactivity.

7.3 Laser Ablation and Self-Organization of Matter

7.3.1 Laser Ablation

Laser ablation belongs to one of the most prominent techniques to manufacture CNTs and was first used by Smalley et al. [17, 18] in 1995. The main idea of this method is to use the radiation of high power laser to distinguish the high temperature at a local place of a graphite target. Vapourization from a carbon target starts immediately. The quality of the produced CNTs depends on the environment factors such as type of inert gas, temperature, pressure, type of catalysts as well as on laser power and frequency.

Figure 7.9 represents a schematic chart of the equipment for laser ablation. Radiation of YAG:Nd laser (300 mJ/pulse at 532 nm wavelength, second harmonic)

Fig. 7.8 A schematic chart of graphene edge cuts. Corners (yellow), armchair (red) and zigzag (blue) arrangements are the places of interest (Adapted according to [12])

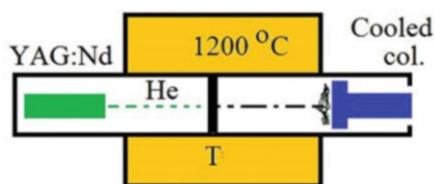
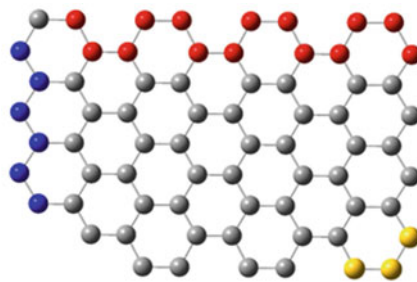


Fig. 7.9 Schematic chart of equipment for laser ablation. Radiation of YAG:Nd laser is pointed to carbon target (T). Evaporated carbon particles are collected on cooled collector (col). Environment of inertial gas (Ar or He), furnace heated until 1200 °C

is focused on carbon target (T). After focusing, the density of energy must exceed the value of 3 J/cm^2 , when pulse duration is 8 ns. The carbon target is placed in a quartz tube furnace heated until about 1200 °C. The environment of the target consists of inertial gas at 500 Torr pressure (Ar or He). The evaporated carbon particles and the reaction products including CNTs are collected on a cooled collector (col) (self-assembling technique). The vapour condensation process on the cooled collector finishes with layer-to-layer covering as well as formation of CNT due to the influence of catalyst particles.

Using the laser ablation technique, MWCNTs can be produced from the pure graphite and SWCNTs from a composite consisting of graphite and any transition metal (nickel, cobalt, etc.). As in the case of the arc discharge technique, the graphite target must be enriched by metal particles as catalysts. The standard composition of the carbon target contains 98.8% of graphite and 1.2% of cobalt/nickel. Using this equipment, SWCNT can be manufactured with a diameter in the range of about $1.0 \div 1.6 \text{ nm}$.

The laser ablation method allows receiving high purity of CNTs (up to 90%) in comparison to the arc discharge one. Moreover, very narrow distribution of diameters can be achieved.

Van de Burgt [19] presented a review of the current situation in the use of the laser ablation technique. Physical parameters, which influence nanotube growth (gas type, selection of catalyst and exchange of thermal energy), were commented and argued from the position of industrial manufacturing.

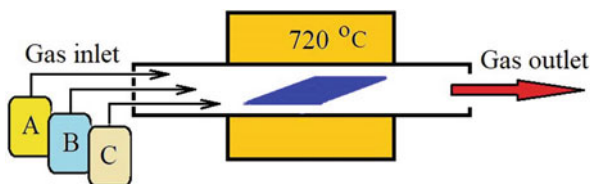


Fig. 7.10 Schematic chart of equipment for chemical vapour deposition (CVD). Quartz tube for flow of hydrocarbons in furnace. Catalyst reactions from metal substrate Fe, Ni and Co (blue). Reservoirs A, B and C are designed for gaseous hydrocarbons (CO, C₂H₂, CH₄) as well as for flow gases (Ar)

One of the most important factors in the laser-assisted synthesis of CNT is the possibility to employ the thermal energy of laser radiation. A great number of CW gaseous lasers such as CO₂, Ar-ion, YAG:Nd, YVO₄:Nd as well as diode lasers could be used.

A special case arises when the resonance frequency of the catalyst nanoparticles is equal to the laser frequency. Conditions of the surface plasmon resonance become excellent. In that case, laser light is efficiently converted into heat inside the catalyst particles. Cao et al. [20] reported the usage of low-power 532 nm CW-laser radiation for local induction of surface plasmon reaction on nanoparticles. Quick heating allows to synthesize the CNTs on nickel and gold particles.

7.3.2 Chemical Vapour Deposition

The catalytic chemical vapour deposition (CVD) method to produce MWCNTs was described by Endo et al. [21]. After several years, Dai et al. [22] announced CVD method to produce SWCNTs adapted CO-based CVD to produce SWNTs. CVD is the most promising method to produce CNT on industrial scale [23].

Figure 7.10 represents a schematic chart of the equipment for CVD. Carbon sources are hydrocarbon gases such as carbon monoxide (CO), acetylene (C₂H₂), methane (CH₄) and benzene (C₆H₆). Quartz tube is designed for the flow of hydrocarbons with heating to 600 ÷ 1200 °C inside the furnace. Inertial gases such as Ar could be used as flow gases. Passing the hydrocarbon vapour through a quartz tube occurs in 60 min. The vapour of hydrocarbons is thermally decomposed at sufficiently high temperature. The presence of the metal catalyst outside the furnace initiates self-organization processes of carbon. Fe, Ni and Co as transition metals are suitable for such purposes. Catalyst material (also in liquid or gaseous form) can be placed inside the furnace. Atomized carbon is condensed by creating certain form of CNT (growing processes). Depending on the temperature, SWCNTs and MWCNTs can be produced.

Cassell et al. [24] reported the semi-continuous system for commercial production of highly crystalline and pure CNTs. Combination of the classical CVD method and the subsequent high-temperature thermal treatment takes place. Takeuchi et al. [25] estimated the CVD method as a unique for industrial usage for large-scale production of CNT. Inami et al. [26] reported applications of alcohol catalytic CVD for growth of SWCNTs using Co catalyst film. Three types of heat treatment were investigated.

The advantages of the CVD method are the following: (1) relatively high purity in comparison to arc discharge, (2) lower temperature range and (3) low power input.

7.4 Simulations of Growth: Sporadic and Stimulated

7.4.1 CNT Growth Mechanism

Since the discovery of CNTs in the 1990s, their growth has been treated as an unresolved task so far. Since the demand for CNTs growth remains as the purpose for the future, industrial production of several fixed parameters for CNTs is outspread. The control of quantity and quality is connected with fundamental questions about the growth mechanism of CNTs – sporadic and stimulated. Because of the large gradients in the energy exchange processes and the difficulties that arise as a result of surface microcontrol and nanocontrol, the laser ablation method, as well as the arc discharge method, relates to sporadic methods.

Otherwise, the chemical vapour deposition (CVD) method belongs to stimulated methods (driving the experiment due to the contribution of the catalysis).

Firstly, catalysed decomposition of hydrocarbon as an exothermic process occurs at a high temperature:



The reaction begins when the hydrocarbon of the reagent enters a short contact with the catalyst. Reaction products such as atomic and/or molecular hydrogen are not involved in following reactions: they remain in the near surrounding as pollutants. After decomposition, carbon atoms cover the catalyst surface creating an amorphous film (some sort of ‘dissolving’ of the catalyst particle occurs).

Secondly, the coating of the metal surface with carbon is a temperature-limited and diffusely limited process. Due to that, some limit of metal covering by carbon could be achieved. By overstepping this limit, carbon starts to crystallize (endothermic process) to pass to a more energetically stable form. Now it is necessary to estimate how the substrate interacts with the catalyst. Due to the interaction strength, two types of CNT growth mechanisms are present: the tip-growth mechanism and the base-growth mechanism [27].

7.4.2 *The Tip-Growth Mechanism*

The surface of the substrate is covered with a catalyst. Let us assume the catalyst as surface structured – spherical metal nanoparticles which could be placed on the substrate surface without forming a strong contact. Van der Waals forces keep the catalyst particle fixed using a small surface of the interconnect area. In that case, the substrate weakly interacts with the catalyst. Figure 7.11 represents several stages of reaction path, when the interaction of catalyst to substrate is weak. Hydrocarbon decomposes on the top of the nanoparticle, carbon atoms begin covering the surface of the nanoparticle starting from the top to the bottom. In such conditions, the formation of the inhomogeneous amorphous layer begins (Fig. 7.11a). Deposition continues until the top of nanoparticle is fully covered by carbons.

Due to the temperature and concentration gradients of the deposited carbon on the surface, carbon starts crystallizing to form pentagons and hexagons (fragments of fullerene) on the top (Fig. 7.11b). The process of crystallization continues from the top particle to the side particle with the formation of the fullerene hemisphere. After that, a tubular form of the carbon (CNT) starts growing. Due to interactions in the hemisphere zone, the nanoparticle is attracted to the fullerene network. Filling X area (between nanoparticle and substrate) by crystallized carbon stimulates the process of CNT growth which is related to pushing the nanoparticle off the surface of the substrate (Fig. 7.11c).

The growth of CNTs continues until a metal nanoparticle is fully covered by carbons. In this case, the catalytic activity of a metal nanoparticle decreases to zero, following crystallization interrupts. At this step, CNT growth terminates (Fig. 7.11d). This type of CNT growth from top to bottom is called the tip-growth mechanism.

7.4.3 *The Base-Growth Mechanism*

The substrate surface is coated with a catalyst. Let's assume that the catalyst as metal nanoparticles of hemispheric type (surface structured) can be placed on the substrate surface forming a strong contact. Van der Waals forces keep the catalyst particle fixed using a large interconnect surface area. In that case, the substrate strongly interacts with the catalyst.

Figure 7.12 represents several stages of the reaction path, when the interaction of the catalyst and substrate is strong. Hydrocarbon decomposes on the top of the nanoparticle and, carbon atoms begin covering the surface of the nanoparticle starting from top to bottom.

Due to the surface properties, X zone in that case is absent. Any force to push the nanoparticle from the bottom could be organized. Crystallization starts from bottom with development of a tubular structure at the bottom (Fig. 7.12a) and continues with development of a hemisphere at the top (Fig. 7.12b). The growth of the

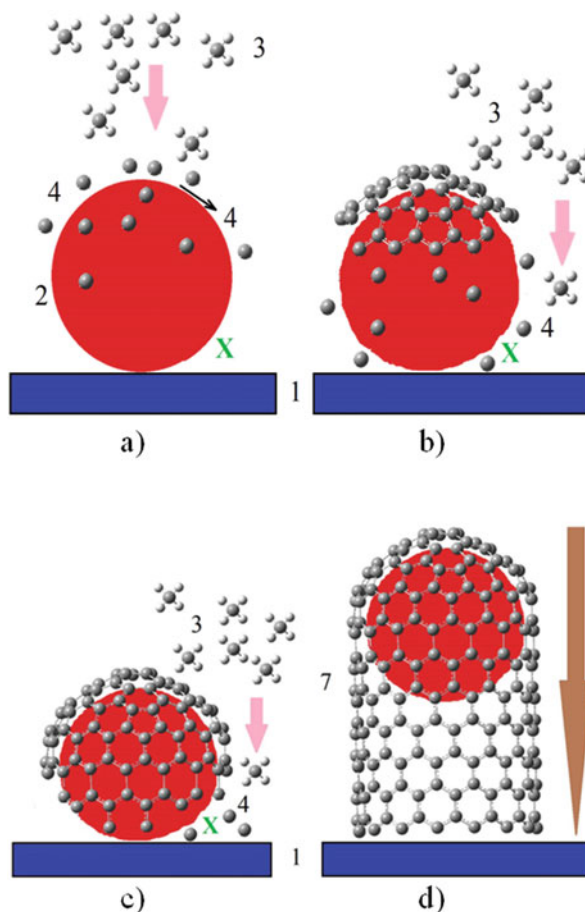


Fig. 7.11 Tip-growth mechanism for CNTs, weak interactions between catalyst and substrate. The direction of growth (from top to bottom) is pointed by a brown arrow: (a) hydrocarbon decomposes at the surface of nanoparticle, carbon atoms cover the catalyst, formation of amorphous layer; (b) crystallization starts, part of fullerene at the top; (c) crystallization is continuing, fullerene and CNTs start growing; (d) catalyst particle is fully covered, crystallization stops. X area (area between spherical nanoparticle and substrate) is denoted as X (green). 1 – substrate (blue); 2 – catalyst as surface structured metal nanoparticle (red); 3 – hot hydrocarbon (in that case methane) is pointed to catalyst; 4 – carbon atoms (adsorbate) are covering the surface of catalyst; 5 – carbon starts to crystallize, and hemisphere of fullerene starts to form; 6 – tubular derivative starts to grow; 7 – CNT with hemisphere of fullerene, CNT growth terminates

hemisphere transforms into the growth of the tubular structure (Fig. 7.12c). The growth of CNTs continues until the metal nanoparticle is fully covered by carbons as in the previous case. At this stage, the growth of CNTs terminates (Fig. 7.12d). This type of CNT growth from bottom to top is called the base-growth mechanism.

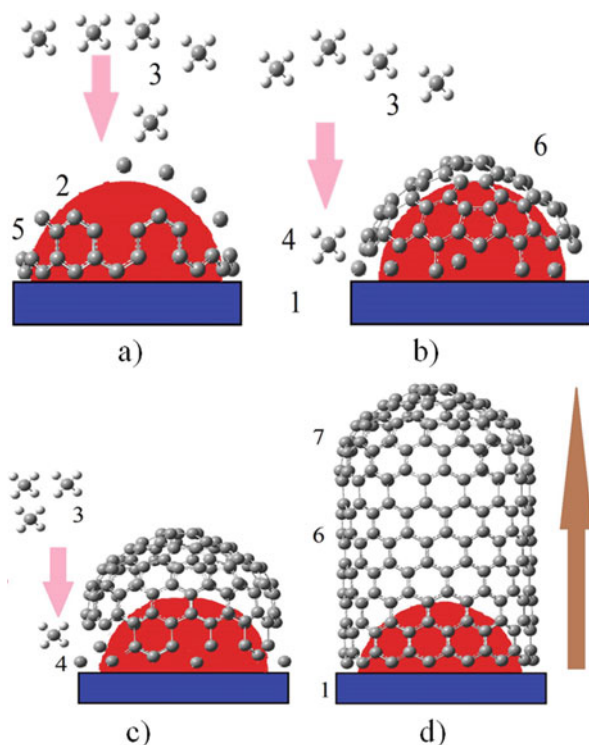


Fig. 7.12 The base-growth mechanism for CNTs, strong interactions between catalyst and substrate. Direction of growth (from bottom to top) is pointed by a brown arrow: (a) crystallization starts from bottom with generation of tubular structure; (b) crystallization continues with generation of hemisphere of fullerene on the top; (c) CNT growing from bottom continues; (d) catalyst particle at the bottom is fully covered, crystallization stops. 1 – substrate (blue); 2 – catalyst as surface structured metal nanoparticle (red); 3 – hot hydrocarbon (in that case methane) is pointed to catalyst; 4 – carbon atoms (adsorbate) are covering the surface of catalyst; 5 – carbon starts to crystallize; tubular fragments start to form; 6 – CNT starts to grow from bottom with formation of hemisphere of fullerene; 7 – CNT growth terminates

7.4.4 Several Control Strategies

Liu et al. [28] declared that the controlled growth of SWCNT with predefined and uniform structures remains a big challenge. Liu observed several strategies of the controlled synthesis of SWCNTs by CVD method.

