

Chapter 1

Introduction

Careful research on different materials reveals that material properties are not only governed by the atomic composition and the chemical bonding, but also by the dimensions of the material (Buffat, 1976). It has been observed that as the size of a material reduce to nanometer scale dimensions, materials exhibit some remarkable properties, resulting in unique physical and chemical characteristics. Novel synthetic approaches have resulted in the development of materials with reduced dimensions. This technology of synthesizing nanoscale materials and devices was named as “nanotechnology” by Norio Taniguchi in 1974 (Taniguchi, 1974).

Carbon, placed at group 14 (IV A), is one of the most important elements in the periodic table. A carbon atom contains 6 electrons, 2 in the first energy level (1s) and the remaining 4 electrons fill the sp hybrid orbital at the second energy level. Owing to its ability to form sp³, sp², and sp hybrids and stable multiple pi and sigma bonds, carbon can form 3D (Diamond and Graphite), 2D (Graphene), 1D (Carbon nanotube), and 0D (Fullerene) materials with a wide variety of physical and chemical properties (Figure 1.1).

Among the different forms of carbon, carbon nanotubes (CNTs) represent one of the most exciting research areas in modern science. Nanotubes are nearly one dimensional structures due to their high length to diameter ratio.

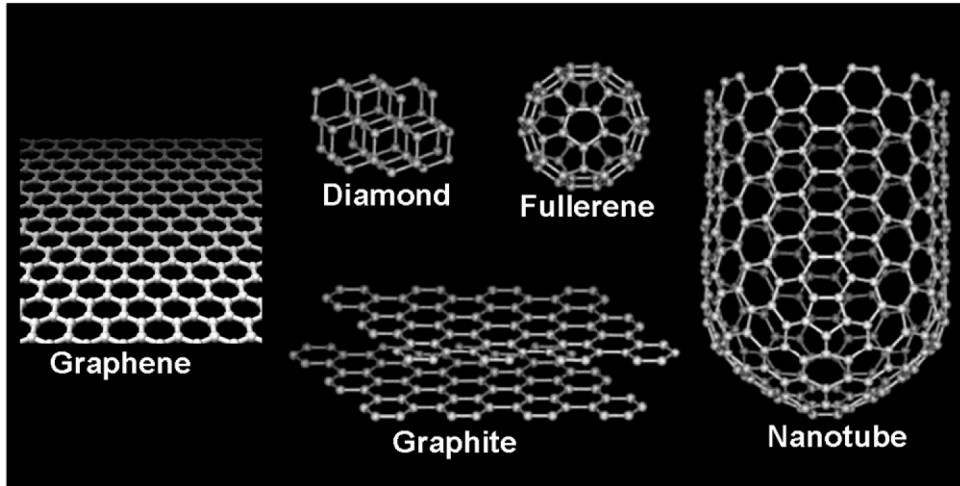


Figure 1.1: Different forms of carbon
(adapted from <http://mrsec.wisc.edu/Edetc/IPSE/educators/activities/carbon.html>)

CNTs exhibit a unique combination of electronic, thermal, mechanical and chemical properties (Chen et al., 1999; Dai et al., 1996a; Qian et al., 2000; Saito et al., 1997; Tans et al., 1998), which promise a wide range of potential applications in key industrial sectors such as nanoelectronics (Herrero et al., 2006), biotechnology (Martin and Kohli, 2003) and thermal management (Kim et al., 2007).

1.1 A brief history of carbon nanotubes

Tubular carbon nanostructures were first observed as early as 1952 by Radushkevich and Lukyanovich (Figure 1.2a), who published this in the Soviet Journal of Physical Chemistry (Radushkevich and Lukyanovich, 1952). Due to the cold war, access to Russian scientific publications for western scientists was not easy. Accordingly this

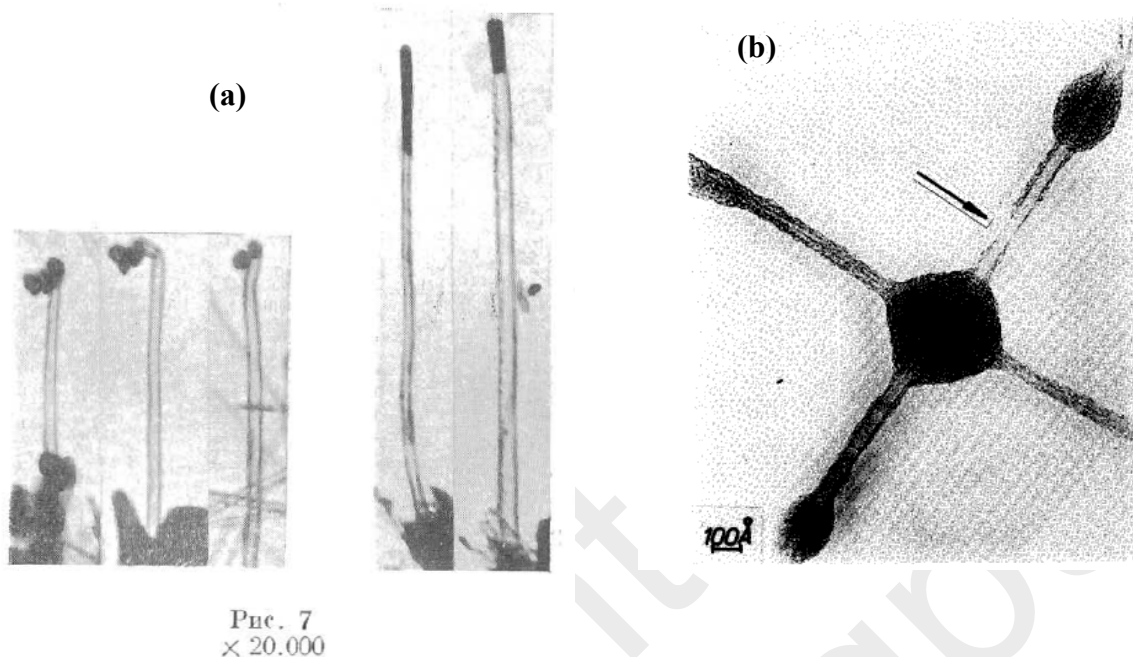


Figure 1.2: Examples of transmission electron microscopy images of carbon nanotubes published by (a) Radushkevich and Lukyanovich (1952) (reprinting permission sought from Nauka Publishers); (b) Oberlin et al. (1976) (reprinted by permission of Elsevier)

discovery was largely unnoticed. A few years later Oberlin et al. (1976) published clear images of hollow carbon fibres with nanometer scale diameters using a vapour growth technique (Figure 1.2b). However, it was not until nearly two decades later, when Iijima reported the observation of CNTs in Nature (Iijima, 1991) that world-wide interest and excitement was generated. Iijima's work is undoubtedly responsible for the explosion of interest in CNT research in the scientific community which resulted in the rapid development of this field. Iijima clearly observed the so-called multi-walled nanotubes (MWCNTs) while studying the soot made from by-products obtained during the synthesis of fullerenes by the electric arc discharge method. Two years later, single-walled carbon nanotubes (SWCNTs) were discovered independently by Iijima at the

NEC Research Laboratory in Japan (Iijima and Ichihashi, 1993) and by Bethune at the IBM Almaden Laboratory in California (Bethune et al., 1993). Since then the field has advanced at a breathtaking pace that is reflected in the number of increased publication (Figure 1.3) along with many unexpected discoveries.

