Chapter-2
2.1 Introduction

The objective of this thesis, as stated in the introductory chapter, is to characterize and measure mechanical and electrical properties of MWCNT grown by the chemical vapour deposition (CVD) method. In this chapter, the preparation process for the MWCNT as adopted in this thesis will be provided. The descriptions include, particulars for the used CVD setup, the precursors, the catalyst the substrate for growth of MWCNT and the process parameters such as pressure temperature, growth time, etc., will be provided.

Prior to the above, a brief review of available methods as available in the literature has been presented that has helped to decide for the suitability of the process as well as related relevant particulars and parameters for preparing specimen MWCNT to be characterized and measured for mechanical and electrical properties, according to the object of the thesis.

There are a number of methods of making carbon nanotubes (CNTs) and fullerenes. Fullerenes were first observed after vaporizing graphite with a short-pulse, high-power laser, however this was not a practical method for making large quantities. CNTs have probably been around for a lot longer than was first realized, and may have been made during various carbon
combustion and vapor deposition processes, but electron microscopy at that time was not advanced enough to distinguish them from other types of tubes.

2.2 Plasma arcing

The first method for producing CNTs and fullerenes in reasonable quantities was by applying an electric current across two carbonaceous electrodes in an inert gas atmosphere. This method is called plasma arcing. It involves the evaporation of one electrode as cations followed by deposition at the other electrode. This plasma-based process is analogous to the more familiar electroplating process in a liquid medium. Fullerenes and CNTs are formed by plasma arcing of carbonaceous materials, particularly graphite. The fullerenes appear in the soot that is formed, while the CNTs are deposited on the opposing electrode. Another method of nanotube synthesis involves plasma arcing in the presence of cobalt with a 3% or greater concentration. As noted above, the nanotube product is a compact cathode deposit of rod like morphology. However when cobalt is added as a catalyst, the nature of the product changes to a web, with strands of 1 mm or so thickness that stretch from the cathode to the walls of the reaction vessel. The mechanism by which cobalt changes this process is unclear, however one possibility is that such metals affect the local electric fields and hence the formation of the five-member rings. [1]

2.3 Arc Method

The carbon arc discharge method, initially used for producing
C50 fullerenes, is the most common and perhaps easiest way to produce CNTs, as it is rather simple. However, it is a technique that produces a complex mixture of components, and requires further purification to separate the CNTs from the soot and the residual catalytic metals present in the crude product.

Arc discharge provides a simple method for vaporizing of carbon into plasma, that lead to the formation of high quality CNTs. An illustration of a typical carbon arc discharge apparatus is shown in figure 2.1. The anode and cathode are carbon rods of 5-20 mm in diameter, and the anode can be moved so that the optimum distance between the anode and cathode can be maintained continuously as the end of the anode is evaporated during CNT growth. The voltage across the anode and cathode is around 20 - 25V DC with a current in the range of 50 - 120A. During operation helium flows through the chamber with a flow rate of 5-15 ml/s and the pressure in the chamber is typically in the order of 500 torr [1].

The CNTs are produced in bundles in the inner region of the cathode, where the temperature is highest. The bundles are aligned in the direction of the current. The yield of CNTs and exactly what kind of CNTs produced are very much dependent on the conditions during growth, even though the spread in diameter is usually narrow.
Fig 2.1

Schematics of an arc discharge apparatus. The anode and cathode, both made primarily of carbon, are positioned at optimal distance while a high current is passed from the anode to the cathode making an arc discharge. During this arc discharge a carbon plasma is formed, and CNTs are deposited on the cathode.

The maximum yield obtained is around 20 % of the evaporated graphite and this is only in the center of the cathode. Also by using different catalyst in the graphite rods it is possible to promote the formation of specific kinds of CNTs, i.e SWCNTs, MWCNTs, ropes of SWCNTs, or bundles of SWCNTs.

Other carbon particles are deposited on the walls of the chamber.
and around the CNTs.