The laser ablation technique is one of the most prominent in the industrial production of CNTs. Reinhardt et al. [29] described the novel equipment consisting of a nanosecond pulsed laser for the generation of transition metal oxide precursors. The catalysed growth of CNTs is ensured in gaseous species (5% H_2 and 95% N_2) at 800 °C. The presented technique is automated for large-scale production of CNTs on demand.

Neyts [30] reviewed a big number of techniques allowing the CNT growth: electric arc discharges, laser ablation, fullerene recrystallization, catalysed CVD (C-CVD) and plasma-enhanced CVD (PE-CVD). Neyts claimed that plasma-enhanced growth can be strongly beneficial. Several advantages of PE-CVD are present for CNT industrial producing.

1. *Low-temperature growth.* Decreasing the temperature allows excluding of generation of additional fragments which damage the tubular structure. Hofmann et al. reported MWCNT growth at 393 K temperature in DC plasma. PE-CVD experiment was organized using a Ni catalysed acetylene and ammonia system. Comparing the energy of thermal CVD (up to 1.5 eV), the PE-CVD activation energy for the growth rate was found to be 0.23 eV, six times less. Surface diffusion of carbon on nickel could be estimated as condition for growth [31].
2. *Effect of electric field.* Electric fields effects are useful in CNT production due to the possibility to make an alignment on demand.
3. *Effect of plasma on the catalyst during the growth.* To understand the processes of covering of catalyst surface by carbon is an interesting task in order to control the reaction pathway. Chiang et al. [32] reported the development of chirality pure SWCNTs in microplasma (pressure 10^5 Pa). By varying the composition of $\text{Ni}_x\text{Fe}_{1-x}$, nanocatalysts, chirality distribution of SWCNTs can be altered. At lower temperature, catalyst of this type may adopt a different surface structure resulting in epitaxial growth. This reference could be estimated as one possible route for chirality-selective synthesis.
4. *Plasma chemistry effects on the catalyst during the growth.* Bogaerts et al. [33] analysed plasma-enhanced growth mechanisms of CNT. In plasma chemistry, the problem of atomic hydrogen is related to the growth control. Atomic hydrogen reacts to methane molecules, creating radicals. Recombination of radicals into C_1H_4 , C_2H_2 , C_2H_4 , C_3H_6 , etc. creates inhomogeneity of the flow. Concentrations of the set of hydrocarbons in the gas phase are temperature dependent. Strong temperature regime and absence of temperature gradients allow controlling of product growth parameters on demand.

7.4.5 Quality Control

Raman spectroscopy belongs to the group of non-invasive non-destructive techniques for identifying the low-frequency vibrational modes in a system. Molecular systems or small clusters could be recognized by characteristic frequencies (so-called fingerprints) which occur as normal vibrations. Due to interaction between external electric field and electronic subsystem of molecule, induced dipole moment will be created. Vibrational (Raman) frequencies depend on behaviour of chemical bonds and symmetry of molecule.

Raman microspectrometry can be used to analyse structural parameters (diameter, chirality) as well as adsorption parameters (presence of adsorbates). Table 7.1 represents Raman modes which are useful for non-invasive identification of structure.

Table 7.1 CNT and graphite: Raman modes

Mode	Structure	Wave number ν (cm ⁻¹)	Formula	Intensity (I)	Source
RB	SWCNT	100 ÷ 350	Eq. (7.2)	Strong	[34, 35]
	DWCNT	100 ÷ 350	Eq. (7.3)	Strong	[34, 35]
G	Graphite	1580		Strong	[36]
	SWCNT	<1580		Strong	[36]
D	Graphite	1330 ÷ 1360		Weak	[36, 37]
	SWCNT	1280 ÷ 1350		Weak	[36, 37]

Table 7.2 Parameters of RB mode function

CNT type	Formula	A (cm ⁻¹ ·nm)	B (cm ⁻¹)	C (cm ⁻¹ ·nm)	D (cm ⁻¹)	Source
SW-RBM	Eq. (7.2)	234	10	–	–	[34, 35]
DW-RBM	Eq. (7.3)	248	0	–	–	[34, 35]
CNT metallic	Eq. (7.4)	227	11.8 ± 1.0	–2.7 ± 1.2	–2.7 ± 0.8	[38]
CNT semicond.	Eq. (7.4)	227	7.3 ± 0.3	–1.1 ± 0.3	–0.9 ± 0.2	[38]

Motion of radial contraction and following expansion represents the radial breathing mode (RB mode) of CNT [34, 35]. Wave number of RBM mode ν is different for SWCNT and DWCNT and depends on the nanotube diameter d :

$$\nu_{\text{RBM}}^{\text{SW}} = \frac{A}{d} + B, \tag{7.2}$$

$$\nu_{\text{RBM}}^{\text{DW}} = \frac{A}{d}. \tag{7.3}$$

Jorio et al. [38] presented revised function for RB mode wave number definition where chiral angle θ is included:

$$\nu_{\text{RBM}} = \frac{A}{d} + B + \frac{C + D(\cos 3\theta)^2}{d^2}. \tag{7.4}$$

Table 7.2 represents parameters of RB mode function. Planar vibrations of carbon atoms (so-called G mode, graphite mode) are present in most graphite-like materials including CNT [36]. All graphite-like carbons which contain any structural defects could be identified by the presence of so-called D mode, disorder-induced mode [36, 37]. For high-quality nanotubes, $Q > 100$:

$$Q = \frac{I_G}{I_D}. \tag{7.5}$$

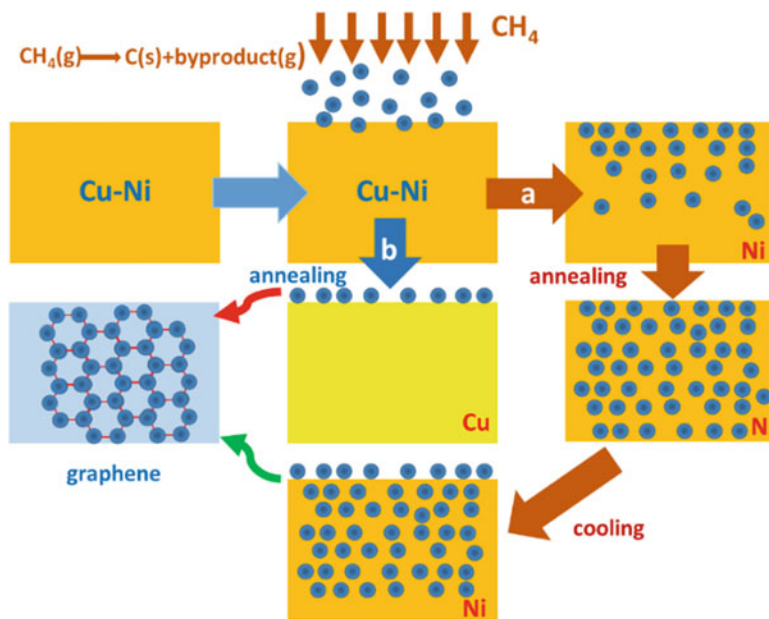


Fig. 7.13 Graphene growth mechanisms. (a) The mechanism of dissolution–precipitation graphene growth. (b) The mechanism of direct deposition graphene growth

7.5 Graphene Growth and Technological Defects

Recently, graphene has become the focus of research due to its properties. The most traditional and technologically popular technique for the synthesis of graphene is the method of chemical vapour deposition [39]. Two basic CVD graphene growth mechanisms have been proposed (see Fig. 7.13) [6, 40]:

- Segregation of surface carbon atoms: It is proposed here that decomposed carbon atoms diffuse into the bulk catalyst (e.g. Ni) during the annealing stage at a high temperature. Then, carbon atoms precipitate on the catalyst during the cooling period.
- Surface deposition of carbon atoms: Carbon atoms here are directly deposited on the catalyst surface (e.g. Cu) without segregation resulting in a graphene layer.

The quality and continuity of the graphene film could be affected by numerous CVD parameters such as temperature, hydrocarbon (e.g. CH_4) concentration, hydrocarbon pressure and cooling rate. The graphene growth mechanism is significantly affected by catalyst type, structure, quality and carbon solubility [41]. Typical catalysts used for graphene growth are polycrystalline Co, Ni, Cu, Pt, Ir and Ru [42–44].

7.5.1 Defects in Graphene

However, there are some physical and chemical conditions during CVD processes when we can observe graphene defects formation. In particular, if graphene films are synthesized by copper-catalysed atmospheric pressure chemical vapour deposition (APCVD) method using a mixture of Ar, H₂ and CH₄ gases, it was found that variations in the reaction parameters, such as reaction temperature, annealing time and growth time, affected the size of the growing graphene domain. Moreover, the reaction parameters influenced the number of layers, degree of defects and uniformity of the graphene films. The increase in growth temperature and annealing time tends to accelerate the graphene growth rate and increase the diffusion length, respectively, thereby increasing the average size of graphene domains [45].

It was experimentally found that the number of pinholes reduced with increase in the growth time. Micro-Raman analysis of the as-grown graphene films confirmed that the continuous graphene monolayer film with low defects and high uniformity can be obtained with prolonged reaction time, under the appropriate annealing time and growth temperature.

The real problem of nanoelectronics is the formation of various interconnects and direct contacts, e.g. graphene–metal, which is an actual technological task for novel electronic nanodevices. It is known that graphene–metal interconnects are characterized by the increased concentration of morphological defects (dangling bonds, spatial disordering). It is necessary to investigate and evaluate the influence of contact architecture and the density of graphene defects on the specific resistance of graphene–metal contacts to forecast electrical properties of prospective nanodevices [46].

Graphene is one of the most promising materials in nanotechnology. The electronic and mechanical properties of graphene samples with high perfection of the atomic lattice are outstanding, but structural defects, which may appear during growth or processing, deteriorate the performance of graphene-based devices. However, deviations from perfection can be useful in some applications, as they make it possible to tailor the local properties of graphene and to achieve new functionalities. In this article, the present knowledge about point and line defects in graphene is reviewed. Particular emphasis is put on the unique ability of graphene to reconstruct its lattice around intrinsic defects, leading to interesting effects and potential applications. Extrinsic defects such as foreign atoms which are of equally high importance for designing graphene-based devices with dedicated properties should be analysed. A short review of typical defects of graphene in connection with technological details is presented in Table 7.3.

Table 7.3 Graphene defects types

Defect type	Defect description
Point defects. Single vacancies. Stone–Wales defect	One of the unique properties of the graphene lattice is its ability to reconstruct by forming non-hexagonal rings. The simplest example is the Stone–Wales (SW) defect, which does not involve any removed or added atoms. Four hexagons are transformed into two pentagons and two heptagons by rotating one of the C–C bonds by 90° [48]
Single vacancies	The simplest defect in any material is the missing lattice atom. Single vacancies (SV) in graphene (or in the outermost layer of graphite) have been experimentally observed by TEM and STM [49]
Multiple vacancies	Double vacancies (DV) can be created either by the coalescence of two SVs or by removing two neighbouring atoms. No dangling bond is presented in a fully reconstructed DV so that two pentagons and one octagon appear instead of four hexagons in perfect graphene. The atomic network remains coherent with minor perturbations in the bond lengths around the defect [50]
Carbon adatoms	Interstitial atoms, as they appear in 3D crystals, do not exist in graphene. This is because placing an atom to any in-plane position, for example, in the centre of a hexagon, would require a prohibitively high energy. Rather than straining the local structure in two dimensions, additional atoms use the third dimension. The energetically favoured position is the bridge configuration [51]
Foreign adatoms	The effect of a foreign (noncarbon) atom on the properties of graphene depends on the bonding between the atom and graphene [52]. If the bond is weak, only physisorption due to van der Waals interaction occurs. If the interaction is stronger, covalent bonding between the foreign atom and the nearest carbon atoms leads to chemisorption
Substitution impurities	Foreign atoms can also be incorporated into graphene as substitutional impurities. In this case, the impurity atom replaces one or two carbon atoms. Boron or nitrogen serve as the natural dopants in carbon structures since they have one electron less or more, respectively, but roughly the same atomic radius. [47, 53]
Topology of defective graphene	It has been known (from the 1980s) that non-hexagonal rings induce local Gaussian curvature in a graphene sheet. In defective graphene, the arrangement of defects determines the local deviation from planarity. Defect domains might be created to induce hillocks or trenches in graphene[54]
1D Defects. Dislocation-like defects	1D defects have been observed in several experimental studies of graphene [55]. Such defects can be thought of as a line of reconstructed point defects with or without dangling bonds [55]
Defects at the edges of a graphene layer	Each graphene layer is terminated by edges with the edge atom being either free or passivated with hydrogen atoms.

(continued)

Table 7.3 (continued)

Defect type	Defect description
	The simplest edge structures are the armchair and the zigzag orientation [56]
Defects in bilayer graphene	Bilayer graphene consists of two stacked monolayers which may or may not be shifted with respect to each other. Similar to graphite, the interlayer distance in bilayer graphene is approximately 3.35 Å, as dictated by the weak van der Waals interaction between the layers. [57].
Electronic structure of graphene in the presence of defects	The electronic structure of graphene with point and line defects was studied in a considerable number of papers [58, 59]

7.6 Simulation of Magnetically Stimulated CVD CNT Growth

CNTs of various chiralities open new wide possibilities for modern nanoelectronics as promising candidates for nanointerconnects in high-speed electronic nanosensing and nanomemory devices [60–66]. We focus our current study on the implementation of advanced simulation models for a proper description of the fundamental electromagnetic properties (electrical resistance, capacitances and impedances) in contacts between carbon nanotubes of different morphologies and metallic substrates of different nature. We also present the model of magnetically stimulated CNT growth for a special case of Fe–Pt metallic nanoparticles, which have unique magnetic properties. We expect that in the presence of magnetic field, the CNTs growth will be more determined from the point of view of possible CNTs morphologies. Moreover, the creation of a CNT forest based on Pt–Fe nanoparticles provides the possibilities to consider this kind of structure as the basic fragment of nanomemory devices, where information bits are located in nanoparticles and the CNT forest provides the necessary spin transport for reading and recording information.