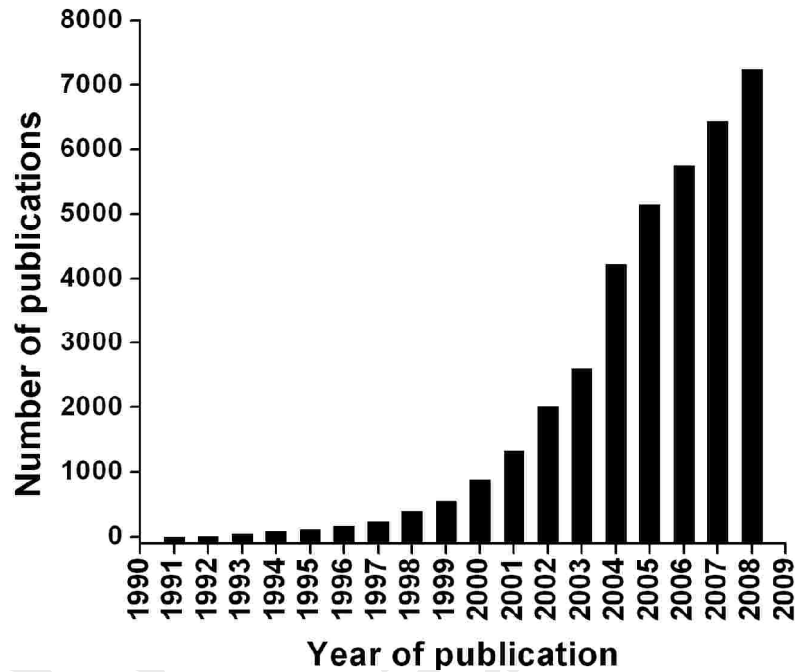


Figure 1.3: The number of papers on carbon nanotubes published annually, from 1991 to 2008 (Data from Scopus, Elsevier)

1.2 Structure

The structure of the CNT can be specified in terms of a vector \vec{C} . This vector is known as the chiral vector and it is formed by joining two crystallographically equivalent points on the original graphene lattice. \vec{C} can be expressed in terms of a set of two integers (n,m) corresponding to graphite vectors \vec{a}_1 and \vec{a}_2 (Figure 1.4)

$$\vec{C} = n \cdot \vec{a}_1 + m \cdot \vec{a}_2, (0 \leq |m| \leq n) \quad \dots(1.1)$$

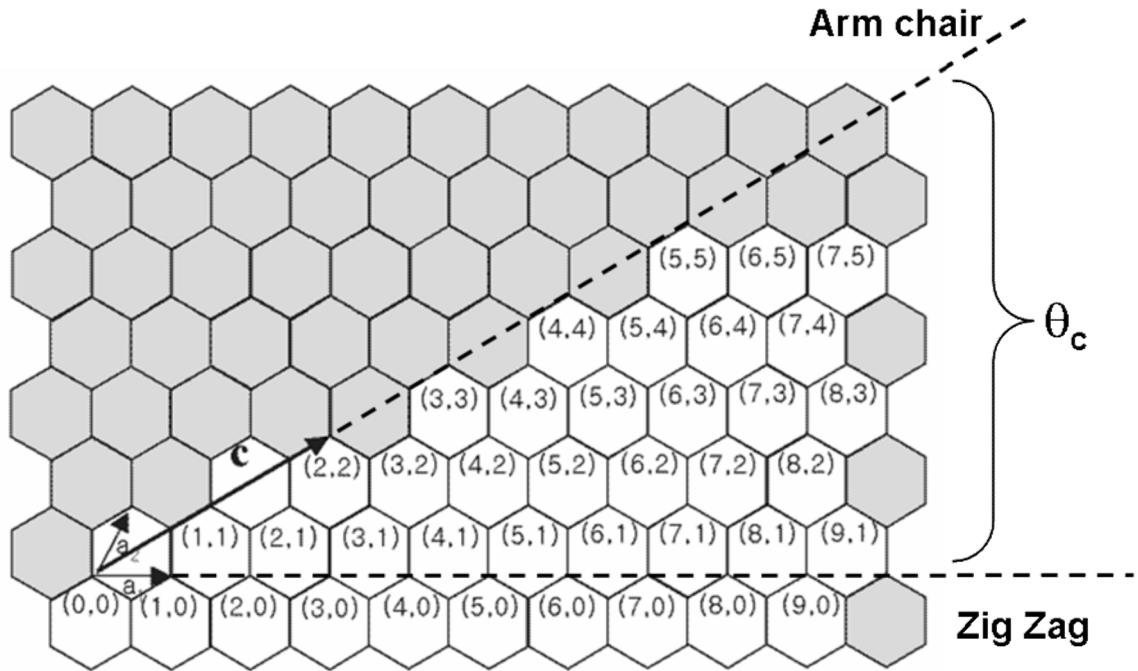


Figure 1.4: Graphene layer defined by unit vectors \vec{a}_1 and \vec{a}_2 and the chiral angle θ_c , the atoms labeled with (n,m) notation (adapted from Dresselhaus et al., 1996)

The integers n and m are also called indexes and determine the chiral angle

$$\theta_c = \tan^{-1}[\sqrt{3}\{m/(m + 2n)\}] \quad \dots(1.2)$$

with respect to the zigzag axis. The direction of the nanotube axis is perpendicular to the chiral vector. Three different types of nanotube structures can be generated by rolling up the graphene sheet into a cylinder along different directions: armchair ($n = m$, $\theta_c = 30^\circ$), zigzag ($m = 0$, $n > 0$, $\theta_c = 0^\circ$), and chiral ($0 < |m| < n$, $0 < \theta_c < 30^\circ$) (Figure 1.5). Armchair CNTs are metallic. Zigzag and chiral nanotubes can be semimetals or semiconductors.

CNTs can be visualized as sheets of carbon atoms rolled up into tubes. There are two types of CNTs: They can consist of one (single-wall) or more (multi-wall) graphitic layers.