The arc discharge method is a simple and cheap way of synthesizing nearly defect-free CNTs. One of the many drawbacks of this method compared to other methods is the poor control of the deposition area. There is no way to produce the CNTs at a desired position in a device using arc discharge. Furthermore the formed CNT will be mixed with several other carbon particles and the need for purification is obvious.

Producing CNTs in high yield depends on the uniformity of the plasma arc, and the temperature of the deposit forming on the carbon electrode. [1]

2.4 Laser Methods

In 1996 CNTs were first synthesized using a dual-pulsed laser and achieved yields of >70wt% purity. Samples were prepared by laser vaporization of graphite rods with a 50:50 catalyst mixture of Cobalt and Nickel at 1200°C in flowing argon, followed by heat treatment in a vacuum at 1000°C to remove the C50 and other fullerenes. The initial laser vaporization pulse was followed by a second pulse, to vaporize the target more uniformly. The use of two successive laser pulses minimizes the amount of carbon deposited as soot. The second laser pulse breaks up the larger particles ablated by the first one, and feeds them into the growing nanotube structure. The material produced by this method appears as a mat of "ropes", 10-20nm in diameter and up to 100pm or more in length. Each rope is found to consist primarily of a bundle of single walled nanotubes, aligned along a common axis. By varying the growth
temperature, the catalyst composition, and other process parameters, the average nanotube diameter and size distribution can be varied.

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 evaporating the carbon source, so it has been unclear how to scale up production to the industrial level using these approaches. 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. [1]

A very efficient way of synthesizing ropes of SWCNT is by using a powerful laser to evaporate a sample primarily made up by graphite. The principle of production is shown in figure 2.2. The graphite (mixed with a small amount of transition metals) target is situated in a furnace, and hit by a laser beam. Opposite the laser is water cooled copper collector just outside the furnace. A steady flow of argon from the laser to the copper collector makes the vaporized carbon flow from the target to the collector, where it will deposit and form ropes of SWCNTs.

The ropes of SWCNT produced will typically have diameters in the range from 10-20 nm and length up to 100 gm. The individual SWCNT have diameters in the range from 1-3 nm.
**Figure 2.2**

*Schematics of a laser ablation apparatus. In this case a Nd YAG laser hits the graphite target heated to 1200 °C and carbon is evaporated. The steady flow of argon sweeps the carbon to the water cooled copper collector, where the carbon deposits forming ropes of SWCNT.*

The distribution of diameters is usually very narrow and the diameter depends on the transition metals mixed in the graphite target as well as temperature, and other experimental parameters.

The laser ablation method is probably the best way of making defect free SWCNT. The drawback of this method is, as in the case of the arc discharge method, the poor control of deposition
area, making the method useless in a device fabrication process.

Furthermore the method is rather costly because of the high powered lasers involved.

2.5 Chemical Vapor Deposition

Chemical vapor deposition of hydrocarbons over a metal catalyst is a classical method that has been used to produce various carbon materials such as carbon fibers and filaments for over twenty years. Large amounts of CNTs can be formed by catalytic CVD of acetylene over Cobalt and iron catalysts supported on silica or zeolite. The carbon deposition activity seems to relate to the cobalt content of the catalyst, whereas the CNTs' selectivity seems to be a function of the pH in catalyst preparation. Fullerenes and bundles of single walled nanotubes were also found among the multi walled nanotubes produced on the carbon/zeolite catalyst.