Thus, in our simulations, we expect to reproduce not only a CNT forest with the predefined morphology but also to develop a prototype of a nanomemory device. The adequate description of CNT chirality [61] is one of the key points for a proper simulation on electric properties of CNT-based nanoelectronic devices. Further development of the cluster approach allowed us to formulate the ‘effective bonds’ model [64] and to carry out a cycle of simulations on electromagnetic properties in various CNT- and graphene (GNRs – graphene nanoribbons)-based metal interconnects (Me = Fe, Cu, Ag, Pt, Au, Pd, Ni) [62, 67]. We consider that this model serves as a tool for understanding the process of CNT growth adequate to the CVD process.

7.6.1 Research Motivation

The main goal of the current research is to understand if there is a relationship between the use of magnetic catalysts and the CVD growth of CNTs, taking into account that most commonly used materials for the growth of CNTs are just Fe, Co and Ni nanoparticles. The nanoparticles of these catalysts are magnetically isotropic. The key question arises: What would happen if one used, instead of Fe, Co and Ni nanoparticles, magnetically anisotropic nanoparticles such as those in the alloy Fe–Pt? The anisotropy of Fe–Pt alloy is due to a spin-orbit coupling of Fe and Pt orbitals. This coupling takes place only if the alloy is formed of alternating planes of Fe and Pt. This particular structure is called L10. In this way, because of the different sizes of the atoms of Fe and Pt, the structure is crushed, and atoms of Fe and Pt are close forming a centred tetragonal phase (*fcc*). This approach allows for the coupling and then the magnetic anisotropy with the magnetization axis perpendicular to such planes. It is essential in this case to find conditions to control the growing CNT chirality. We also should take into account a possible substitutional disorder of $\text{Fe}_x\text{Pt}_{1-x}$ alloy, when the stoichiometry number ‘x’ becomes an additional parameter of CNT growth. No doubt, the diameter of the grown CNTs is also an essential parameter, which is evidently predefined by the created nanoparticle diameter. But again, we should discuss some limitations in the creation of Fe–Pt nanoparticle sizes in connection with the Fe–Pt melting point. However, Fe–Pt nanoparticles demonstrate an extremely strong coercing field, and this promises definite hopes for the controlled CNT growth in the CVD process. We also consider the CVD process of CNT growth as a more predictable one from the point of view of the expected growing CNT parameters (diameter, chirality, morphology of SW or MWCNTs).

Our experience with the nanotubes synthesis by means of the arc discharge brought about large doubts in the possibilities of CNTs growth control. Two cathodes of pure graphite (99.7%) were taken $\varphi = 6$ mm (cathode) and $\varphi = 10$ mm (anode) in diameter. Carbon black was added to iron–platinum powder, and after which the mixture was introduced to complete the filling of the hole. At this point the whole mass was placed in the room. The synthesis was carried out according to the parameters presented here: current 90 A, voltage $\sim 18 \div 20$ V DC, vacuum $\sim 2 \times 10^{-4}$ mbar, gas: He, work pressure 600 mbar and arc duration ~ 15 min.

Some filaments also exit from the outer wall of the cathode but in smaller quantities than found on the anode. The residue of the deposit formed on the upper part of the synthesis chamber was collected. It appeared to be quite little compared to other discharges with other catalysts (Figs. 7.14 and 7.15).

Figure 7.15 shows that filaments are of different nature – some formats are created from these spheres, and others have very fine structures of a few nanometers, probably single-walled nanotubes, covered by these spheres, partly or totally. The question is *what percentage of nanoparticles was originally made or how much*

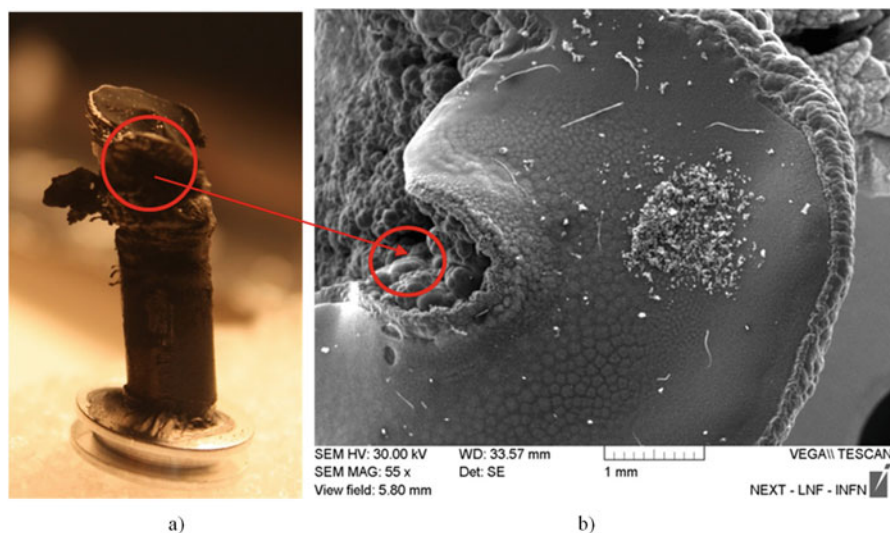


Fig. 7.14 (a) Photo of the cathode filaments exiting out after the synthesis, (b) SEM photo of the cathode surface

iron and platinum and how this underwent a change, during the arc discharge process?

We also take into account the extremely marginal parameters of the Fe–Pt system: Pt has the melting point at $T = 2041.4 \text{ K}$ ($1768.2 \text{ }^{\circ}\text{C}$) and the boiling point at $T = 4098 \text{ K}$ ($3825 \text{ }^{\circ}\text{C}$).

There are four major crystal structure modifications for Fe: below $769 \text{ }^{\circ}\text{C}$ (Curie temperature), it is $\alpha\text{-Fe}$ (α -ferrite) with a body-centred cubic crystal structure and ferromagnetic properties. Ferrite above the critical temperature ($769\text{--}917 \text{ }^{\circ}\text{C}$) is beta-ferrite ($\beta\text{-Fe}$) where it is paramagnetic rather than ferromagnetic, and it is crystallographically identical to $\alpha\text{-Fe}$. Within the interval of $917\text{--}1394 \text{ }^{\circ}\text{C}$, it is $\gamma\text{-Fe}$ (austenite) with acicular cubic crystal structure. At temperatures between $1394 \text{ }^{\circ}\text{C}$ and $1538 \text{ }^{\circ}\text{C}$, the body-centred cubic crystal structure is a more stable form of delta-ferrite ($\delta\text{-Fe}$), the melting point $1538 \text{ }^{\circ}\text{C}$ (1811 K) and the boiling point at $T = 3273 \text{ K}$ ($3000 \text{ }^{\circ}\text{C}$).

Our earlier research proved that close to the arc, the temperature ranges between 4000 and 6000 K and there is a subsequent rapid temperature gradient decrease with the distance from it. Filaments are found nearby the arc itself, more precisely, upstream of it. Taking into account the essentially nonsteady character of the arc discharge process and very high working temperatures, the CNT growth control is practically impossible, and CNT morphologies are nonpredictable.

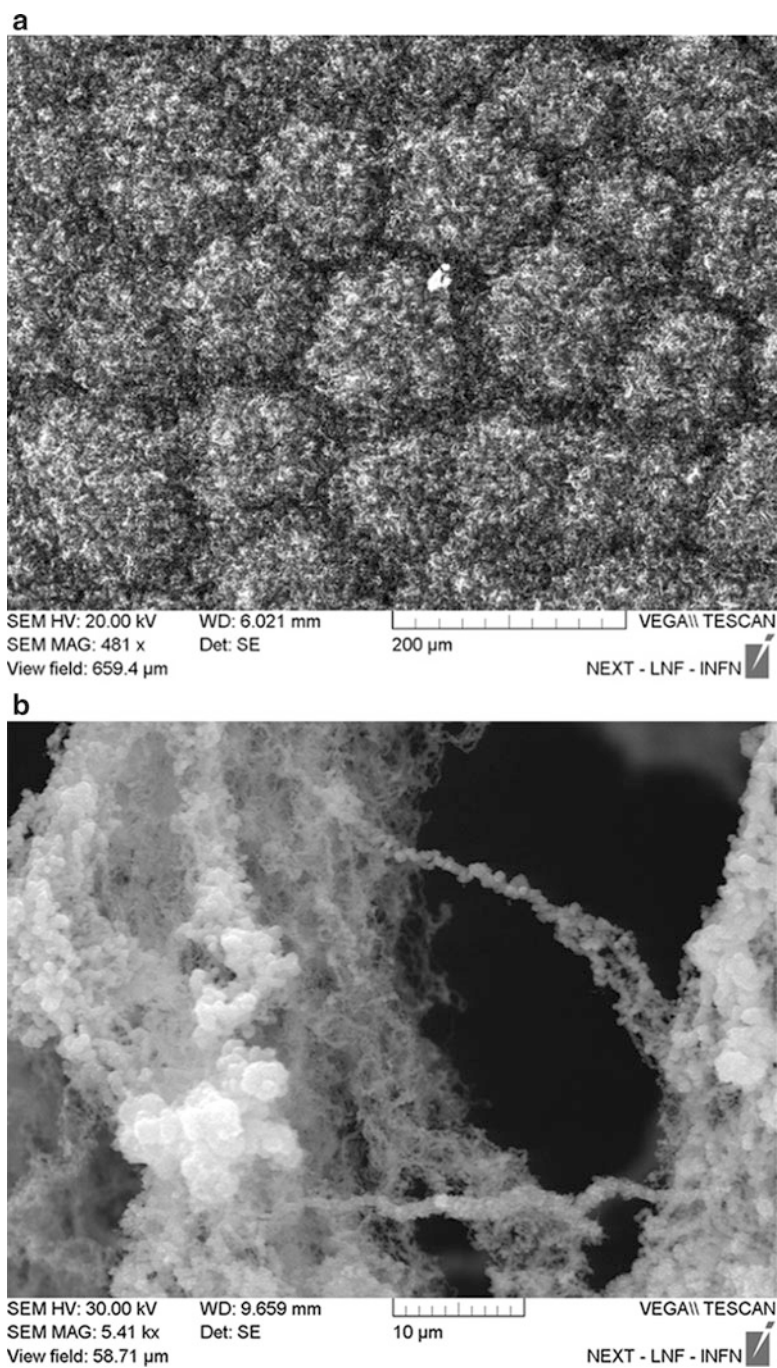


Fig. 7.15 Evolution view of filaments in the arc discharge process (Bellucci–Capobianchi): (a–c) [68–71]

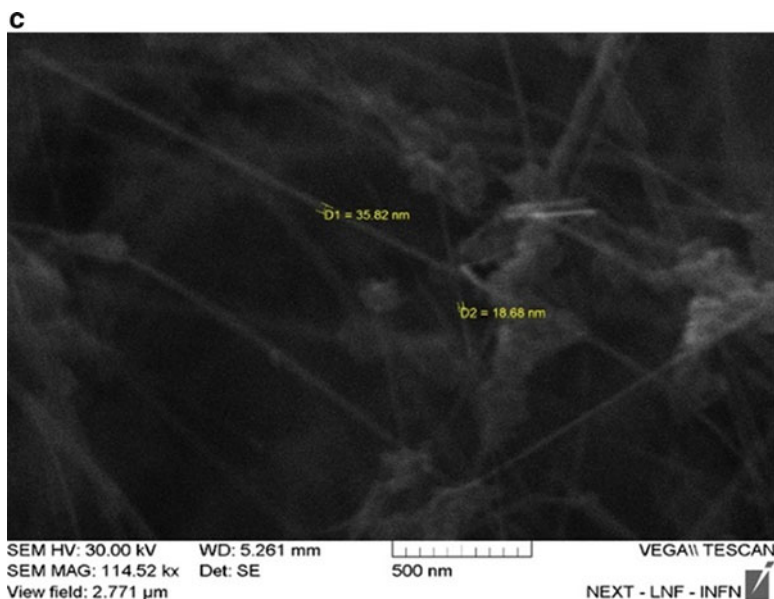


Fig. 7.15 (continued)

7.6.2 *CNT Growth in the Chemical Vapour Deposition Process Based on Metal Nanoparticles*

The CVD (chemical vapour deposition) is a highly versatile approach to producing nanotubes and is, perhaps, the most commonly published technique for nanotube growth often used to synthesize CNTs for commercial applications. The process involves decomposition of a carbonaceous precursor at high temperatures under oxygen-free conditions and reduced atmosphere to produce nanotubes.

CVD process begins with previously made supported catalyst material placed in a furnace. A flow of gaseous carbon precursor is introduced for a given time period follows the heating of the furnace till the appropriate reaction temperature. Heating periods can reach several hours. The reaction product is collected from the reactor walls and support surfaces after cooling. There are various experimental conditions for CVD realization in SWCNTs production procedure. Catalyst and carbon precursors, flow rates, reaction temperatures and batch run times together with support materials are presented when available. There are two growth mechanisms in the CVD process: root (base) and tip growth. In root growth, the catalyst particle stays pinned at the support surface and the support – particle interaction must be taken into consideration. In the tip growth, the catalyst is lifted off from the support surface during CNT growth due to weak support – catalyst interaction. Evaporation of the catalyst metal may take place during CVD synthesis due to the physical

properties of nanosized catalyst particles (nanodrops). The vapourized metal may nucleate and form secondary metal particles away from the surface. The catalytic decomposition reaction may then take place in the gas phase on the surface of the newly formed particles. This product is eventually deposited on the reactor walls.

7.6.3 CVD Process Analysis

The chemical vapour deposition (CVD) process involves decomposition of a carbonaceous precursor at high temperatures. The carbonaceous precursor may be a carbon gas, methane or ethylene, for instance, or it can be in the form of a volatile hydrocarbon solvent such as ethanol, which is generally fed into the reactor with some inert carrier gas. In the reaction chamber, the precursor is decomposed in the presence of a catalyst – usually a transition metal such as iron, cobalt or some similar combination of metals. The catalyst can be introduced in a number of different ways.

The substrate needs to have catalyst nanoparticles providing the growth of CNTs where nanoparticles present the place from which nanotubes start growing. Nanoparticles can be composed of lots of different substances (usually, a metal like Fe, Co, Ni, Mo, Mn, Pd, etc.) [72].

The substrate is then heated to the temperature of about 700–800 °C under H₂. As the nanoparticles heat up, the hydrogen pulls oxygen out from the nanoparticles, leaving behind metallic nanoparticles.