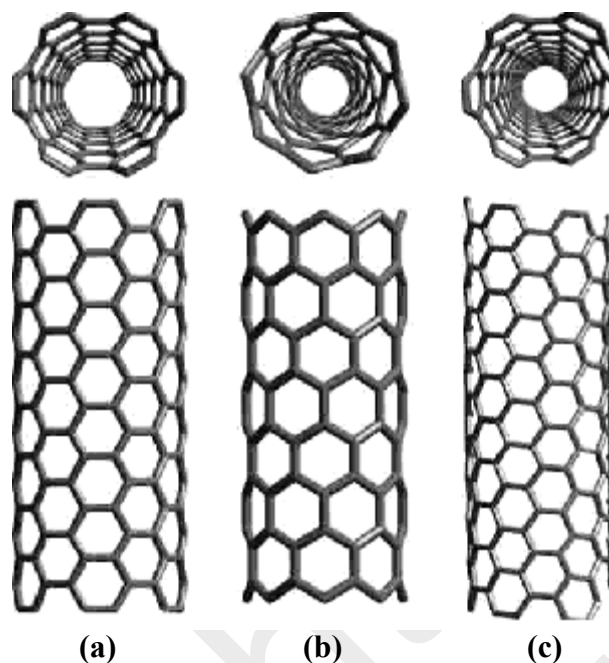


Figure 1.5: Cross sectional (top) and plan view (bottom) schematics of various types of single-walled carbon nanotubes (a) Armchair nanotube; (b) Zigzag nanotube and (c) Chiral nanotube

The structure of a SWCNT can be thought of as a single atomic layer thick sheet of graphite (called graphene) rolled into a seamless cylinder such that the lattice of carbon atoms remains continuous around the circumference. Depending on the roll-up direction SWCNTs can have different structures namely zigzag, armchair or chiral (Figure 1.5). The term zigzag and armchair refer to the arrangement of hexagons around the circumference of a CNT.

MWCNTs consist of multiple layers of graphitic sheets rolled in on themselves to form a tube shape. The structure of multi-walled nanotube can be explained on the basis of two models– the “Russian doll” model and the “Parchment model” (Figure 1.6).

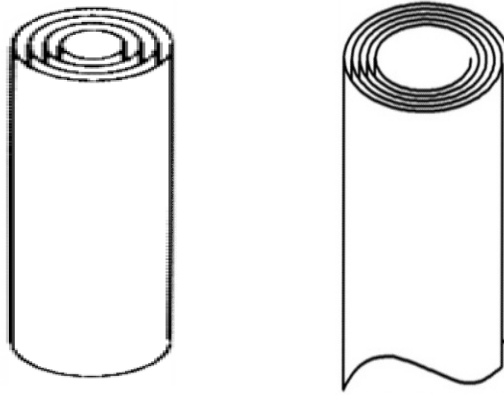


Figure 1.6: Schematics of (a) Russian doll and (b) Swiss roll model of multi-walled carbon nanotube

In the “Russian doll” model, sheets of graphite are arranged in concentric cylinders while in the “Parchment model”, a single graphene sheet is rolled in around itself multiple times to form a spiral, like a roll of paper or parchment. The “Parchment model” is often described as the “Swiss roll” model. However, there are reports (Maniwa et al., 2001; Martinez et al., 2007; Zhou et al., 1994) on the structure of MWCNTs which indicate that the structure of MWCNTs may be a mixture of “Russian doll” and “Swiss roll” structures. Evidence has also been found about the presence of zigzag, armchair and chiral tubes within the same MWCNT (Zhang et al., 1993; Zhang et al., 1994a; Zhang et al., 1994b).

1.3 Properties

The exotic electronic properties of nanotubes have received a lot of attention from the research community. Nanotubes possess remarkable electronic properties due to their extremely small size and highly symmetric structure. The unparalleled electronic properties, for example the quantum wire like behavior of a SWCNT, SWCNT bundles,

and MWCNTs as well as the metallic and semiconducting characteristics of a SWCNT have been established both theoretically and experimentally (Bockrath et al., 1997; Charlier et al., 2007; Chico et al., 1996; Odom et al., 2000; Wildoer et al., 1998). Experimental observation confirms that confinement effect due to the tube circumference is responsible for these phenomena. In the case of electron transport in the metallic nanotubes, as the allowed electronic states are very limited with respect to graphite, therefore the conduction occurs through well separated discrete electron states as in a quantum wire. Consequently, the conduction is of ballistic type, i.e. electrons pass along the nanotubes without any scattering. Effectively, the electrons move without experiencing any resistance and subsequently dissipate no energy. Thereby, metallic nanotubes are capable of conducting high current without producing heat which is one of the highly desirable criteria for the construction of nanoscale circuits. The electron transport in semiconducting nanotubes is much more complicated. However, experimental evidence for extremely high mobilities has been established (Durkop et al., 2004).

Nanotubes also show extraordinary thermal properties. SWCNTs have thermal properties similar to graphite at room and elevated temperatures but unusual behavior at low temperatures because of the effects of phonon quantization (Hone et al., 1999; Yamamoto et al., 2004). This indicates that heat conduction in a nanoscale structure can be quantized since only a small number of phonons are active in the nanoscale device at very low temperatures (Angelescu et al., 1998; Rego and Kirczenow, 1998). Ballistic transport of phonons has also been reported by Brown et al. (2005) using a temperature sensing

scanning probe microscope. Theoretical calculations along with experimental measurements reveal that the thermal conductivity at room temperature for SWCNT ropes and MWCNTs may vary between 1800 and 6000 W/(m·K) (Hone et al., 1999; Yi et al., 1999) whereas more than 3000 W/(m·K) is evidenced (Kim et al., 2001) from measurements on a single MWCNT.

Semiconducting SWCNTs have a direct band gap which is the most important criteria for use in optical and optoelectronic applications. Optical properties of nanotubes have been investigated by employing resonant Raman (Rao et al., 1997), fluorescence (Hartschuh et al., 2003), and ultraviolet to the near infrared (UV-VIS-NIR) spectroscopies (Hagen and Hertel, 2003). Furthermore, electrically induced optical emission (Misewich et al., 2003) and photoconductivity (Freitag et al., 2003) measurements have been reported for individual SWCNTs. Theoretical calculations and experimental measurements reveal that there is a difference in the absorption coefficient spectra for nanotubes due to the strong dependence of nonlinear optical properties on the diameter and symmetry of the tubes.

CNTs are also recognized as the stiffest and strongest material known to date featuring high flexibility and large breaking stress with low density. The axial component of sigma bond and sp^2 rehybridization in nanotubes is mainly responsible for their unparallel mechanical properties. Several research groups have reported the Young's modulus and tensile strength of SWCNTs and MWCNTs (Lukić et al., 2005; Treacy et al., 1996; Wong et al., 1997; Yu et al., 2000a) based mainly on the techniques of transmission electron microscopy (TEM) (Demczyk et al., 2002), scanning electron microscopy

(SEM) (Yu et al., 2000b) and atomic force microscopy (AFM) (Guhados et al., 2007). While there is some scatter in the reported values of Young's modulus and tensile strength observed in these studies, it can be concluded that the Young's modulus of the nanotubes is around 1000 GPa, approximately five times higher than steel while their tensile strength can be up to 50 GPa, around fifty times higher than steel (although higher values for both Young's modulus and tensile strength have been observed in some studies). However, it is important to realize that Young's modulus can vary with tube diameter but stiffness always increases with the increase of the diameter of the tube. The experiment carried out by Falvo et al. (1997) using AFM provides further evidence of extraordinary resilience of CNTs. They found that the CNT could be bent repeatedly through large angles without fracturing.