Some researchers are experimenting with the formation of CNTs from ethylene. Supported catalysts such as iron, cobalt, and nickel, containing either a single metal or a mixture of metals, seem to induce the growth of isolated single walled nanotubes or single walled nanotubes bundles in the ethylene atmosphere. The production of single walled nanotubes, as well as double-walled CNTs, on molybdenum and molybdenum-iron alloy catalysts has also been demonstrated. CVD of carbon within the pores of a thin alumina template with or without a Nickel catalyst has been achieved. Ethylene was used with reaction temperatures of 545°C for Nickel-catalyzed CVD, and 900°C for
an uncatalyzed process. The resultant carbon nanostructures have open ends, with no caps. Methane has also been used as a carbon source. In particular it has been used to obtain 'nanotube chips' containing isolated single walled nanotubes at controlled locations. High yields of single walled nanotubes have been obtained by catalytic decomposition of an H\textsubscript{2}/CH\textsubscript{4} mixture over well-dispersed metal particles such as Cobalt, Nickel, and Iron on magnesium oxide at 1000°C. It has been reported that the synthesis of composite powders containing well-dispersed CNTs can be achieved by selective reduction in an H\textsubscript{2}/CH\textsubscript{4} oxide such as Al\textsubscript{2}O\textsubscript{3} or MgAl\textsubscript{2}O\textsubscript{4} and one or more transition metal oxides. The reduction produces very small transition metal particles at a temperature of usually >800°C. The decomposition of CH\textsubscript{4} over the freshly formed nanoparticles prevents their further growth, and thus results in a very high proportion of single walled nanotubes and fewer multi walled nanotubes. [1] Chemical vapor deposition (CVD) is a collective name for several different methods.

They all involve the vaporization of carbon and the use of catalyst particles. The carbon vapor is supplied by a hydrocarbon. The hydrocarbon is heated in a two zone flow reactor with a steady low flow of H\textsubscript{2} in some cases mixed with an inert carrier gas. The gas flow transports the carbon molecules to a zone with a higher temperature (around 900- 1100°C) where a reaction happens on the catalyst particles creating CNTs. The catalyst particles are either contained in the hydrocarbon such as iron(II) phthalocyanine (A zone 1 temperature of 550±°C is used) [36] or deposited on a surface by means of imprint, electron beam deposition, or a lithography method.
Figure 2.3
Schematics of a two zone flow reactor. The hydrocarbon is placed in a zone with a temperature that vaporizes the hydrocarbon (Yellow). A steady flow of H2 transport the carbon molecules to a zone with a temperature of 900-1100°C (Red) where a reaction takes place on catalyst particles creating MWCNT.

The use of a deposited catalyst particles has a great advantage compared to methods were the catalyst is supplied in the hydrocarbon. The exact growth positions for the CNT can be determined. Electric field alignment can also be controlled revealing great perspectives in terms of integrating CVD-grown CNT in actual electrical devices.

The diameter and number of shells can to some extend be controlled by the type and size of catalyst particles as well as source gas. The growth is also dependent on parameters such as
Temperature and gas-flow. Usually the CVD process makes MWCNTs with a relatively high defect density.

2.6 Ball Milling

Ball milling and subsequent annealing is a simple method for the production of CNTs. Although it is well established that mechanical attrition of this type can lead to fully nano porous microstructures, it was not until a few years ago that CNTs of carbon and boron nitride were produced from these powders by thermal annealing. Essentially the method consists of placing graphite powder into a stainless steel container along with four hardened steel balls. The container is purged, and argon is introduced. The milling is carried out at room temperature for up to 150 hours. Following milling, the powder is annealed under an inert gas flow at temperatures of 1400°C for six hours. The mechanism of this process is not known, but it is thought that the ball milling process forms nanotube nuclei, and the annealing process activates nanotube growth. Research has shown that this method produces more multi walled nanotubes and few single walled nanotubes. [1]

2.7 Other Methods

CNTs can also be produced by diffusion flame synthesis, electrolysis, use of solar energy, heat treatment of a polymer, and low-temperature solid pyrolysis. In flame synthesis, combustion of a portion of the hydrocarbon gas provides the elevated temperature required, with the remaining fuel conveniently serving as the required hydrocarbon reagent.
Hence the flame constitutes an efficient source of both energy and hydrocarbon raw material. Combustion synthesis has been shown to be scalable for high-volume commercial production. [1]

The CVD process has appeared as the most promising method in CNT synthesis due to its relatively low cost and high yield production. It has been applied both in the absence and in the presence of a substrate. The former is a gas phase homogeneous process based on the decomposition of two precursors, one for the metal catalyst and the other for carbon. The latter is a heterogeneous process which uses either bulk catalysts or supported catalysts. Both processes appear very sensitive to the nature and structure of the catalytic system and to the operation conditions.