At the target temperature, a carbon-containing gas such as ethylene (or some others, e.g. alcohol vapour) is introduced. At these temperatures, the gas partly decomposes, giving carbon-containing fragments and other molecules. These fragments and molecules then work their way onto the catalyst nanoparticles, where they stick and then break down into carbon. The carbon dissolves with some probability into or on the nanoparticle. When a critical concentration of carbon is reached in the nanoparticle, the addition of just a little bit more carbon from the vapour causes carbon to precipitate as a crystal.

When carbon crystallizes under the atmospheric pressure (like in CVD), it crystallizes into flat sheets of hexagonally patterned carbon. But because the nanoparticle is so small and has such a high curvature, when the carbon crystallizes out, it is constrained into a cylindrical shape in the form of a carbon nanotube.

Additional carbon atoms on the nanoparticle provide further nanotube growth, which stops when the carbon-containing gas is turned off if the substrates cool down or for a number of other reasons that can influence the nanotube or catalyst nanoparticles.

Tuning the appropriate parameters, it is possible to obtain a huge amount of CNTs in a cheap and quick way. Also it is the technique enabling the growth of CNTs with specific characteristics: particular diameter, length and orientation (alignment) and family (multi- or single wall).

Table 7.4 Most commonly used catalyst metals for the CVD method [73, 75]

Catalyst			Temperature (°C)	Carbon source
Metal	Catalyst type	Preparation method		
Fe	Ultrafine particle	Decomposition of metallocene	1,060	Benzene
	Silica support	Pore impregnation	700	Acetylene
	Zeolite or clay support	Ion exchange	700	Acetylene
	Graphite support	Impregnation	700	Acetylene
	Ultrafine particle	Decomposition metal of carbonyl	800	Acetylene
	Silica support	Sol-gel process	700	Acetylene
Co	Ultrafine particle	Laser etching of Co thin film	1,000	Triazine
	Ultrafine particle	Decomposition metal of carbonyl	800	Acetylene
	Silica support	Pore impregnation	700	Acetylene
	Zeolite or clay support	Ion exchange	700	Acetylene
	Graphite support	Impregnation	700	Acetylene
Ni	Graphite support	Impregnation	700	Acetylene
	Ultrafine particle	Decomposition of Ni (C ₈ H ₁₂) ₂	800	Acetylene
Mo	Ultrafine particle	Decomposition of Mo* ^a	800	Acetylene
Mn	Ultrafine particle	Decomposition metal of carbonyl	800	Acetylene
Pd	Ultrafine particle	Decomposition metal of carbonyl	800	Acetylene

^aMo* = (NH₄)₂₅ ± 5[Mo₁₅₄(NO)₁₄O₄₂₀(OH)₂₈(H₂O)₇₀] 350H₂O

It has been well known for a long time that carbon nanotubes are synthesized by catalytic decomposition of hydrocarbon [73] in the reactor, where metal nanoparticles are presented as a catalyst on a substrate. Catalyst metals mostly used for these purposes are listed in the following Table 7.4. Hydrocarbon such as methane adsorbed on the catalytic particle surface releases carbon during decomposition, which dissolves and diffuses into a metal particle. When a supersaturated state is reached, carbon precipitates in a crystalline tubular form.

It is necessary to emphasize that it will be possible to grow CNTs using a gas, both as a catalyst and as hydrocarbon. If a stream of catalyst particles can be injected into the flowing feedstock, it is possible to produce nanotubes in the gas phase. This approach is amenable for scale-up to large-scale production. Sen et al. [74] first reported such a possibility when they used ferrocene or nickelocene as a source of the transition metal and benzene as a carbon source.

This approach yielded MWNTs, whereas their later work [76] with gas-phase pyrolysis of acetylene using a metallocene yielded SWNTs with diameters around 1 nm [75]. CVD-produced CNTs are curved and have high amount of defects,

mainly after the purification in the acid bath; it is needed to remove metal nanoparticles inside of tubes.

The main interests related to iron-containing nanoparticles are focused on their potential applications as high-quality magnetic materials. Thus, a new generation of iron–metal nanoparticles is studied to be used as a catalyst in growing CNTs, with a magnetic nanomaterial inside, making it possible to design a precise carbon nanomagnetic device for drug delivery diagnostics.

For example, iron nanoparticles have been widely used as a catalyst for CVD synthesis of multiwalled carbon nanotubes, [77] while iron–molybdenum can act as a very efficient catalyst for the synthesis of either single-walled or multiwalled carbon nanotubes with the CVD method [78–83].

To prevent the magnetic behaviour of these iron nanocompounds, it is necessary to grow carbon nanotubes of nanocompounds below the Curie temperature. Typically, the growth temperature is around 600–700 °C at the atmospheric pressure [84].

The potential applications of carbon nanotubes grown for semiconductor and sensor devices are presented for CMOS industrial applications [85]. The low-temperature growth of vertically aligned carbon nanotubes (CNTs) at high growth rates by a photothermal chemical vapour deposition (PTCVD) technique using a Ti/Fe bilayer film as a catalyst is presented in [86]. The bulk growth temperature of the substrate is as low as 370 °C, and the growth rate is up to 1.3 μmin^{-1} , at least eight times faster than the values reported by traditional thermal CVD methods. It should be recognized that the mechanism of CNTs growth is not obvious enough. Technological growth characteristics may differ in detail, although the concept remains the same. The mechanism of carbon atom deposition on metal catalyst nanoparticles with the subsequent nucleation of CNTs can be considered one of the most effective and practically important. Crystal (e.g. Si) nanoparticles with a set diameter created on a substrate give a high probability of producing CNTs with the regulated diameter. However, the problem of controlling the chirality of CNTs remains a pressing one. Among more effective catalysts, it is possible to distinguish Pt, Pd, Cu, Ag, Au, Si, SiC, Ge and Al_2O_3 [87] in addition to the earlier investigated Mg, Ti, Cr, Mn, Fe, Co, Ni, Sn and Pb [88–90](see also Table 7.5).

7.6.4 Advantages of CVD

Compared to the discharge and laser ablation methods, CVD is a simple and economic technique for synthesizing CNTs at low temperatures and ambient pressures. Arc- and laser-grown CNTs are superior to the CVD-grown ones. In yield and purity, CVD has advantages over the arc and laser methods. Considering CNTs in relation to structure or architecture control, CVD is the only answer. CVD is versatile in the sense that it offers harnessing plenty of hydrocarbons in any state (solid, liquid or gas), enables the use of various substrates and allows CNT growth

Table 7.5 Comparison of catalysts for SWCNTs growth [88–90]

Type	State	SWCNT size for growth (nm)	Catalysis for cracking	Carbon solubility	Growth temperature for ethanol (°C)	Growth rate
Fe, Co, Ni	Liquid/solid	<10	Yes	High	600–950	High
Pt, Pd	Liquid/solid	<5	No?	High	850–950	High
Au, Ag, Cu	Liquid/solid	<5	No	Low	850–950	High
Ge	Liquid/solid	<5	No	Low?	850–950	Low?
Si, SiC	Solid	<5	No	No?	850–950	Low
Al ₂ O ₃	Solid	<5	No	No	850–950	Low

in a variety of forms, such as powder, thin or thick films, aligned or entangled, straight or coiled nanotubes or a desired architecture of nanotubes on predefined sites of a patterned substrate. It also offers better control over the growth parameters zone, while carbon crystallization (being an endothermic process) absorbs some heat from the metal precipitation zone. This precise thermal gradient inside the metal particle keeps the process going on. This last advantage is the most essential one [87]. Taking only two main CNT parameters, namely, CNT diameter and chirality, the problem cannot be solved well enough. There are two marginal cases of CVD growth.

Tip-growth model – the catalyst–substrate interaction is weak (metal has an acute contact angle with the substrate); hydrocarbon decomposes on the top surface of the metal; carbon diffuses down through the metal, and CNT precipitates out across the metal bottom, pushing the whole metal particle off the substrate; as long as the top of the metal is open for fresh hydrocarbon decomposition, CNT continues to grow longer and longer; the metal is fully covered with the excess carbon and its catalytic activity ceases and the CNT growth stops.

Base-growth model – the catalyst–substrate interaction is strong; initial hydrocarbon decomposition and carbon diffusion take place similar to that in the tip-growth case; the CNT precipitation fails to push the metal particle up, so the precipitation is compelled to emerge out of the metal apex; carbon crystallizes out as a hemispherical dome, which then extends up in the form of seamless graphitic cylinder; subsequent hydrocarbon deposition takes place on the lower peripheral surface of the metal, and a dissolved carbon diffuses upward; CNT grows up on the catalyst nanoparticle base.

7.6.5 CNT Precursors

Most commonly used CNT precursors are methane [91, 92], ethylene [76, 78] acetylene [93], benzene [78] xylene [94] and carbon monoxide [95].

SWCNTs were first produced from the disproportionation of carbon monoxide at 1200 °C, in the presence of molybdenum nanoparticles [22], and later they were produced from benzene [96], acetylene [76], ethylene [97], methane [98], cyclohexane [99] and fullerene [100] by using various catalysts. It means that the working temperature and pressure of the CVD process can be changed in a wide range of ways and the kinetics of carbon atoms deposition can also be widely varied.

In 2002 the low-temperature synthesis of high-purity SWCNTs from alcohol on Fe–Co-impregnated zeolite support was carried out [101], and since then, ethanol has become the most popular CNT precursor in the CVD method worldwide [102–104].

A special interest in binary catalysts becomes principal now. The unique feature of ethanol is explained by the fact that ethanol-grown CNTs are almost free from amorphous carbon, owing to the etching effect of OH radical [105]. Later, vertically aligned SWCNTs were also grown on Mo–Co-coated quartz and silicon substrates [106, 107]. It has been shown that intermittent supply of acetylene in ethanol CVD significantly assists ethanol in preserving the catalyst activity, thus, enhancing the CNT growth rate [108].

Generally, low-temperature CVD (600–900 °C) yields MWCNTs, whereas high-temperature (900–1200 °C) reaction favours SWCNT growth. It means that SWCNTs have a higher energy of formation (presumably owing to small diameters and the fact that high curvature bears high strain energy). Probably, this is the reason that MWCNTs are easier to grow than SWCNTs.

Recent developments in the nanomaterials synthesis and characterization have enabled many new catalysts for the CNTs growth. Apart from popularly used transition metals (Fe, Co, Ni), a range of other metals (Cu, Pt, Pd, Mn, Mo, Cr, Sn, Au, Mg, Al) have also been successfully used for horizontally aligned SWCNT growth on quartz substrates [109]. It has been also proposed that the active catalyst is Au–Si alloy with about 80 at% Au [110].

7.6.6 CNT Growth Control

It is a general experience that the catalyst particle size dictates the tube diameter. The particle size dependence and a model for iron-catalysed growth of CNTs have been reported in [111]. Metal nanoparticles of the controlled size, pre-synthesized by other reliable techniques, can be used to grow CNTs of the controlled diameter [112].

Influence of a catalyst material and concentration. The additional advantage of using the bimetallic catalyst is that CNTs can be grown at a much lower

temperature -550°C . For example, the melting point of the mixture of Fe and Co is lower than their individual melting points. Moreover, alloys are known to be better catalysts than pure metals. These trends suggest that tri-metallic catalysts should also give interesting results, though the interpretation of the results would be more complicated.

Influence of temperature. There are investigations of the temperature effect on camphor CVD in a wide range of temperatures $500\text{--}1000^{\circ}\text{C}$ [113]. It was noticed that camphor did not decompose below 500°C . At 550°C very short-length tubes emerged from the zeolite pores suggesting that the catalyst activity, and hence the CNT growth rate, was quite low at 550°C . However, the CNT growth abruptly increased at 600°C , and a profound growth was observed all around the zeolite pores. At 650°C and above, the growth rate was so enormous that hardly a zeolite particle could be located amid nanotubes. The CNT diameter is increased with the growth temperature increase. Very pure CNTs, almost free from metallic impurity, were produced up to 750°C . From 750°C onward, both the diameter and the diameter distribution range increased drastically. It is supposed that at high temperature, the metal atoms agglomerate into bigger clusters leading to thick CNTs. At 850°C and above, SWCNTs began to take shape alongside with MWCNTs, and the volume of SWCNTs increased with the increasing temperature. For instance, at 900°C , samples of large bundles of SWNTs can be observed. The CVD temperature plays the central role in CNT growth. For a fixed metal concentration, the increasing CVD temperature enlarges the diameter distribution. It should also be noted that MWCNTs and SWCNTs can be selectively grown as a function of CVD temperature if the catalyst concentration is properly optimized [113, 114].

Influence of pressure. For the controlled growth of CNTs by CVD, the vapour pressure of the hydrocarbon in the reaction zone is another very important parameter. For gaseous hydrocarbons, a desired vapour pressure in the CVD reactor can be maintained by a limited gas flow rate and the controlled suction with a rotary pump [115]. In the case of a liquid hydrocarbon, its vapour pressure is controlled by its heating temperature before it enters the reactor [116]. However, for a solid hydrocarbon such as camphor, it is quite problematic to control its vapour pressure. It becomes a function of three parameters: camphor mass, its vapourization temperature and the flow rate of argon – the carrier gas. By proper optimization of these three parameters, the influx of camphor vapour to the zeolite bed and its decomposition rate were balanced to a great extent, and a record growth of MWCNTs was achieved at atmospheric pressure by CVD. Pure SWCNTs (free from MWCNTs) have been selectively obtained from camphor CVD at low pressures ($10\text{--}40$ Torr) where the camphor vapour pressure is quite in tune with the low metal concentration [117]. It is important to note that the melting point of nanoparticles below 10 nm falls abruptly, e.g. 5 nm Fe and Co particles can melt at about 850°C and 640°C , respectively. It leads to essential limitations in the CVD process of small diameter ($< 5\text{ nm}$) CNTs growth.

Schematic representation of the basic steps of SWCNT growth on a metal catalyst is usually simulated in three steps [118]:

1. The diffusion of single C atoms on the surface of a catalyst.
2. The formation of an sp^2 graphene sheet floating on the catalyst surface with edge atoms covalently bonded to the metal.
3. The root incorporation of diffusing single C atoms. It has been shown that carbon atoms diffuse only on the outer surface of the metal cluster. At first, a graphene cap is formed which floats over the metal, while the border atoms of the cap remain anchored to the metal. Subsequently, more C atoms join the border atoms pushing the cap up and, thus, constituting a cylindrical wall.