High reactivity and strong sensitivity of CNTs to chemical or environmental interactions is due to the curvature of the tube. A carbon atom in the sidewall, or in a closed end cap, has three bonds to its nearest neighbor carbon atoms. Carbons at the termination of an open ended tube only have two bonds. Therefore, it is easy to introduce foreign molecules into the structure. Thus, CNTs can be functionalized by the preferential addition of one or more species. Functionalization is a way to enhance properties for specific applications such as for the development of nanotube-based composite (Tasis et al., 2006).

1.4 Synthesis methods

There are many methods by which CNTs can be produced, including but not limited to arc discharge, laser ablation and chemical vapor deposition (CVD). These three synthesis methods of CNT can be classified into two main categories depending on the growth temperature. High temperature routes are the electric arc method and the laser ablation method whereas medium temperature routes are based on CVD processes. Present work focuses on CVD synthesis since this method can be relatively easily extended to bulk production.

The high temperature process involves sublimation of graphite in an inert atmosphere and condensing the resulting vapor under a high temperature gradient. The difference between the various processes is the method used for subliming graphite. An electric arc formed between two electrodes is used for sublimation of graphite in case of the arc discharge method. An ablation induced by a laser is used for sublimation of graphite in case of the laser ablation technique.

1.4.1 Arc discharge

Arc discharge was used by Bacon in 1960 to produce carbon whiskers (Bacon, 1960), around 50 years ago. Later, in 1990, Krätschmer and his co-workers employed the arc discharge technique to produce fullerenes (Krätschmer et al., 1990) while Iijima used arc evaporation for the synthesis of MWCNTs in 1991 (Iijima, 1991). The first synthesis of SWCNTs in 1993 also involved arc evaporation using metal impregnated electrodes. Since then arc evaporation remains an important method for nanotube synthesis. This

method creates CNTs through an arc discharge generated between two graphite electrodes placed face to face, separated by approximately 1mm in the airtight chamber (Figure 1.7) that is usually filled with inert gas at low pressure. In general, a low voltage (~ 12 to 25 V) and high current (50 to 120 A) power supply is used for arc discharge.

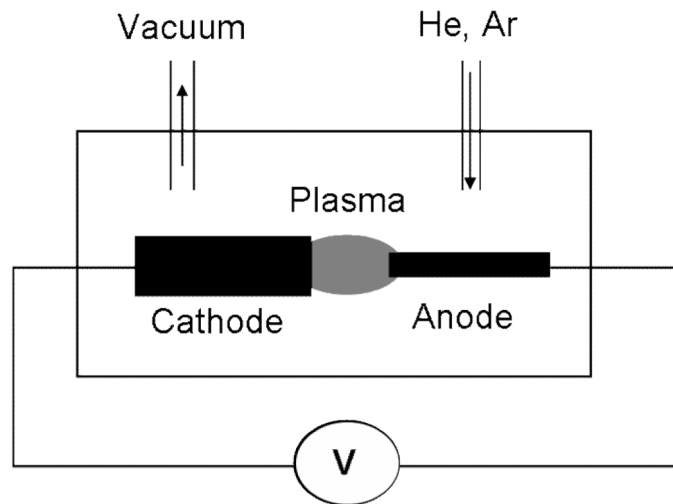


Figure 1.7: Schematic of the arc discharge technique

The electrical discharge creates a high temperature between the two electrodes resulting in the sublimation of the carbon contained in the graphite electrode. During sublimation, the carbon atoms eject from the solid and form plasma. These atoms move toward the colder zones within the chamber, allowing a nanotube deposit to accumulate on the cathode. The type of nanotube that is formed in arc discharge process depends crucially upon the presence of metal catalysts. If small amounts of transition metals such as Fe, Co, Ni, Pt, Pd or Y are introduced in the target graphite, then SWCNTs become the dominant product (Journet et al., 1997; Yudasaka et al., 2002). Radial growth of SWCNTs has also been observed using lanthanum (Saito et al., 1995). In the absence of such metals, the formation of MWCNT is favored. The metal is typically introduced into this reaction via

the anode in two predominant methods, drilled hole or uniformly dispersed. In the drilling method, a several centimeter hole is drilled into the end of the anode graphite rod and filled with the catalyst and graphite powder. The other type of anode has the catalyst uniformly dispersed within the rod and is easier to fabricate. Physical conditions of the arc discharge for efficient CNT production include parameters such as potential drop between electrodes, current density in the arc, the inter-electrode spacing, plasma temperature, stability of the plasma formed between the electrodes, inert gas pressure and cooling of electrodes (Ebbesen and Ajayan, 1992; Seraphin et al., 1993). Different type of gases e.g. He, Ar, CH₄, H₂, N₂, CF₄ and organic vapors have been used (Ando 1994; Cui et al., 2004; Shimotani et al., 2001; Yokomichi et al., 1998; Zhao et al., 2004). Researchers are trying to improve the method of arc discharge technique in terms of experimental ease, quality of nanotubes and production quantity. To reduce the process cost, several efforts have been made, e.g. under water growth of nanotubes has been demonstrated (Zhu et al., 2002) which does not require vacuum or a water cooled chamber. Similarly, instead of graphite, coal has been used as the electrode material (Qiu et al., 2003). As the growth temperature of the arc discharge method is higher than that of other CNT production methods, therefore the crystallinity and perfection of arc grown CNTs are generally higher than other methods. However, the wide range of CNTs produced in arc discharge method have varying morphologies and suffer from a variety of defects such as amorphous carbon matter deposited on the inside and outside of the CNT walls. Moreover, the CNTs from the arc discharge are often covered with amorphous carbon, which contains metallic particles in the case of metal-carbon co-evaporation. Many purification methods have been developed to purify the nanotubes

produced by arc evaporation, e.g. oxidation (Ebbesen et al., 1994), bromination (Chen et al., 1996), chromatography (Duesberg et al., 1998), intercalation (Ikazaki et al., 1994) and combined wet grinding, hydrothermal treatment and oxidation (Sato et al., 2001). In recent years, interest in purifying arc grown tubes has decreased due to the increased focus on in catalytically grown nanotubes. Consequently, there are no completely satisfactory ways of achieving pure arc grown CNTs at present.