2.8 Powder catalysts vs supported catalysts

Baker and coworkers have undertaken extensive studies of CNF (Carbon Nano Fibers) production using a series of unsupported mono and bimetallic catalyst powders [2-8]. Unsupported powder catalysts are highly efficient for a high CNF yield [9, 10], but lead mainly to the production of CNFs. Another major shortcoming of power catalysts is that one has little control over the size and structures of the final CNFs. This is mainly due to the uncontrolled changes of the catalyst precursors during the reduction and subsequent carbon growth processes. In order to produce small structured CNFs with a controlled size, it is necessary to disperse the metal catalyst particles on a suitable support [9].
Anderson et al. [11, 12] demonstrated that major modification in the growth of CNFs can be achieved when metals are used in a supported form than in a powder form. The use of support material generated CNFs with width dictated by the dimensions of the supported metal particles [11]. The support may also alter the precipitation faces of the catalyst particle, which in turn influences the structural characteristics of the CNFs. For example, CNFs grown from iron powder from CO/H₂ at 600°C possess a platelet structure, whereas CNFs grown on the silica supported iron possess a tubular structure [9].

Therefore, using supported catalysts is essential for the control of both the size and morphologies of the catalyst particles. Nevertheless, the use of supported catalysts suffers the problem of removal of the support without damage to the carbon. More seriously, only a low productivity can be achieved, most probably due to the low active metal loading, but also possibly due to the metal support interaction, which is not favored for a high carbon yield [13].

2.8.1 Catalyst supports

While powder and supported metals exhibit different reactivity and CNT growth characteristics, metals on different supports seem also to have different activity and CNT growth due to different nature and strength of the metal-support interactions. The effects have been manifested in many studies [13-17].

Park et al. [14] studied the catalyst support effects in the carbon growth from ethylene decomposition on supported Ni catalyst. It was found that the characteristics of CNFs generated
can be readily manipulated by a judicious choice of the support materials. The occurrence and ramifications of Ni/support interactions, in terms of Ni particle size/morphology/orientation, are related to the carbon structure/dimensions and yield. de los Arcos et al. [17] found that formation of thin tubes and fast growth rate were associated with the underlying Al2O3 layer, whereas thick MWNTs were grown from Fe on the TiN and TiO2 layers. The influence has been attributed to a combination of chemical and morphological changes induced in the catalyst due to the catalyst-substrate interaction.

The support may have impact on the product quality. Li et al. [18] found that MgO was the best for CNT synthesis from methane decomposition compared with other supports such as SiO2, Al2O3, ZrO2 and CaO.

The support effects have also been documented quite extensively by the B.Nagy group [19-22]. Interestingly, for acetylene and methylacetylene decomposition on supported Ni, Co, or Fe catalysts, Hernadi [22] disclosed that the catalyst supports have more influence on CNT selectivity than the metallic particle itself.

A good summary of the effects of metal-support interaction was given by Anderson et al. [11]: it induces electronic perturbations throughout the metal; it generates significant differences in metal morphology and the arrangement of the surface atoms; it exerts an influence of the growth characteristics of the supported metal particles; and it possibly modifies the chemistry of the system.
2.8.2 Catalyst precursors

The growth rate, diameter, and crystallinity of the CNTs can be manipulated by the selection of the catalyst precursors. Several studies have focused on supported Ni, Fe, Co catalysts for CNT growth from acetylene decomposition [23-26]. Lee et al. [23] used silicon support and found that the growth rate shows the order of Ni > Co > Fe. The average diameter follows the sequence of Fe, Co, and Ni. The structures of CNTs reveals almost same morphology regardless of catalyst but the crystallinity is better from Fe than Ni and Co. Soneda et al. [25] used MgO support and found that Co is the most effective catalyst for MWNT synthesis, because of a significantly high production rate and high quality tubes with a narrow diameter distribution. Huang et al. [26] used TiO₂ support and concluded that Ni is the best catalyst for the growth of aligned CNTs. Therefore, the outcome of the CNT synthesis is a complex interplay among the metal precursors, the support, and the reaction conditions.