7.6.7 Magnetically Stimulated CNT CVD Growth on Fe–Pt Catalysts

The key question for a CVD process of CNTs growth is the formation of initial interconnects between substrates (catalyst nanodrops). This step predefines the future morphology of the created CNTs. Computer simulation of CNT–metal interconnects is an effective way in formulation of technological recommendations. Our systemic theoretical approach in a wide scale simulations and modelling is based on multiple scattering theory and effective media approximation [119]. This is a reasonable and constructive way to solve a set of marginal condensed media problems in cases of essential structural disordering.

7.6.8 Effective Bonds Model for CNT–Fe–Pt Interconnect Electromagnetic Properties

CNT–Fe–Pt interconnect atomistic structures are in compliance with the proposed ‘effective bonds’ model. The ‘effective bonds’ are responsible for mechanical, electronic, magnetic and electrical properties of interconnects. The common consideration of two marginal carbon structures (CNTs and GNRs) is induced by the similar technological problems in respect of these materials for the modern nanoelectronics [120].

We have developed structural models for CNT–Me and GNR–Me junctions, based on their precise atomistic structures of clusters, which take into account the CNT chirality effect and its influence on the interconnect resistance for Me (= Fe, Ni, Cu, Ag, Pd, Pt, Au) as well as the predefined CNT (or GNR) geometry. These atomistic structures are in compliance with the proposed ‘effective bonds’ model.

Our main interest in this particular case is focused entirely on CNT–Me interconnects, when the modelling of CNT growth on metal surfaces is combined with the controlled electromagnetic properties in the interconnect area. To ensure a predictable interconnect morphology, the permanent magnetic field is used that accompanies the growth, and magnetic drops are used as growth catalysts that provide for the special composition of Fe–Pt with unique magnetic properties. The

results of our simulations show that interconnects resistance and the number of effective bonds can be considered as indicators of chirality. Figures 7.16, 7.17, 7.18, 7.19 and 7.20 demonstrate the numbers of effective bonds via CNT diameters, chirality angles and CNT–Me interconnect resistances and impedances. It means that resistances and the number of effective bonds in the interconnect space are indicators of CNTs morphology.

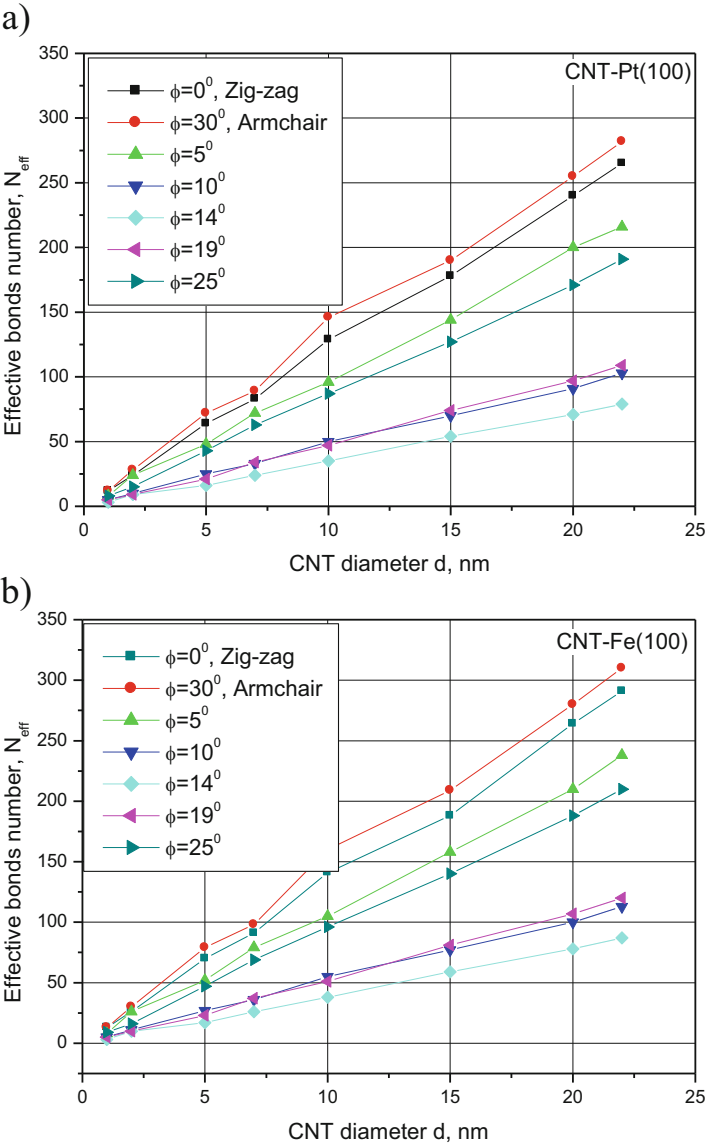


Fig. 7.16 Effective bonds number via CNT diameter: (a) CNT–Pt and (b) CNT–Fe

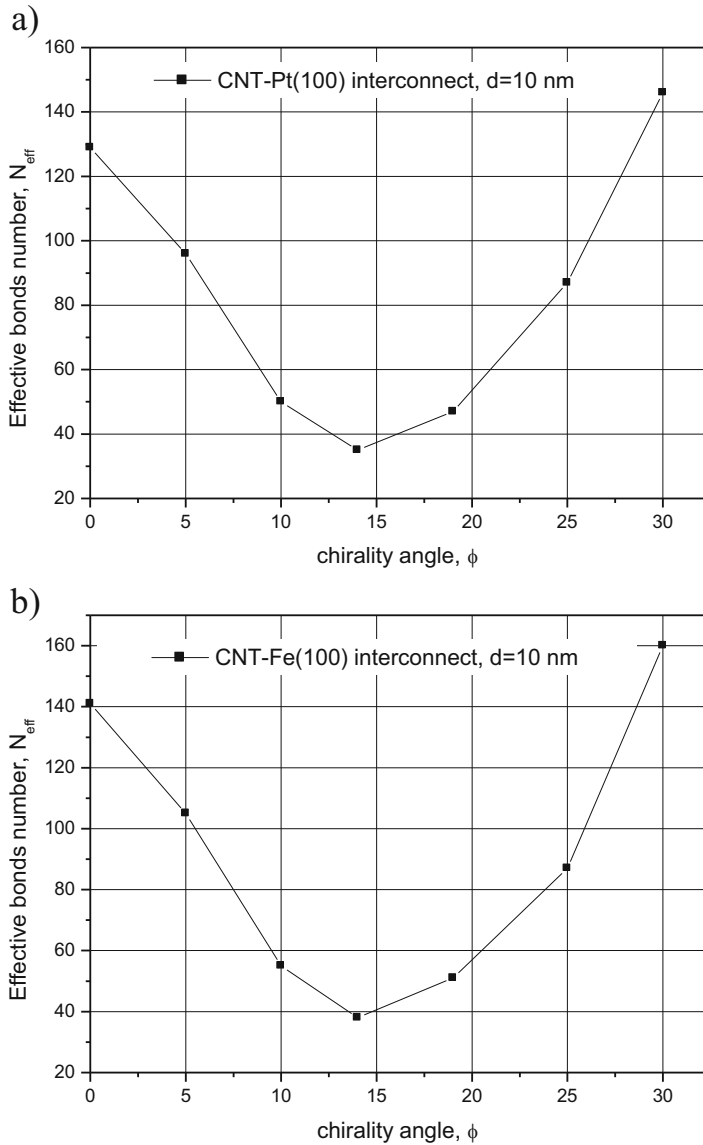


Fig. 7.17 Effective bonds number via CNT chirality for the diameter $d = 10$ nm: (a) CNT-Pt and (b) CNT-Fe

7.6.9 CNT- $\text{Fe}_x\text{Pt}_{1-x}$ Interconnect Formation

There is a relation between the use of magnetic catalysts and the CVD growth of CNTs determining the most commonly used materials for the CNT growth – Fe, Co and Ni. The nanoparticles of the latter catalysts are magnetically isotropic. Magnetism of the particles of catalysts brings order into the process of CVD growth.

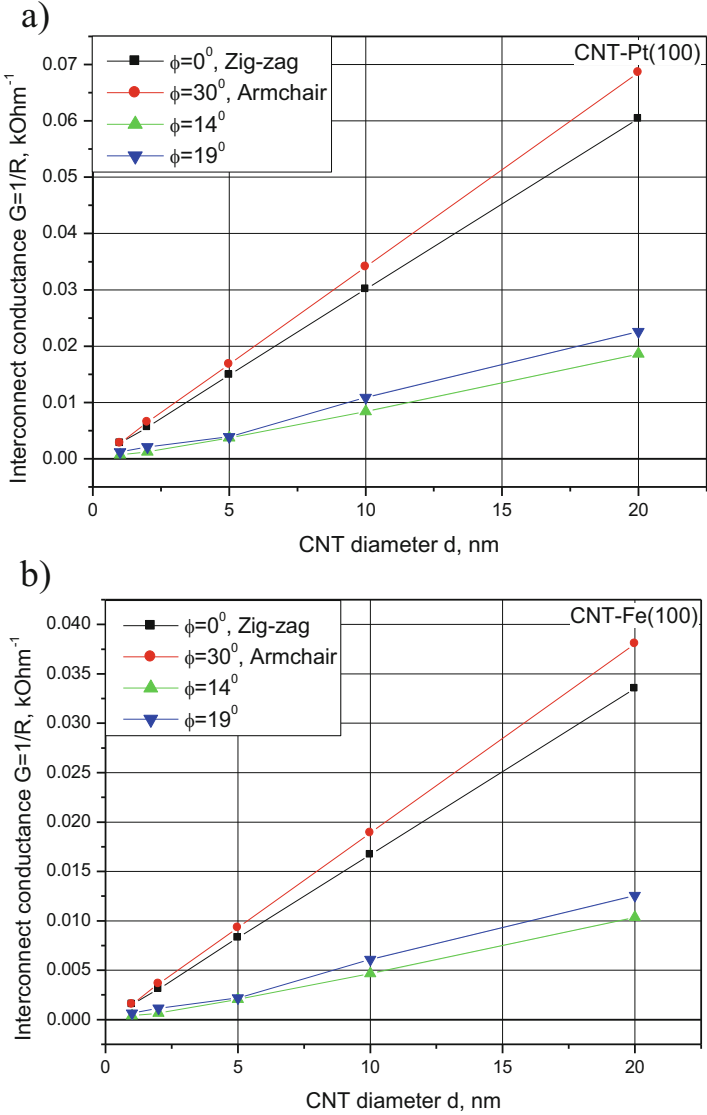


Fig. 7.18 Interconnect conductance via CNT diameter: (a) CNT–Pt and (b) CNT–Fe

Actual class of Fe–Pt nanodrops as possible catalysts in a CVD process has the diameter ranging from 5 to 30 nm. The stable and predictable creation of definite sizes of nanodrops is a basis for the output growth of CNTs with the expected morphology. Their magnetic properties are essentially changed in dependence on their size. Magnetization orientation of nanodrops in a Fe–Pt system is regulated in competition of the heat factor and collective magnetization of the nanodrop

Fig. 7.19 Resistances of zigzag SWCNT–metal interconnects in comparison

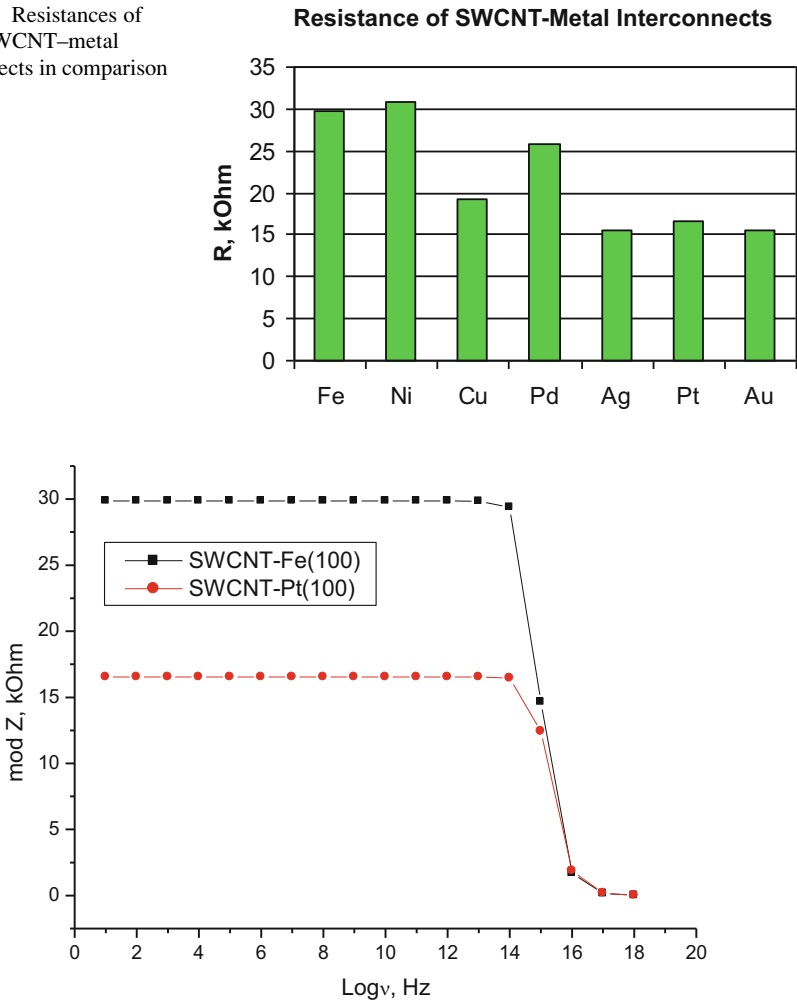


Fig. 7.20 Impedances of SWCNT–Fe and Pt interconnects in comparison

ferromagnetic state. Magnetization of nanodrops becomes non-stable for small sizes. This also means additional technological complications in magnetically controlled CMTs CVD growth. Fe–Pt nanoparticles containing a near-equal atomic percentage of Fe and Pt are an important class of magnetic nanomaterials. They are known to have a chemically disordered face-centred cubic (*fcc*) structure or a chemically ordered face-centred tetragonal (*ftt*) structure.

Additional possibilities in controlling the process of CVD growth open up the ways to use magnetically anisotropic nanoparticles such as those in the alloys with a different substitutional disorder (e.g. $\text{Fe}_x\text{Pt}_{1-x}$), to manage the CVD process with the formation of the predefined CNT chiralities. Besides, the stimulation of the

process by means of the external magnetic field activates magnetic moments of the catalyst and the deposited carbon atoms. This also means that we can control the number of effective bonds inside interconnects. We pay a special attention to Pt and Fe substrates as possible elements for nanoelectronic and nanomagnetic devices considering interconnect fundamental properties and magnetically stimulated nanoproceses on Fe–Pt L_{10} nanoparticles [59–61, 121].