1.4.2 Laser ablation

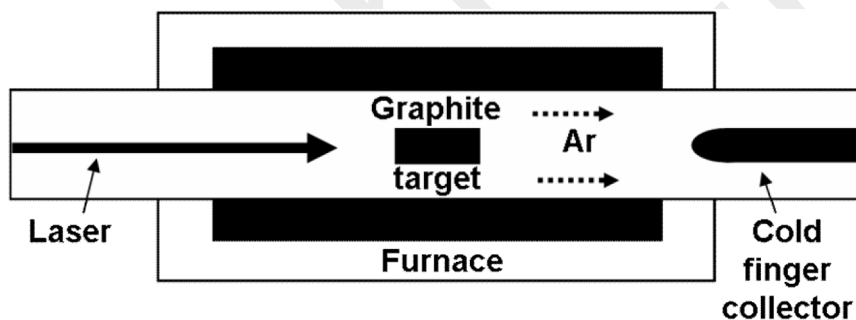


Figure 1.8: Schematic of the laser ablation technique

Historically, production of fullerenes was originally obtained by a laser ablation technique (Kroto et al., 1985). In this process, ablation of a graphite target with a focused laser beam is realized in an inert atmosphere at low pressure (Figure 1.8). Typically a Nd:YAG (Guo et al., 1995a) or CO₂ (Kokai et al., 1999) laser is used as a source. Since the energy density of lasers is much higher than that of other vaporization devices, a laser is suitable for materials with a high boiling temperature such as carbon. Two kinds of methods were developed and they use either a pulsed laser (Guo et al., 1995b) or a continuous laser (Maser et al., 1998). The laser evaporates a solid target of graphite (or

graphite and catalyst) into a background gas which is gently flowing through a quartz tube inside a high temperature oven. During the vaporization process the flowing argon gas sweeps the produced soot inside the quartz tube. The nanotubes nucleate in the vapor phase, coalesce, get carried away by the flowing argon and condense downstream on the water-cooled copper collector. The felt-like material, when scraped off the wall, contains MWCNTs or SWCNTs depending on the experimental conditions. As with the electric arc method, MWCNTs are obtained when using a pure graphite target and SWCNTs when the target is a mixture of graphite and metallic catalysts such as Ni-Co or Ni-Y mixtures (Maser et al., 1998). Nanotubes are accompanied by amorphous carbon, metal particles, and carbon onions as in electric arc techniques. Therefore the nanotubes produced by this synthesis method also need extensive purification before use.

Arc discharge and laser vaporization are currently the principal methods for obtaining small quantities of high quality CNTs. However, both methods suffer from drawbacks. The first is that both methods involve high purity graphite rods, consumption of a large amount of energy and low yield of CNTs. So, these techniques are not economically advantageous to scale up and less favorable for nanotube production at an industrial level. The second issue relates to the fact that vaporization methods grow CNTs in highly tangled forms, mixed with unwanted forms of carbon and/or metal species. The CNTs thus produced are difficult to purify, manipulate, and assemble for building nanotube-device architectures for practical applications. Controlled synthesis on substrates with ordered nanotube structures has not been possible by these methods. This need is satisfied by CVD and related techniques.

1.4.3 Chemical vapor deposition

There are many types of CVD that can be used in the manufacture of CNTs, but the predominant types are thermal and plasma enhanced which are categorized according to the energy source. When a conventional heat source such as a resistive or inductive heater is used, the technique is called thermal CVD whereas when a plasma source is used to create a glow discharge it is called plasma enhanced CVD (PECVD). This section focuses primarily on thermal CVD as it was employed in the present work.

In the early 1970s, notable work on formation of filamentous carbon by catalytic decomposition of hydrocarbon gases was carried out by several research groups (Baker et al., 1972; Baird et al., 1974; Ruston et al., 1969). Few years later Oberlin et al. (1976) published clear images of hollow carbon filaments using a similar technique. More in-depth studies on the synthesis of carbon filaments were performed in the 1980s. Audier et al. (1981) studied the effect of shape of the catalyst particle on the nanotube growth. Tibbetts (1984) found that it is energetically favorable for the carbon filament to create a hollow core when the outer surface is a curved (0001) basal plane. Baker (1989) reported different growth modes of filamentous carbon and also investigated the influence of the metal-support interaction on them. The observation of high quality MWCNTs by Iijima in 1991 stimulated huge interest in the synthesis of CNTs. In 1993, Yacamán et al. (1993) reported the synthesis of carbon microtubules by catalytic decomposition of acetylene over Fe particles. These carbon microtubules are similar to the helical structure reported by Iijima in 1991. Synthesis of SWCNT using CVD was demonstrated by Dai et al. (1996b) by metal-catalyzed disproportionation of carbon monoxide. Aligned CNT growth

was demonstrated in 1996 by a Chinese group who used a technique in which Fe nanoparticles were embedded in mesoporous silica and that was used to catalyze the decomposition of acetylene at 700 °C (Li et al., 1996). The spatially selective growth of nanotubes was exhibited in 1998 using a patterned Si surface by CVD (Kong et al., 1998). In the same year growth of CNTs using plasma CVD was also achieved using Fe as a catalyst (Ren et al., 1998). However the CNTs produced by CVD process contain residual metal catalyst particle and support material. These impurities can be removed far more easily than in case for arc grown tubes, as shown by a number of groups (Andrews et al., 2001; Chen et al., 2002; Huang et al., 2003; Zhang et al., 2006). It seems that the most successful methods involve high temperature annealing in vacuum. Thus, with the implementation of the CVD process, it became possible to produce a large amount of CNTs directly on the desired substrate with high purity and large yield and at a much lower temperature compared to vaporization methods.

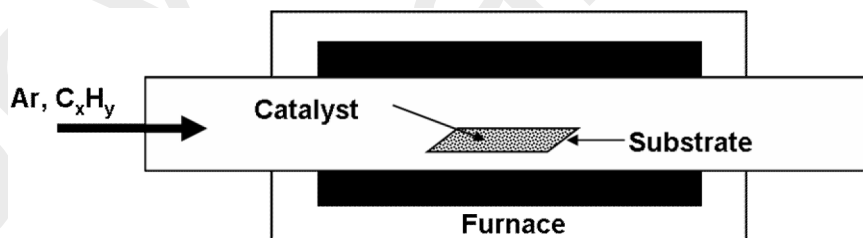


Figure 1.9: Schematic of the chemical vapor deposition technique

A schematic experimental setup for thermal CVD growth is depicted in Figure 1.9. In thermal CVD, an inert gas is used for purging and a hydrocarbon is used as the feedstock. The substrate with catalyst overlayer is placed inside the reactor. A typical growth run involves several steps. Purging of the reactor is done with the inert gas until the reactor

reaches the desired growth temperature. Then the inert gas flow is switched to the feedstock for the specified growth period. During the growth period, decomposition of the feedstock gas is catalyzed by catalytic nanoparticles, which also serve as nucleation sites for the initiation of CNT growth. At the end, the feedstock gas flow is switched back to the inert gas and the reactor is allowed to cool down. Materials grown over the catalyst are collected upon cooling the system to room temperature. Care must be taken during cool down since exposure to air at elevated temperatures can cause damage to the CNTs. Several types of hydrocarbon have been used as feedstock e.g. acetylene (Zhong et al., 2009), methane (Homma et al., 2002), propane, etc. These feedstock gases decompose in the presence of catalyst and produce carbon, e.g., $C_3H_8 \rightarrow 2 C + CH_4 + 2 H_2$ (Hussain et al., 2008).

1.4.3.1 Catalyst

The pathways for the synthesis of CNTs by CVD can be categorized into catalytic and non-catalytic methods (Derycke et al., 2002; Schneider et al., 2008). There are several ways by which catalyst can be prepared for the CNT growth by CVD. A stream of catalyst particles can be injected into the flowing feedstock to produce nanotubes in the gas phase using a floating or unsupported catalyst approach. In contrast, the catalyst can be deposited on the substrate before loading it inside the reactor. This is called supported catalyst approach.