When the transitional metals are alloyed with another metal, both the carbon yield and the structure of the CNTs can be changed dramatically. This has been demonstrated most extensively by Baker and co-workers with powder catalysts [6, 7, 27]. They have been able to tailor the carbon nanostructures by designing different alloy catalysts. For supported metal catalysts, a similar effect has been observed [28-30]. The ratio of bimetallic catalyst is also important [9, 31]. For CO decomposition on Co-Mo catalysts at 700°C, it was found that a particle with low Co content (<15 at.%) tends to produce a long CNT, while a particle with high Co content (>85%) tends to
produce onion-like structure [31].

Even the origin of the metal precursors [32] or the catalyst preparation procedures [33] might play a role. Serp et al. [32] found that among iron chloride, iron sulphate, and iron carbonyl, Fe$_3$(CO)$_{12}$ was the best precursor, producing longest fibers from methane.

2.8.3 Gas precursors

Systematic studies of the relationship between the nature of the carbon-containing gas and the structure of the resulting CNFs are very scarce. The intrinsic activity of the gases will of course determine the CNF growth rate over different catalysts. Hernadi et al. [34] observed that over supported iron or cobalt catalysts, the activity of acetylene is higher than that of ethylene and propylene, which are in turn higher than methane. Flame synthesis of CNTs has shown that Fe reacts preferentially with CO/H$_2$ to produce SWNTs, while Ni reacts preferentially with C$_2$H$_2$/H$_2$ to produce nanofibers [35]. Therefore, the activity of the gases seems to be metal dependent which again illustrates the complex interplay between the gases and the metal precursors.

Interestingly, Toebes et al. [36] reported opposite reactivity of CNF production from the decomposition of CH$_4$, CO/H$_2$, or C$_2$H$_4$/H$_2$ over supported Ni or powder Ni catalyst at 550°C. They found that the small supported Ni particles need gases with a relatively low activity, like CH$_4$ or CO to produce CNFs. The large unsupported Ni only produces CNFs using C$_2$H$_4$. The CNF yield has been attributed to a subtle interplay between the nickel particle size and consequently the exposed crystal planes on the
one hand and the reactivity of the gases on the other.

Otsuka et al. [37] have shown the effect of the gas precursors on the structure and crystallinity of the CNFs from the decomposition of different hydrocarbons on Ni/SiO2 catalysts. Zigzag fiber structure was formed from methane, and a rolled fiber structure was formed from alkenes and acetylene. The degree of CNF graphitization was in the order, alkanes > alkenes > acetylene.

2.8.4 Temperature

The temperature appears to influence the CNT yield differently depending on the specific reaction system. Kukovecz et al. [38] reported that the amount of CNTs increases with increasing temperature from acetylene decomposition. Takenaka et al. [39] found that the CNF yield decreases with increasing temperature from methane decomposition. The CNT yield might also decrease with temperature due to catalyst particle sintering at high temperatures [40].

The effect of temperature on the structures of CNTs has been investigated on Fe/SiO2 by acetylene decomposition from 600 to 1050°C and gas pressure of 0.6 and 760 Torr. At low gas pressure, the CNTs are completely hollow at low temperature and bamboo-like at high temperature. While at 760 Torr, all the CNTs are bamboo-like structure regardless of temperature [41]. Therefore, the effect of temperature on carbon structures depends on the gas pressure. Takenaka et al. [39] reported fishbone CNFs at 500°C but MWNT at 700°C from methane decomposition on Ni/SiO2. In addition, the diameter and
diameter distribution of the nanotubes will increase with increasing temperature [41-43].

Finally, the reaction temperature influences the graphitic order of CNFs. It has normally been found carbon fibers with more ordered or more disordered carbon after growth at high and low temperatures, respectively [44, 45].

2.8.5 Pressure

Studies of the effect of gas pressure on the production of CNTs and CNFs are less performed. Higher pressures will normally increase the carbon yield but decrease the CNT selectivity [46, 47]. From acetylene decomposition over supported Fe and Co catalyst, Hernadi et al. [46] reported that carbon deposit increases with higher pressure, but leads to worse selectivity and many other kinds of carbon structures.