7.6.10 Magnetic Properties of Fe–Pt Alloys

The unique magnetic properties of Fe–Pt alloys are an open field for research to correlate different CNT techniques in terms of the catalyst role in entirely different range of temperatures and pressures. Carbon nanotubes grow using bimetallic nanoparticle Fe–Pt as a catalyst [122–125]. Since the mid-1930s, Fe–Pt alloys have been known to exhibit high coercivities due to high magnetocrystalline anisotropy of the L_{10} FePt phase, but their high cost prevented these alloys from widespread applications in the past. In Fe–Pt alloys, both Fe and Pt atoms carry a magnetic moment: the induced magnetic moment on the Pt sites and the enhanced magnetic moment on the Fe sites. A wide variety of the magnetic structure types in the Fe–Pt alloys is evidently the consequence of various atomic configurations around Fe atoms, which, in turn, has a considerable effect on the electronic structure of these alloys (see Fig. 7.21, Table 7.6 and eutectic phase diagram of Fe–Pt alloy (<http://www.himikatus.ru/art/phase-diagr1/Fe-Pt.php>)).

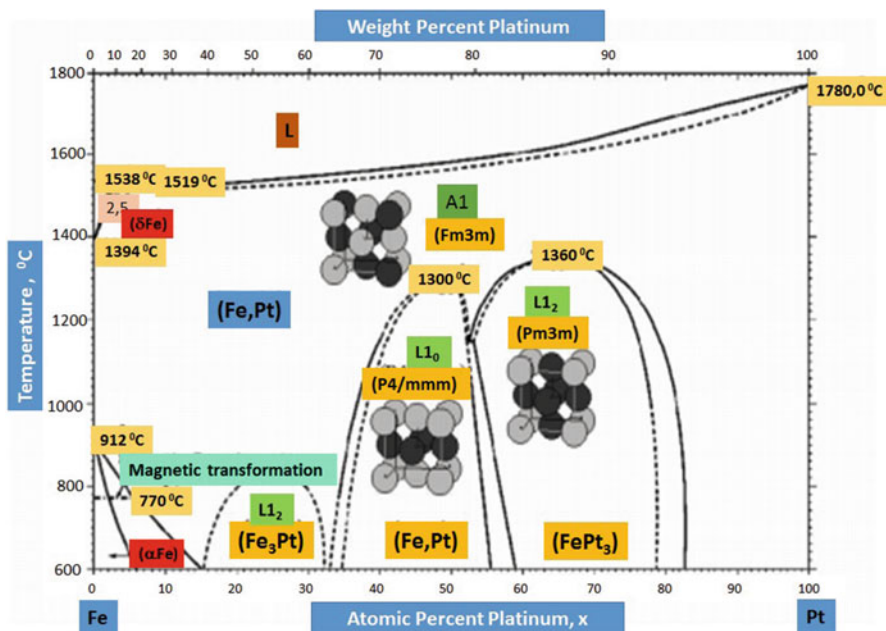
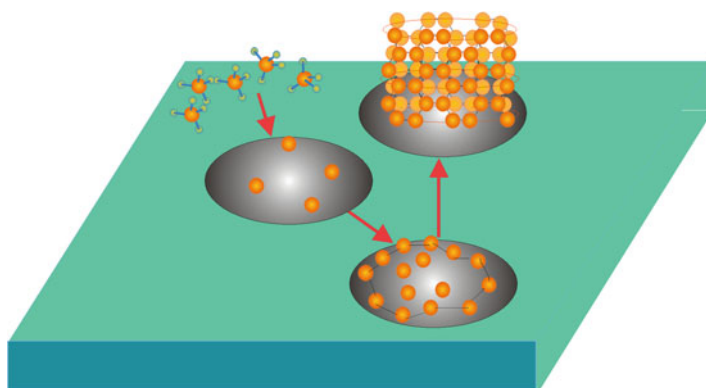


Fig. 7.21 Eutectic phase diagram of Fe–Pt alloy (<http://www.himikatus.ru/art/phase-diagr1/Fe-Pt.php>)

Table 7.6 Specific magnetic structures of Fe–Pt systems

Magnetic structure	Behaviour	Curie temperature (K)
$L1_2$ Fe ₃ Pt	<i>Ferromagnetic</i>	410
$L1_0$ FePt	<i>Ferromagnetic</i>	750
$L1_2$ FePt ₃	Paramagnetic	273

**Fig. 7.22** A fragment of the CNT CVD process growth on nanoparticle surfaces

To obtain the Fe–Pt alloy in $L1_0$ phase, we use a new chemical synthesis strategy reported in detail in our previous works [59–61, 121]. By planetary ball milling of nanocrystals of a particular precursor, $[\text{Fe}(\text{H}_2\text{O})_6]\text{PtCl}_6$ and NaCl were grounded and then annealed at 400 °C (300 °C – less than typically used temperature) in reductive atmosphere. After washing, we obtain FePt $L1_0$ NPs with selected size as a function of the fraction $[\text{Fe}(\text{H}_2\text{O})_6]\text{PtCl}_6$ and NaCl used. By varying the precursor ratio, we are able to avoid the coalescence phenomena and obtain single-crystal NPs with the size around 6 nm, not agglomerated.

7.6.11 Magnetically Stimulated CNT Growth

The formation of the initial optimal perimeter for carbon–metal (Fe–Pt) bonds is a synergetic process with a minimal free energy (see Fig. 7.22).

The nanoparticle diameter determines with a certain error the diameter of a CNT. The number of effective bonds defines the morphology of the future CNT (see Fig. 7.23, armchair, chiral, zigzag CNTs,) in terms of chirality. Obviously, there is a considerable uncertainty in the morphology of the future CNTs, owing to sporadic thermal dynamics of the deposited carbon atoms.

According to our model, the process can be considerably streamlined using even minor diamagnetic properties of carbon atoms at the expense of magnetic field and strong induced ferromagnetism of the nanoparticle. It becomes evident that the

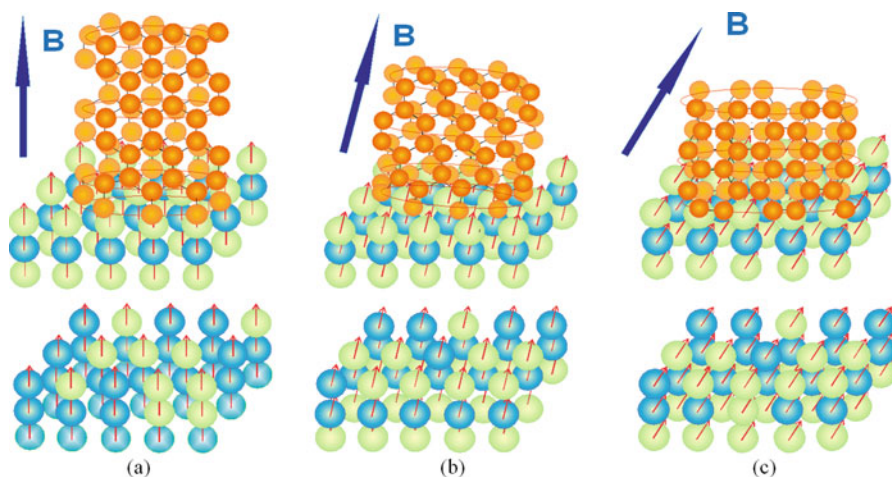


Fig. 7.23 Magnetically stimulated orientation of magnetic moments of atoms in model interconnects during the CNT controlled growth with the expected chiralities under the directed magnetic field B with the orientation angle $\phi = \Theta_B$: (a) armchair CNT, magnetic field B with the orientation angle Θ_B , where B is the magnetic induction and the chirality angle is $\phi = 0^\circ$; (b) chiral CNT $0 < \phi < 30^\circ$ and (c) zigzag CNT, $\phi = 30^\circ$

nanoparticle composition Fe–Pt and its atomic structure (including the short-range order) play a primary role in the process of CNT growth stimulated by the magnetic field of CVD.

Nucleation in the process of CNT growth in cases of the ordered Fe–Pt nanoparticles is more stable and has principal advantages in relation to the CNT controlled growth compared with the cases of any kind of anisotropic Fe–Pt nanocatalysts [126].

The availability of substitutional disorder and anisotropy in Fe–Pt nanodrops used for CNT CVD controlled growth is a negative factor for the production of CNTs with predictable morphologies. There are some essential negative features of disorder in Fe–Pt nanodrops for the CVD process:

1. C atoms chemical binding preferences (C–Fe bonds are stronger than C–Pt ones).
2. A higher structural anisotropy leads to higher relaxation times of a nanodrop structure [127].
3. Disorder effects in Fe–Pt lead to sporadic magnetization phenomena.

Thus, it is important to control the process of formation of nanodrop structures corresponding to $L1_0$ (Fe–Pt) and $L1_2$ (Fe_3Pt) systems with reliable magnetism and adequate cooling rates, when relaxation processes in nanodrops are accomplished.

As it has already been mentioned, Fe–Pt nanoparticles containing a near-equal atomic percentage of Fe and Pt are an important class of magnetic nanomaterials. They are known to have a chemically disordered face-centred cubic (*fcc*) structure or a chemically ordered face-centred tetragonal (*ftt*) structure.

7.6.12 *Model of CVD CNT Growth with the Probabilistically Predefined Morphology*

Magnetically stimulated CNT CVD model formulation looks as follows (see Figs. 7.22 and 7.23):

- Effective bonds are responsible for the future chirality of CNT in the CVD processes.
- The permanent magnetic field provides the alignment of CVD growth.
- The binding with the Fe–Pt nanoparticle has a probabilistic character; the probability of binding of C atoms with Fe atoms is preferable as compared to Pt atoms.
- The composition of Fe–Pt atoms in a nanoparticle and the atomic structure ordering are essential for chirality of the obtained CNTs.
- The diameter of the future CNT is correlated with the nanoparticle size.
- The direction of the magnetic field stabilizes the direction of CNT forest growth and is a tool of the growth control.
- The ordering of a nanoparticle atomic structure, as well as a substitutional disorder or arbitrary disorder of a nanoparticle, is responsible for the magnetic state of the nanoparticle, which is essential for the possible future nanomemory devices.

Even a very strong magnetic field is not able to suppress thermal fluctuations of magnetic moments in carbon atoms. It is a different thing when carbon diamagnetic atoms appear on the surface of a catalyst in the ferromagnetic condition where magnetism induced by the external field can be very strong and is able to correct the behaviour of carbon atoms by suppressing thermal fluctuations.

At the same time, the growth control over chiral and non-chiral nanotubes essentially depends on stoichiometric composition of Fe–Pt nanoparticles. The beginning of the nucleation process with the growth of nanotubes might be connected with stochastic fluctuations of the magnetic moment in a carbon atom relative to the direction of the local magnetic field in a nanoparticle. Distribution of the fluctuation angle obeys the Gaussian law (see Fig. 7.24):

$$f(\theta) = \frac{1}{\sigma\sqrt{2\pi}} \cdot \exp\left(-\frac{(\theta - \theta_B)^2}{2\sigma^2}\right), \quad (7.6)$$

where σ^2 is the angular dispersion of thermal fluctuations of the magnetic moment angle of a carbon atom. To evaluate this dispersion, the potential energy change of the magnetic moment under the influence of the thermal energy should be evaluated: $\mu_C B(1 - \cos \theta_T) \approx k_B T_{\text{CVD}}$, where μ_C is the induced magnetic moment of a carbon atom $\mu_C = 1.25\mu_B$ (see evaluations in [125], $\mu_B = 5.788 \cdot 10^{-5}$ eV/T, B is the magnetic induction of the catalyst surface, $\theta_T = \theta - \theta_B$, T_{CVD} is the operating temperature of the CVD process, $k_B = 8617\,3324(78) \cdot 10^{-5}$ eV/K is the Boltzmann constant. Hence, $2 \sin \frac{2\theta_T}{2} \approx \frac{k_B T_{\text{CVD}}}{\mu_C B}$. Taking into consideration one of the main

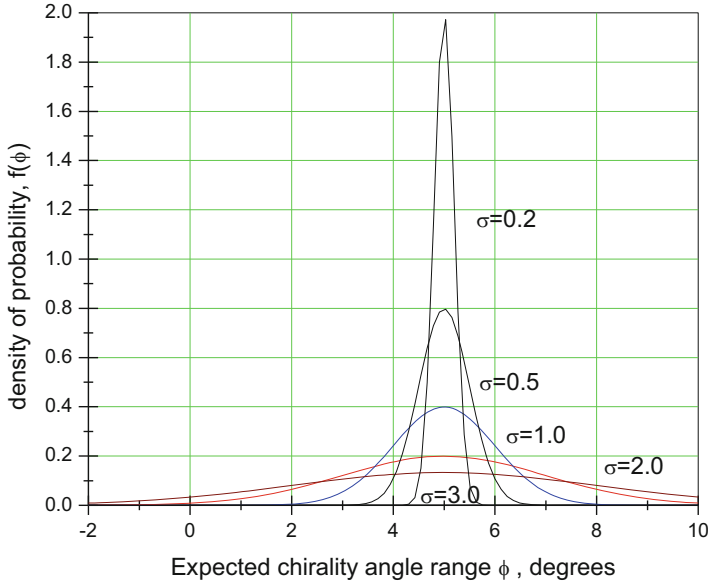


Fig. 7.24 The predictable scattering of chiralities for nanotubes of approximately similar diameters

problems of the nanotubes growth control – the chirality control – it is necessary to seek for the small fluctuation angle θ . Then, $\sigma^2 = \theta_T^2 = \frac{2k_B T_{CVD}}{\mu_C B}$.

The condition of the small fluctuation angle (e.g. $\theta < 10^\circ$) at a certain temperature of the CVD process imposes limitations on the values of the demanded magnetic induction B .

Taking into account the ratio between the chirality angle and the direction of the magnetic field $\phi = \theta_B$, Fig. 7.24 displays the predictable scattering of chiralities for nanotubes of approximately the same diameter.

We are also able to evaluate the necessary value of the magnetic field B providing the expected chirality angles scattering, e.g. $\sigma = 0.2$ (appr. 12°) leads to the B evaluation for the CVD process temperature $T_{CVD} = 700^\circ\text{C}$ as $B = \frac{2k_B T_{CVD}}{\sigma^2 \mu_C} \approx \frac{16755}{\sigma^2 \mu_C} \approx 57895 \approx 6 \cdot 10^4 \text{ Tesla}$. For small angle dispersions $\sigma^2 = \theta_T^2 = \frac{2k_B T_{CVD}}{\mu_C B}$

the high local magnetic field on the nanoparticle surface is necessary. The result also strongly depends on the carbon atom magnetic moment μ_C .