In the unsupported catalyst approach, a volatile compound containing the catalytic element, e.g. iron pentacarbonyl ($Fe(CO)_5$), ferrocene ($Fe(C_5H_5)_2$), or nickelocene

$(\text{Ni}(\text{C}_5\text{H}_5)_2)$ is used as the catalyst source. The nanotubes form in the vapor phase and condense onto cold surfaces. However, the transition metal sources vaporize at temperatures much lower than that for the gas phase pyrolysis of the carbon sources and a two zone furnace is generally required to produce CNTs by the unsupported catalyst approach. In this method, smaller catalyst clusters tend to evaporate fast and are very unstable. Very large clusters are also not ideal for nanotube growth because they favor graphitic overcoating. Declustering or breakup of large clusters also happens in the reactor. It is the competition between various processes (clustering and evaporation) that creates favorable size clusters (Dateo et al., 2002). Tuning of various parameters e.g. temperature, flow rates of various gases, injection velocity of the catalyst precursor, residence time, etc., is needed to obtain reasonable quantities of nanotubes. Sen et al. (1997) first reported the unsupported catalyst approach and they used ferrocene or nickolecene as a source of the transition metal and benzene as the carbon source. Nikolaev et al. (1999) used CO disproportionation aided by Fe clusters created from $\text{Fe}(\text{CO})_5$ to grow CNTs. Cheung et al. (2002) reported the synthesis of nanocluster solutions with distinct and nearly monodisperse diameters of 3.2, 9 and 12.6 nm for three different protective agents used, respectively. Addition of protective agents in the solution prevented the nanoparticles from aggregation. Hence, for large scale continuous production of nanotubes, the floating catalyst approach is suitable. But the major drawback is that CNTs can not be grown with site selectivity. Site selective growth of CNTs is a prerequisite for several device applications of CNTs.

The methods for the preparation of catalyst in case of supported catalyst approach can be divided into two categories: one is solution based catalyst preparation technique and the other is the physical evaporation technique. There are numerous methods for preparing catalysts from solutions, for example sol-gel process (Ermakova et al., 2001; Pan et al., 1999), co-reduction of precursors (Chen et al., 1997), impregnation (Venegoni et al., 2002), reverse micelle method (Ago et al., 2000), spin coating of catalytic solution (Choi et al., 2003) etc. Furthermore, it should be noted that a mixture of transition metal containing compounds is used in the above methods. Usually it is difficult to determine the optimum concentration of each constituent in a trial and error approach because the number of trials is large. Cassell et al. (2001) pioneered a combinatorial optimization process for catalyst discovery for the growth of MWCNTs. This rapid throughput approach coupled with characterization techniques allows development of catalyst libraries with minimal number of growth experiments.

In the physical deposition technique, metal can be evaporated or sputtered to be deposited on the substrate. The metal, if deposited at room temperature, will generally be amorphous and form a nearly smooth film on the surface of the substrate. Upon annealing, the equilibrium shape may be reached. To know this shape, the Young's equation describing a contact between two phases A and B and the ambient atmosphere has to be considered:

$$\gamma_A = \gamma_{AB} + \gamma_B \cdot \cos \theta \quad \dots(1.3)$$

where γ is the corresponding interface energies (Figure 1.10).

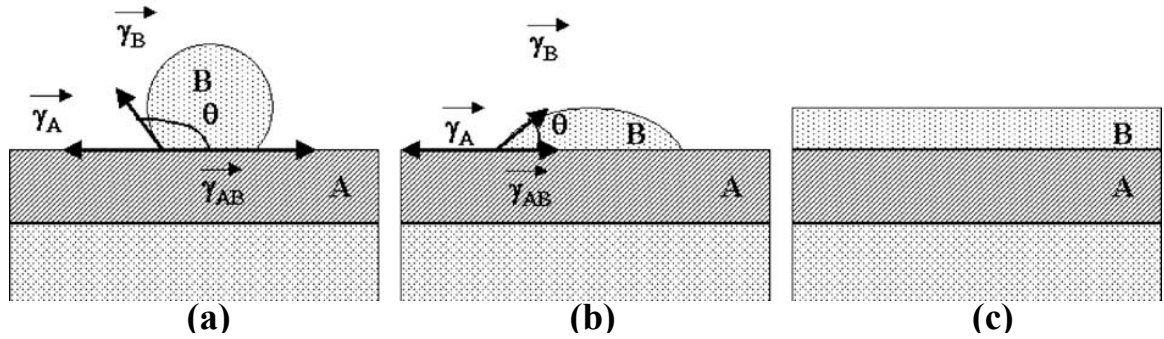


Figure 1.10: Conditions of the surface energies of substrate (A), deposit (B) and interface A–B in determining the type of growth: island or Volmer–Weber growth for (a) non-wetting; (b) wetting and (c) layer-growth

As $\theta \rightarrow 0$, $\gamma_A \rightarrow \gamma_{AB} + \gamma_B$, in this case, the growth is expected to occur layer by layer.

When $\theta > 0$, $\gamma_A < \gamma_{AB} + \gamma_B$ and discrete three-dimensional island-like clusters form as shown in Figure 1.10.

It has been observed that the catalyst on the substrate must be in the form of particles instead of smooth, continuous films. The latter do not appear to yield nanotubes. Thus, the property of island growth is required for obtaining nanoparticles on a substrate by physical deposition. After deposition, usually performed at room temperature, annealing allows the atoms to rearrange themselves and reach the energetically most favored configuration. This method has been widely used to obtain nanoparticles of catalyst material to grow CNT. For breaking up the thin film obtained after deposition, many authors reported the use of NH_3 (Yoon et al., 2002) or H_2 (Wang et al., 2001) during annealing. The surface energies γ_A and γ_B used above are defined relative to the atmosphere gas and thus a change in the gas can dramatically change the final shape of B on A. Delzeit et al. (2001) have shown that introduction of a metal underlayer (such as

Al) can be used instead of any chemical pretreatment steps to create a rough surface. Physical techniques such as electron gun evaporation (Merkulov et al., 2000), thermal evaporation (Chhowalla et al., 2001), pulsed laser deposition (Gao et al., 2003), ion-beam sputtering (Delzeit et al., 2002), and magnetron sputtering (Han et al., 2000) have been successfully used in catalyst preparation.

A wide variety of catalytic species can be used to produce CNTs in CVD growth based on their hydrocarbon decomposition ability, carbon solubility, stability, morphology etc. Different transition metals (e.g. Fe, Ni, Co) and their alloys (e.g. Fe-Mo, Cu-Co, Ni-Ti) have been extensively used to grow CNTs by CVD (Hofmeister et al., 2004; Ižák et al., 2008; Liao et al., 2003; Siegal et al., 2002; Singh et al., 2007; Wang et al., 2001). Noble metals (e.g. Au, Ag) (Takagi et al., 2006), semiconductors (Takagi et al., 2007) and even SiO₂ nanoparticles (Huang et al., 2009) behave as catalyst for nanotube growth. In 2006, Deck and Vecchio described a detailed study of the catalytic growth of CNTs using a wide variety of transition metal catalysts (Deck and Vecchio, 2006). They found that Fe, Co and Ni were the only active catalysts, with Cr, Mn, Zn, Cd, Ti, Zr, La, Cu, V and Gd showing no activity. They suggested that the key to catalytic activity is the solubility of the carbon in the metals. However, metals like Cu, Pt, Pd, Mn, Mo, Cr, Sn, Au, Mg and Al have been used to grow CNTs as reported by Yuan et al. (2008). These observations indicate that the catalyst–growth dynamics–feedstock picture is not yet complete, and there is much more to explore.