Speaking about the possible errors in diameters of growing nanotubes, their evaluation from beneath is defined by the minimal variations in parameters of the chirality vector $\vec{c} = (n, m)$ Δn and Δm , which are equal 1.

Taking into consideration the formula for calculating the diameter of CNT:

$$d = \frac{\sqrt{3}a}{\pi} \sqrt{m^2 + n^2 + mn},$$

where $a = 0,142$ nm is the distance between the neighbouring carbon atoms in the graphite plane.

The relationship between chirality indices (n and m) and the angle ϕ is given by the ratio:

$$\sin \phi = \frac{m\sqrt{3}}{2\sqrt{m^2 + n^2 + mn}}. \quad (7.7)$$

Then the minimum relative error in the diameter of CNT is possible to define as:

$$\epsilon_d = \frac{\Delta d}{d} \approx \frac{\sqrt{5m^2 + 5n^2 + 8mn}}{2(m^2 + n^2 + mn)}. \quad (7.8)$$

Particularly, in the case of armchair CNT ($m = 0$) $\epsilon_d \approx \sqrt{5}/2n$, and in the case of zigzag CNT ($m = n$), $\epsilon_d \approx 1/(2\sqrt{2}n)$.

Thus, errors in the diameter of growing CNTs are incorporated in discrete morphological properties. But these minimum estimates are only reinforced, given the obvious errors in the size of catalyst nanoparticles are taken into consideration.

References

1. Li Y H, Wang S, Wei J, Zhang X, Xu C, Luan Z, Wu D, Wei B **2002** Lead adsorption on carbon nanotubes *Chemical Physics Letters* **357**(3–4) 263–6
2. Iijima S, Ajayan P M, Ichihashi T **1992** Growth Model for Carbon Nanotubes *Physical Review Letters* **69**(21) 3100–3
3. Iijima S, Ichihashi T **1993** Single-shell carbon nanotubes of 1-nm diameter *Nature* **363** 603–5
4. Bethune D S, Kiang C H, De Vries M S, Gorman G, Savoy R, Vazquez J, Beyers R **1993** Cobalt-catalysed growth of carbon nanotubes with single-atomic-layer walls *Nature* **363** 605–7
5. Ando Y, Zhao X **2006** Synthesis of Carbon Nanotubes by Arc-discharge method *New Diamond and Frontier Carbon Technology* **16**(3) 123–37
6. Ando Y, Iijima S **1993** Preparation of Carbon Nanotubes by Arc-Discharge Evaporation *Japanese Journal of Applied Physics* **32**(2) L107–9
7. Somu C, Karthi A, Sing S, Karthikeyan R, Dinesh S, Ganesh N **2017** Synthesis of various forms of carbon nanotubes by arc discharge methods - comprehensive review *International Research Journal of Engineering and Technology (IRJET)* **04**(01) 344–54
8. Maria K H, Mieno T **2015** Synthesis of single walled carbon nanotubes by low-frequency bipolar pulsed arc discharge method *Vacuum* **113** 11–8
9. Berkman J A, Jagannatham M, Reddy R D, Haridoss P **2015** Synthesis of thin bundled single walled carbon nanotubes and nanohorn hybrids by arc discharge technique in open air atmosphere *Diamond and Related Materials* **55** 12–5
10. Sugai T, Yoshida H, Shimada T, Okazaki T, Shinohara H. **2003** New synthesis of high-quality double-walled carbon nanotubes by high temperature pulsed arc discharge *Nano Letters* **3**(6) 769–73

11. Jong Lee S, Koo Baik H, Yoo J, Hoon Han J **2002** Large scale synthesis of carbon nanotubes by plasma rotating arc discharge technique *Diamond and Related Materials* **11** 914–7
12. Eftekhari A, Garcia H **2017** The necessity of structural irregularities for the chemical applications of graphene *Materials Today Chemistry* **4** 1–16
13. Brayfindley E, Irace E E, Castro C, Karney W L **2015** Stone–Wales Rearrangements in Polycyclic Aromatic Hydrocarbons: A Computational Study *J. Org. Chem.* **80**(8) 3825–31
14. Stone A J, Wales D J **1986** Theoretical studies of icosahedral C₆₀ and some related structures *Chemical Physics Letters* **128**(5–6) 501–3
15. Letardi S, Celino M, Cleri F, Rosato V **2002** Atomic hydrogen adsorption on a Stone–Wales defect in graphite *Surface Science* **496** 33–8
16. Meyer J C, Kisielowski C, Erni R, Rossell M D, Crommie M F, Zettl A **2008** Direct Imaging of Lattice Atoms and Topological Defects in Graphene Membranes *Nano Letters* **8** (11) 3582–6
17. Guo T, Nikolaev P, Rinzler A G, Tomanek D, Colbert D T, Smalley R E **1995** Self-Assembly of Tubular Fullerenes *J. Phys. Chem.* **99** 10694–7
18. Guo T, Nikolaev P, Thess A, Colbert D T, Smalley R E **1995** Catalytic growth of single-walled nanotubes by laser vaporization *Chem. Phys. Lett.* **243** 49–54
19. van de Burgt Y **2014** Laser-assisted growth of carbon nanotubes — A review *Journal of Laser Applications* **26**(3) 032001–18
20. Cao L, Barsic D N, Guichard A R, Brongersma M L **2007** Plasmon-Assisted Local Temperature Control to Pattern Individual Semiconductor Nanowires and Carbon Nanotubes *Nano Letters* **7**(1) 3523–7
21. Endo M, Takeuchi K, Igarashi S, Kobori K, Shiraishi M, Kroto H W **1993** The production and structure of pyrolytic carbon nanotubes *J. Phys. Chem. Solids* **54** 1841–8
22. Dai H, Rinzler A G, Nikolaev P, Thess A, Colbert D T, Smalley R E **1996** Single-wall nanotubes produced by metal-catalyzed disproportionation of carbon monoxide *Chem. Phys. Lett.* **260** 471–5
23. Karthikey S, Mahalingam P, Kartnik M **2009** Large Scale Synthesis of Carbon Nanotubes *E-Journal of Chemistry* **6**(1) 1–12
24. Cassell A M, Raymakers J A, Kong J, Dai H **1999** Large Scale CVD Synthesis of Single-Walled Carbon Nanotubes *Journal of Physical Chemistry B* **103**(31) 6484–92
25. Takeuchi K, Hayashi T, Kim Y A, Fujisawa K, Endo M **2014** The state-of-art science and applications of carbon nanotubes *Nanosystems: Physics, Chemistry, Mathematics* **5** (1) 15–24
26. Inami N, Mohamed M A, Shikoh E, Fujiwara A **2007** Synthesis-condition dependence of carbon nanotube growth by alcohol catalytic chemical vapor deposition method *Science and Technology of Advanced Materials* **8** 292–5
27. Kumar M **2011** Nanotube synthesis and growth mechanism *In: InTech Carbon Nanotubes - Synthesis, Characterization, Applications* Sery Nanotechnology and Nanomaterials Ed by Yellampalli S Ch 8
28. Liu C, Cheng H M **2013** Carbon nanotubes: controlled growth and application *Materials Today* **16**(1/2) 19–28
29. Reinhardt H, Hellmann C, Nürnberger P, Kachel S, Hampp N **2017** Free Form Growth of Carbon Nanotube Microarchitectures on Stainless Steel Controlled via Laser-Stimulated Catalyst Formation *Adv. Mater. Interfaces* **4** 1700508–1–7.
30. Neyts E **2012** PECVD growth of carbon nanotubes: From experiment to simulation *Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena* **30** 030803
31. Hofmann S, Ducati C, Robertson J **2003** Low-temperature growth of carbon nanotubes by plasma-enhanced chemical vapor deposition *Applied Physics letters* **83** 135–7
32. Chiang W H, Sankaran R M **2009** Linking catalyst composition to chirality distributions of as-grown single-walled carbon nanotubes by tuning Ni(x)Fe(1-x) nanoparticles *Nature Materials* **8** 882–6

33. Bogaerts A, Eckert M, Mao M, Neyts E **2010** Computer modelling of the plasma chemistry and plasma-based growth mechanisms for nanostructured materials *J. Phys. D: Appl. Phys.* **44** 174030
34. Fantini C, Jorio A, Souza M, Strano M S, Dresselhaus M S, Pimenta M A **2004** Optical Transition Energies for Carbon Nanotubes from Resonant Raman Spectroscopy: Environment and Temperature Effects *Phys. Rev. Lett.* **93** 147406
35. Souza Filho A G, Chou S G, Samsonidze G G, Dresselhaus G, Dresselhaus M S, An Lei, Liu J, Swan Anna K, Unlu M S, Goldberg B B, Jorio A, Grüneis A, Saito R **2004** Stokes and Anti-Stokes Raman Spectra of Small-Diameter Isolated Carbon Nanotubes *Physical Review B*. **69**(11) 115428
36. Eklund P C, Holden J M, Jishi R A **1995** Vibrational modes of carbon nanotubes; Spectroscopy and theory *Carbon* **33** 959–72
37. Hennrich F, Krupke R, Lebedkin S, Arnold K, Fischer R, Resasco D E, Kappes M M **2005** Raman Spectroscopy of Individual Single-Walled Carbon Nanotubes from Various Sources *J. Phys. Chem. B* **109** 10567–73
38. Jorio A, Fantini C, Pimenta M A, Capaz R B, Samsonidze G G, Dresselhaus G, Dresselhaus M S, Jiang J, Kobayashi N, Gruneis A, Saito R **2005** Resonance Raman spectroscopy (n,m)-dependent effects in small-diameter single-wall carbon nanotubes *Phys. Rev. B* **71** 075401
39. Seah Ch-M, Chai S-P, Mohamed A R **2014** Mechanisms of graphene growth by chemical vapour deposition on transition metals *Carbon* **70** 1–21
40. Li X, Cai W, Colombo L, Ruoff R S **2009** Evolution of graphene growth on Ni and Cu by carbon isotope labelling, *Nano Letters* **9**(12) 4268–72
41. Baraton L, He Z, Lee C, Cojocaru C, Châtelet M, Maurice J, Lee Y, Pribat D **2011** On the mechanisms of precipitation of graphene on nickel thin films *Europhysics Letters* **96** (4) 46003–1–6
42. Cabrero-Vilatela A, Weatherup R S, Braeuninger-Weimer P, Caneva S, Hofmann S **2016** Towards a general growth model for graphene CVD on transition metal catalysts *Nanoscale* **8** (4) 2149–58
43. Sun J, Nam Y, Lindvall N, Cole M T, Teo K B K, Park Y W, Yurgens A **2014** Growth mechanism of graphene on platinum: Surface catalysis and carbon segregation *Appl. Phys. Lett.* **104** 152107
44. Li X, Cai W, Colombo L, Ruoff R S **2009** Evolution of Graphene Growth on Ni and Cu by Carbon Isotope *Nano Lett.* **9** (12), 4268–72
45. Kang C, Jung D H, Nam J E, Lee J S **2014** Correlating defect density with growth time in continuous graphene films *J Nanosci Nanotechnol.* **14**(12) 9169–73
46. Krishna Bharadwaj B, Nath D, Pratap R, Raghavan S **2016** Making consistent contacts to graphene: effect of architecture and growth induced defects *Nanotechnology* **27** (20) 205705–1–6
47. Banhart F, Kotakoski J, Krasheninnikov A V **2011** Structural Defects in Graphene *ACS Nano* **5**(1) 26–41
48. Stone A J, Wales D J **1986** Theoretical Studies of Icosahedral C₆₀ and Some Related Species *Chem. Phys. Lett.* **128** 501–3
49. Ugeda M M, Brihuega I, Guinea F Gomez-Rodriguez, J M **2010** Missing Atom as a Source of Carbon Magnetism *Phys. Rev. Lett.* **104** 096804
50. El-Barbary A A, Telling R H, Ewels C P, Heggie M I, Briddon P R **2003** Structure and Energetics of the Vacancy in Graphite *Phys. Rev. B* **68** 144107
51. Lehtinen P O, Foster A S, Ayuela A, Krasheninnikov A V, Nordlund K, Nieminen R M **2003** Magnetic Properties and Diffusion of Adatoms on a Graphene Sheet *Phys. Rev. Lett.* **91** 017202
52. Banhart F **2009** Interactions between Metals and Carbon Nanotubes: At the Interface between Old and New Materials *Nanoscale* **1** 201–13
53. Krasheninnikov A V, Lehtinen P O, Foster A S, Pyykkö P, Nieminen R M **2009** Embedding Transition-Metal Atoms in Graphene: Structure, Bonding, and Magnetism *Phys. Rev. Lett.* **102** 126807

54. Lusk M T, Wu D T, Car L D **2010** Graphene Nanoengineering and the Inverse Stone-Thrower-Wales Defect *Phys. Rev. B* **81** 155444
55. Lahiri J, Lin Y, Bozkurt P, Oleynik I I, Batzill M **2010** An Extended Defect in Graphene as a Metallic Wire *Nat. Nanotechnol.* **5** 326–9
56. Koskinen P, Malola S, Häkkinen H **2009** Evidence for Graphene Edges Beyond Zigzag and Armchair *Phys. Rev. B* **80** 073401
57. Xia F, Farmer, D. B.; Lin, Y.; Avouris, Ph. **2010** Graphene Field-Effect Transistors with High On/Off Current Ratio and Large Transport Band Gap at Room Temperature *Nano Lett.* **10** 715–8
58. Pedersen T G, Flindt C, Pedersen J, Mortensen N A, Jauho A-P, Pedersen K **2008** Graphene Antidot Lattices: Designed Defects and Spin Qubits. *Phys. Rev. Lett.* **100** 136804
59. Yazyev O V, Louie S G **2010** Electronic Transport in Polycrystalline Graphene *Nat. Mater.* **9** 806–9
60. Shunin Yu and Kiv A (Eds) *Nanodevices and Nanomaterials for Ecological Security* **2012** Series: NATO Science for Peace Series B - Physics and Biophysics (Heidelberg: Springer Verlag) 363p
61. Shunin Yu N, Zhukovskii Yu F, Burlutskaya N Yu, Gopejenko V I, Bellucci S **2012** Properties of CNT- and GNR-Metal Interconnects for Development of New Nanosensor Systems In: *Nanodevices and Nanomaterials for Ecological Security* Series: NATO Science for Peace Series B - Physics and Biophysics Eds Yu Shunin and A Kiv (Heidelberg: Springer Verlag) 237–62
62. Shunin Yu N, Zhukovskii Yu F, Gopejenko V I, Burlutskaya N, Lobanova-Shunina T, Bellucci S **2012** Simulation of Electromagnetic Properties in CNT and Graphene Based Nanostructures *Journal of Nanophotonics* **6**(1) 061706–1–16
63. Shunin Yu N, Schwartz K K **1997** Correlation between electronic structure and atomic configurations in disordered solids In: *Computer Modelling of Electronic and Atomic Processes in Solids* Eds R C Tennyson and A E Kiv. Kluwer Academic Publisher: Dordrecht/Boston/London 241–57
64. Shunin Yu N, Zhukovskii Yu F, Gopejenko V I, Burlutskaya N, Bellucci S **2011** *Ab Initio* Simulations on Electric Properties for Junctions Between Carbon Nanotubes and Metal Electrodes *Nanoscience and Nanotechnology Letters* **3**(6) 816–825
65. Economou, E L **2006** *Green's Functions in Quantum Physics Solid State* **7** (Berlin/Heidelberg: Springer Verlag)
66. Ziman J M **1979** *Models of Disorder* (New York-London: Cambridge University Press) Chapter 10
67. Shunin, Yu N, Zhukovskii Yu F, Burlutskaya N, Bellucci S. **2012** *Journal of Nanoelectronics and Optoelectronics* **7**(1) 3–11
68. Capobianchi A, Colapietro M, Fiorani D, Foglia S, Imperatori P, Laureti S, Palange E **2009** General strategy for direct synthesis of L1₀ nanoparticle alloys from layered precursor: the case of FePt *Chem. Mater.* **21**(10) 2007–9
69. Capobianchi A, Campi, G, Camalli M, Veroli C Z **2009** Crystal and molecular structure of the saline complex hexaquaairon(II) hexachloroplatinate, [Fe(H₂O)₆][PtCl₆] *Kristallogr* **224** (8) 384–8
70. Faustini M, Capobianchi A, Varvaro G, Grosso D **2012** Bifunctional FePt@MWCNTs/Ru Nanoarchitectures: Synthesis and Characterization *Chem. Mater.* **24** 1072–9
71. Bellucci S Carbon nanotubes: physics and applications **2005** *Physica Status Solidi (c)* **2** (1) 34–47
72. Moisala A, Nasibulin A G, Kauppinen E I **2003** The role of metal nanoparticles in the catalytic production of single-walled carbon nanotubes – a review *J. Phys. Condens. Mater.* **15** S3011–35
73. Baker R T K, Hams P S **1978** *Chemistry and Physics of Carbon* **14** Eds P L Walker Jr and P A Thrower (New York: Marcel Dekker) 83p
74. Sen R, Govindaraj A, Rao C N R **1997** Metal-filled and hollow carbon nanotubes obtained by the decomposition of metal-containing free precursor molecules *Chem. Phys. Lett.* **267** (3) 276–80

75. *Carbon Nanotubes Science and Applications* 2005 Ed Meyyappan (Florida: CRC Press LLC Google e-Book)
76. Satishkumar B C, Govindraj A, Sen R, Rao C N R **1998** B–C–N, C–N and B–N nanotubes produced by the pyrolysis of precursor molecules over Co catalysts *Chem. Phys. Lett.* **293** (1) 47–52
77. Xie S., Chang B, Li W, Pan Z, Sun L, Mao J, X. H. Chen, L. X. Qian, W. Y. Zhou **1999** Synthesis and Characterization of Aligned Carbon Nanotube Arrays *Adv. Mater.* **11** 1135–9
78. Cassell A M, Raymakers J A, Kong J, Dai H J **1999** Large Scale CVD Synthesis of Single-Walled Carbon Nanotubes *Phys. Chem. B* **103** 6484–9
79. Su M, Zheng B, Liu J **2000** A scalable CVD method for the synthesis of single-walled carbon nanotubes with high catalyst productivity *Chem. Phys. Lett.* **322** 32–6
80. Su M, Li Y, Maynor B, Buldam A, Lu J P, Liu J J **2000** Lattice-Oriented Growth of Single-Walled Carbon Nanotubes *Phys. Chem. B* **104** 6505–12.
81. Fan S S, Chapline M G, Franklin N R, Tomblor T W, Cassell A M, Dai H **1999** Self-oriented regular arrays of carbon nanotubes and their field emission properties *Science* **283** 512–4
82. Cheng H M, Li F, Su G, Pan H Y, He L L, Sun X, Dresselhaus M S **1998**. Large-scale and low-cost synthesis of single-walled carbon nanotubes by the catalytic pyrolysis of hydrocarbons *Appl. Phys. Lett.* **72** 3282–4
83. Li Y, Liu J Z, Wang Z **2001** Preparation of monodispersed Fe-Mo nanoparticles as the catalyst for CVD synthesis of carbon nanotubes *Chem. Mater.* **13** 1008–14
84. Lee D C, Mikulec F V, Korgel B A **2004** Carbon nanotube synthesis in supercritical toluene *Amer. Chem. Soc.* **126**(15) 4951–7
85. Chen G Y, Jensen B, Stolojan V, Silva S R P **2011** Growth of carbon nanotubes at temperatures compatible with integrated circuit technologies *Carbon* **49**(1) 280–5
86. Shang N G, Tan Y Y, Stolojan V, Papakonstantinou P, Silva S R P **2010** High-rate low-temperature growth of vertically aligned carbon nanotubes *Nanotechnology* **21** (50) 505604
87. Kumar M, Ando Yo **2010** Chemical vapor deposition of carbon nanotubes: a review on growth mechanism and mass production *Journal of Nanoscience and Nanotechnology* **10** (6) 3739–58
88. Takagi D, Hibino H, Suzuki S, Kobayashi Y, Homma Y **2007** Carbon Nanotube Growth from Semiconductor Nanoparticles *Nano Lett.* **7** 2272–5
89. Takagi D, Homma Y, Hibino H, Suzuki S, Kobayashi Y **2006** Single-Walled Carbon Nanotube Growth from Highly Activated Metal Nanoparticles *Nano Lett.* **6** 2642–5
90. Liu H, Takagi D, Ohno H, Chiashi Sh, Chokan T, Homma Yo **2008** Growth of Single-Walled Carbon Nanotubes from Ceramic Particles by Alcohol Chemical Vapor Deposition *Appl. Phys. Express* **1** 014001–3
91. Hernadi K, Fonseca A, Nagy J B, Bernaerts D, Lucas A A **1996** Fe-catalyzed carbon nanotube formation *Carbon* **34**(10) 1249–57
92. Kong J, Cassell A M, Dai H **1998** Chemical vapor deposition of methane for single-walled carbon nanotubes *Chem. Phys. Lett.* **292**(4) 567–74
93. Li W Z, Xie S, Qian L X, Chang B H, Zou B S, Zhou W Y, Zhao R A, Wang G **1996** Large-scale synthesis of aligned carbon nanotubes *Science* **274** 1701–3
94. Wei B Q, Vajtai R, Jung Y, Ward J, Zhang R, Ramanath G, Ajayan P M **2002** Microfabrication technology: organized assembly of carbon nanotubes *Nature* **416** 495–6
95. Nikolaev P, Bronikowski M J, Bradley R K, Rohmund F, Colbert D T, Smith K A, Smalley R E **1999** Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide *Chem. Phys. Lett.* **313** 91–7
96. Cheng H M, Li F, Sun X., Brown S D M., Pimenta M A., Marucci A, Dresselhaus G, Dresselhaus M S **1998** Bulk morphology and diameter distribution of single-walled carbon nanotubes synthesized by catalytic decomposition of hydrocarbons *Chem. Phys. Lett.* **289** 602–10
97. Hafner J H, Bronikowski M J, Azamian B R, Nikolaev P, Rinzler A G, Colbert D T, Smith K A, Smalley R E **1998** Catalytic growth of single-wall carbon nanotubes from metal particles *Chem. Phys. Lett.* **296** 195–202

98. Flahaut E, Govindaraj A, Peigney A, Laurent C, Rao C N R **1999** Synthesis of single-walled carbon nanotubes using binary (Fe, Co, Ni) alloy nanoparticles prepared in situ by the reduction of oxide solid solutions *Chem. Phys. Lett.* **300**(1–2) 236–42
99. Gruneis A, Rummeli M H, Kramberger C, Grimm D, Gemming T, Barreiro A, Ayala P, Pichler T, Kuzmany H, Schamann C, Pfeiffer R, Schumann J, Buchner B **2006** Novel catalysts for low temperature synthesis of single wall carbon nanotubes. *Physica Status Solidi (b)* **243** 3054–7
100. Maruyama S, Miyauchi Y, Edamura T, Igarashi Y, Chiashi S and Murakami Y **2003** Single-walled carbon nanotubes catalytically grown from mesoporous silica thin film *Chem. Phys. Lett.* **375** 553–9
101. Maruyama S, Kojima R, Miyauchi Y, Chiashi S, Kohno M **2002** Low-temperature synthesis of high-purity single-walled carbon nanotubes from alcohol *Chem. Phys. Lett.* **360**(3) 229–34
102. Okubo S, Sekine T, Suzuki S, Achiba Y, Tsukagoshi K, Aoyagi Y and Kataura H **2004** Purification of Single-Wall Carbon Nanotubes synthesized from Alcohol by Catalytic Chemical Vapor Deposition *Jpn. J. Appl. Phys.* **43** L396–8
103. Gruneis A, Rummeli M H, Kramberger C, Barreiro A, Pichler T, Pfeiffer R, Kuzmany H, Gemming T, Buchner B **2006** High quality double-wall carbon nanotubes with a defined diameter distribution by chemical vapor deposition from alcohol *Carbon* **44** 3177–82
104. Nasibulin A G, Moisala A, Jiang H, Kauppinen E I **2006** Carbon nanotube synthesis from alcohols by a novel aerosol method *J. Nanopart. Res.* **8** 465–75
105. Murakami Y, Miyauchi Y, Chiashi S, Maruyama S **2003** Direct synthesis of high-quality single-walled carbon nanotubes on silicon and quartz substrates *Chem. Phys. Lett.* **377** (1) 49–54
106. Murakami Y, Chiashi S, Miyauchi Y, Hu M, Ogura M, Okubo T, Maruyama S **2004** Growth of vertically aligned single-walled carbon nanotube films on quartz substrates and their optical anisotropy *Chem. Phys. Lett.* **385**(1) 298–303
107. Maruyama S, Einarsson E, Murakami Y, Edamura T **2005** Growth process of vertically aligned single-walled carbon nanotubes *Chem. Phys. Lett.* **403**(4–6) 320–3
108. Xiang R, Einarsson E, Okawa J, Miyauchi Y and Maruyama S **2009** Acetylene-Accelerated Alcohol Catalytic Chemical Vapor Deposition Growth of Vertically Aligned Single-Walled Carbon Nanotubes *J. Phys. Chem. C* **113** 7511–5
109. Yuan D, Ding L, Chu H, Feng Y, McNicholas T P, Liu J **2008** Horizontally Aligned Single-Walled Carbon Nanotube on Quartz from a Large Variety of Metal Catalysts *Nano Lett.* **8** (8) 2576–9
110. Ward J, Wei B Q, Ajayan P M **2003** *Chem. Phys. Lett.* **376**(5–6) 717–25
111. Morjan R E, Nerushev O A, Sveningsson M, Rohmund F, Falk L K L, Campbell E E B **2004** Growth of carbon nanotubes from C 60 *Appl. Phys. A* **78**(3) 253–61
112. Ago H, Komatsu T, Ohshima S, Kuriki Y, Yumura M **2000** Dispersion of metal nanoparticles for aligned carbon nanotube arrays *Appl. Phys. Lett.* **77**(1) 79–81
113. Kumar M, Ando Y **2005** Controlling the diameter distribution of carbon nanotubes grown from camphor on a zeolite support *Carbon* **43**(3) 533–40
114. Li W Z, Wen J G, Ren Z F **2002** Effect of temperature on growth and structure of carbon nanotubes by chemical vapor deposition *Appl. Phys. A* **74**(3) 397–402
115. Li W Z, Wen J G, Tu Y, Ren Z F **2001** Effect of gas pressure on the growth and structure of carbon nanotubes by chemical vapor deposition *Appl. Phys. A* **73**(2) 259–264
116. Maruyama S, Murakami Y, Shibuta Y, Miyauchi Y, Chiashi S **2004** Generation of single-walled carbon nanotubes from alcohol and generation mechanism by molecular dynamics simulations. *J. Nanosci. Nanotechnol.* **4** 360–7
117. Kumar M and Ando Y **2008** Gigas growth of carbon nanotubes *Defence Sci. Journal* **58** (4) 496–503
118. Raty J-Y, Gygi F, Galli G **2005** Growth of Carbon Nanotubes on Metal Nanoparticles: A Microscopic Mechanism from *Ab Initio* Molecular Dynamics Simulations. *Phys. Rev. Lett.* **95** 096103–7
119. Bellucci S, Micciulla F, Shunin Yu, Zhukovskii Yu, Gopejenko V, Burlutskaya N **2015** Memory Nanodevices Based on Carbon Nanotube-Fe-Pt Interconnects: Electromagnetic

- Simulations and Magnetically Stimulated Nanotube Growth *Journal of Materials Science and Engineering B* **5** (3–4) 120–34
120. Shunin Yu **2015** *Spintronic Nanomemory and Nanosensor Devices Based on Carbon Nanotube-Fe-Pt Interconnects: Models and Simulations* LAP LAMBERT Academic Publishing
121. Bellucci S., Zhukovskii Yu F, Gopejenko V I, Burlutskaya N, Shunin Yu N **2012** Interconnects fundamental properties and magnetically stimulated nanoprocesses on Fe-Pt substrates *CIMTEC2012 Theses* June 10–14 Montecatini Terme Tuscany Italy 78
122. Sun A C, Kuo P C, Chen S C, Chou C Y, Huang H L, Hsu J H **2004** Magnetic properties and microstructure of low ordering temperature L10L10 FePt thin films *J. Appl. Phys.* **95** (11) 7264–6
123. Elkins K, Li D, Poudyal N, Nandwana V, Jin Zh, Chen K, Liu J P 2005 *J. Phys. D* **38** 2306–9
124. Yan M L, Sabirianov R F, Xu Y F, Li X Z, Sellmyer D J 2004 *IEEE Trans. on Magnetics* **40** (4) 2470–2
125. Kim Y-H, Choi J, Chang K J, Tománek D **2003** Defective fullerenes and nanotubes as molecular magnets: An *ab initio* study *Phys. Rev. B* **68** 125420
126. Medwal R., Sehdev N, Annapoorni S J **2012** Order–disorder investigation of hard magnetic nanostructured FePt alloy *J Phys. D Appl. Phys.* **45** 055001–7
127. Arabshahi H, Hematabadi A, Bakhshayeshi A, Ghazi M **2012** Temperature Dependence and Magnetic Properties of FePt Nanoparticles via Monte Carlo Simulation *World Applied Programming* **2**(8) 415–20