1.4.3.2 Growth mechanisms

Thermal CVD relies on thermal decomposition of carbonaceous gas molecules. The general growth process of CNTs by CVD is based on the mechanism proposed by Baker et al. (1972) known as the vapour-liquid-solid (VLS) mechanism (hydrocarbon vapor \rightarrow metal-carbon liquid \rightarrow crystalline carbon solid). The VLS synthesis mechanism can be used in the synthesis of many types of one dimensional nanostructures and generally consists of the three primary steps of absorption, saturation, and structure extrusion. The VLS process is energized by heat, which forces the metal catalyst into a molten state and also begins cracking the carbonaceous gases. Once gas decomposition has started, the carbon species begin to diffuse into the catalyst to form a metal-carbon solution. As more and more carbon elements are incorporated into the catalyst, the concentration of carbon exceeds the solubility limit of the catalyst particle and consequently, the metal-carbon solution become supersaturated. When a supersaturated state is reached, carbon precipitates at the surface of the particle in its stable form and leads to the formation of a carbon tube structure. At this juncture two different scenarios are possible (Figure 1.11).

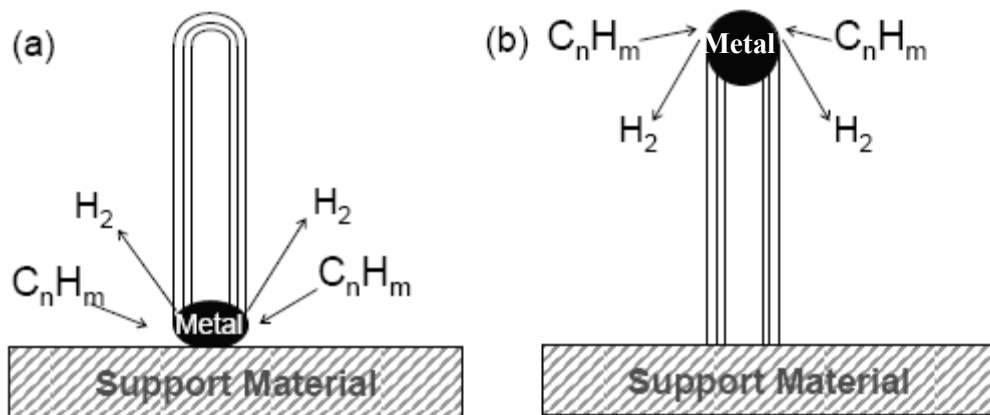


Figure 1.11: Schematic representation of the two typical carbon nanotube growth modes, (a) Base growth mode and (b) Tip growth mode

If the particle adherence to the surface is strong, then carbon precipitates from the top surface of the particle and the filament continues to grow with the particle attached to the substrate. This is called the base growth model. In cases where the particle adherence to the surface is weak, then carbon precipitation occurs at the bottom surface of the particle and the growing filament lifts the particle as it grows. In this case, the top end of the filament contains the catalyst particle, and the resultant scenario is called tip growth. Vinciguerra et al. (2003) suggest that tip growth or root growth of CNTs depends solely on the strength of the interaction of the catalyst particle with the substrate. However, the nature of the driving force for carbon diffusion through the catalyst particles is a subject of debate. The driving force could be temperature (Yang and Yang, 1985) or concentration gradient (Nielsen and Trimm, 1977) within the particle.

The key step in temperature-driven carbon diffusion mechanism was believed to be the diffusion of carbon species through the particle from the exposed and hotter front surface on which the exothermic decomposition of hydrocarbons occurs, to the cooler rear surfaces on which carbon is precipitated (endothermic process) from the solid solution (Baker, 1989). The cooler surfaces are generally in contact with the support face. There is considerable experimental evidence to support this mechanism (Massaro and Petersen, 1971). However, a temperature-driven dissolution-precipitation mechanism cannot provide a rational explanation for the endothermic pyrolysis of some hydrocarbons, e.g. methane decomposition.

Concentration-driven carbon diffusion mechanism involves a concentration gradient across the catalyst particle in contact with hydrocarbon on one side and with a graphitic precipitation on the other side. Carbon growth involves a fast gas phase reaction (decomposition of hydrocarbon), carbon atom dissolution in the metal, and carbon precipitation as graphitic structures at the opposite side of the catalyst particle.

So far it has been assumed that the catalytic growth of CNTs involves the volume diffusion of carbon through a catalyst particle. An alternative mechanism based on surface diffusion of carbon around the catalyst particle (Figure 1.12) was put forward by Baird and colleagues in 1974 (Baird et al., 1974) and elaborated by Oberlin in 1976 (Oberlin et al., 1976). In 2004, Helveg et al. reported the study of nanotube growth using a controlled atmosphere TEM (Helveg et al., 2004). This study provides quite compelling evidence for the surface diffusion mechanism.

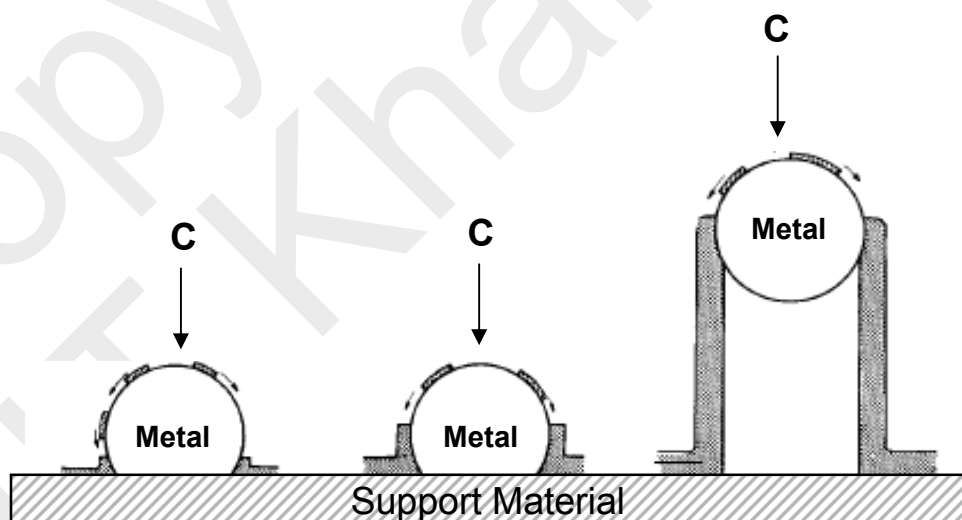


Figure 1.12: An illustration of the growth mechanism based on the surface diffusion of carbon around the metal particle

For a catalyst particle of unchanging size, the growth of CNTs should continue until the hydrocarbon is shut off, either by removing the feedstock from the reaction area or by amorphous or graphitic carbon fully coating the particle, blocking the gas. Additionally, in the case of base growth, growth may slow down or stop due to slow diffusion of hydrocarbons down to the nanoparticle at the bottom of the CNT. If nothing impedes the source of carbon to the nanoparticle, and nothing impedes the nanotube extrusion, the growth should be continuous. In reality, there are competing reactions at the nanoparticle site, such as the formation of graphitic shells and the deposition of amorphous carbon. As a result, in suboptimal growth conditions, amorphous carbon can coat the nanoparticle, preventing feedstock from reacting with the particle and cutting off the carbon source, terminating the growth. Alternatively, if the nanotube exiting the particle encounters an excessive external force, the energy for forming a nanotube might exceed the energy necessary to form a graphitic carbon shell, at which point the nanoparticle will coat itself with a carbon shell, cutting itself off from the carbon feedstock.

1.4.3.3 Growth morphologies

Both SWCNT and MWCNT are produced using catalytic CVD. They often have different morphologies depending on the process parameters. Apart from common structures such as zigzag, armchair and chiral nanotubes in case of SWCNT and hollow MWCNT, some special structures like filled and bamboo-like nanotubes are also observed. Their growth mechanisms can be explained with the help of VLS mechanism and are described in detail in Chapter 3. A unique feature of the bamboo-like CNTs is that they offer high surface area, high density of defects and unique inner closed cells,

which have extended potential applications to electrochemical bio-sensing (Heng et al., 2005) and hydrogen storage (Jang et al., 2005). The application of bamboo-like CNTs as an electrically conductive additive and anode material for lithium ion batteries has also been reported (Zou et al., 2008).

On the other hand, CNTs filled with magnetic materials have important applications in magnetic force microscopy, magnetoresistance sensors, high density magnetic recording media and biology (Kuo et al., 2003; Monch et al., 2005; Palen 2008; Winkler et al., 2006). They can be also used for microwave absorption (Narayanan et al., 2009) and even in medical sciences for drug delivery (Popov et al., 2007).

1.5 Motivation, objectives and organization of thesis

In today's world of nanotechnology, CNTs have become a very promising material and have attracted wide attention both in the research and industrial communities due to their unique structure, novel properties and potential applications. To utilize the unique properties of CNTs in real devices, the nanotubes need to be synthesized over desired substrates. Currently, CVD appears to be the most effective method to achieve this. However, the challenge in the creation of reproducible nanotube-based architectures consisting of arrays of tubes is evidently great. Furthermore, an essential step towards the application of nanotubes is an understanding of nanotube growth and the role of the metal catalyst involved in the synthesis process. Thus, CVD process variables need to be examined intensively to achieve controlled and reproducible growth of nanotubes (Grobert, 2006).

It has been found that the structure of the nanotubes depends on the growth parameters such as reaction temperature, catalyst, reaction gas etc. The growth temperature is especially crucial for selective and controlled growth of CNTs. Unfortunately, despite tremendous progress in synthesizing CNTs, reports on the systematic comparative study of the growth temperature effect on the CNTs are still relatively scarce. Moreover, prior to CNT synthesis, high temperature hydrogen treatment of the catalyst is an important step in order to produce contamination free catalyst and for the removal of the oxides that may exist over the catalyst surface (Takagi et al., 2007). During this procedure, heating above a certain temperature causes catalyst clusters to coalesce and form macroscopic islands. This process is based on cluster diffusion and depends on their density and surface diffusion constant at a given substrate temperature (Jak et al., 2000). These clusters act as a catalyst surface and the cluster size plays a critical role in CNT growth. Therefore, a detailed comparative study on the effects of pre-heating on CNT growth, morphology and microstructure is of importance to achieve a controllable growth of CNTs.

The CVD synthesis of CNTs on plain substrates generally requires catalyst metal deposition over the substrate, which is time consuming and the uniformly deposited area is also finite. These limitations can be overcome by employing spin coating of the catalyst material onto the desired substrate. Moreover, magnetic metal encapsulated CNTs are of great interest due to their distinct magnetic properties compared to the bulk ferromagnetic material (Grobert et al., 1999; Mühl et al., 2003). The cavity of the CNTs can also be used to incorporate metal clusters in order to create novel nanostructured

materials with new electronic or magnetic properties as a consequence of the large surface-to-volume ratio of the confined materials and the interaction between the confined materials and the inner walls of nanotube (Karmakar et al., 2005; Solan et al., 2002). Other than the geometrical advantage of a cylindrical shaped nanostructure design, the carbon shells protect the confined metals from oxidation thus ensuring their long-term stability in the core.

For synthesis of metal filled CNTs, several authors have used a floating catalyst method along with dual zone CVD (Deck and Vecchio, 2005; Leonhardt et al., 2003; Müller et al., 2006; Zhang et al., 2002). The obtained CNTs are in bundles grown on the CVD reactor walls or vertically aligned on Si substrates. However, there are many technical barriers to achieve magnetic metal encapsulated CNT-based electronic devices. The placement of CNTs in the desired position is crucial for CNT integration in such devices. From a practical point of view, to achieve CNT-based electronics, the growth and placement of CNTs should be executed in a manner compatible with current microelectronic processes for large scale fabrication. In this regard, photolithography is one of the most important and effective patterning techniques for microfabrication and is comprehensively used in integrated circuit technology. The lithographically patterned growth approach is feasible with discrete catalytic nanoparticles and scalable on large wafers for producing massive arrays of magnetic material filled CNT.

Objectives of the present investigation

Taking into account the above scope the following objectives were adopted for the investigation

1. To understand the effect of CVD process variables on CNT growth and improve the quality
 - i) Catalyst
 - a) Variation in physical form of catalyst (elemental metal and metal complex)
 - b) Variation of catalytic element (Fe and Ni)
 - ii) Temperature
2. To demonstrate site selective growth of catalyst filled CNTs using a simple process.

Organization of the thesis

This thesis focuses on the growth of MWCNTs on Si using the CVD technique in a resistance heated furnace, the characterization of the CNTs using standard techniques and the improvement of the growth quality with site selectivity. The whole thesis is organized into five chapters. The structure of the thesis is as follows: Chapter 1 contains a general introduction to CNT and the current directions in research related to this material. The experimental details of the growth procedures and characterization techniques which have been used in this thesis have been described in Chapter 2. The results of the growth of MWCNTs on Si(111) substrates using elemental metal catalyst by CVD and the influence of different experimental parameters such as growth temperature, pre-heating temperature and nature of catalytic elements on nanotube growth are presented in Chapter 3. Chapter 4 discusses the results obtained from experiments performed using metal complex as catalyst. Lithographically defined site selective growth of partially catalyst filled MWCNTs is also described. Finally, the thesis concludes with a summary in Chapter 5.