Some studies have observed an optimum partial pressure [48-50]. Liu et al. [48] discovered a critical methane partial pressure (-0.4 atm) for SWNT synthesis on supported Fe catalyst. Below this value, the production rate is proportional to the partial pressure. Li et al. [50] found that the yields of CNTs increase significantly with the gas pressure from acetylene decomposition over Fe/SiO₂ catalyst, reached 600% at 600 Torr and then decreases with further increase of gas pressure. Li et al. [50] also observed a change in the internal structures: completely hollow structure at low pressure but bamboo structure at high pressure.
2.8.6 Hydrogen

The role of hydrogen has been described quite extensively in both the VGCF and CNT literature. Hydrogen is known to either accelerate [40, 51-53] or suppress [42] the formation of CNTs. The most significant effect of hydrogen is to change the orientation of the graphite sheets [44, 51], which has been illustrated nicely by Jiao and Nolan. Jiao et al. [54, 55] found that when no hydrogen was present, only closed forms of carbon deposits such as MWNTs were produced from CO. As the hydrogen partial pressures increased to 0.1 vol%, the filament with open edges was observed. The number of open edges and the angle between the graphite sheets and the axis increased with increasing H$_2$ concentration. Nolan et al. [56] found that carbon deposition from CO resulted in encapsulated carbon only when hydrogen was absent. Nolan et al. [57] proposed that hydrogen atoms serve to satisfy valences at the free edges of graphite sheets. Without hydrogen, carbon will deposit in closed forms such as shells and nanotubes. Equations were derived to calculate the minimum number of hydrogen atoms necessary to form a CNF. Nolan et al. [58] further derived thermodynamic expressions for the relationship between filament cone angle and hydrogen partial pressure. Therefore, the orientation of graphite basal planes of carbon filaments can be tailored.

2.8.7 Particle size

Though it is widely accepted that the final CNT diameter is determined by the starting catalyst particle size, the relationship between tube diameters and sizes of initial catalyst particles can
be complicated by particle mobility, sintering and redispersion. Catalyst particles could either be aggregated by contact with the reactant [59], or be changed by the deposited carbon [60]. Kukovitsky et al. [61] investigated more systematically the dependence of CNT diameter on the size of the Ni catalyst: At low temperature of 700°C, the nanotube growth is conducted through the solid tip catalyst and the tube diameter reproduces essential features of original particle size distribution. At 800°C, it grows via liquid catalyst particle by extrusion mode and tubes exhibit universal Gauss-like distribution irrespective of the catalyst particle sizes.

Recently it has been noticed that the catalyst particle size is an important factor in CNT growth rate [39, 62, 63]. Indeed, it has been shown decades ago both experimentally and theoretically that the carbon filament growth rate increases with decreasing catalyst particle size [64, 65]. Some recent studies showed that the CNT growth rate and productivity are higher on the larger particles [66], while others found that the growth rate is higher on smaller particles [16]. This suggests that there is probably an optimum particle size for CNT growth, which has been implicitly demonstrated [47, 67, 68]. Peigney et al. [47] examined the decomposition of CH₄/H₂ on a-Al₁.₉Fe₀.₁₀ solid solution. Almost all the CNTs have an inner diameter in the range of 1-6 nm, indicating that the catalyst particles active for CNT formation are in this size range. Another study showed that the hematite particles with a 8-20 nm size range are involved in the formation of MWNTs during C₂H₂ decomposition at 700°C [67]. In addition to the above discussed parameters, other factors such as run duration [40, 69], phosphorus [70], and
sulfur [71, 72] etc. have been found to influence the CNF and CNT growth.

Therefore, the growth of CNTs is a very complex process which involves the interplay of all the process parameters.

The synthesis of SWNT needs additional notice. The lack of methods for large scale synthesis has limited fundamental research and application development of this unique material. A yield of 550% relative to the weight of metal [73], or 120% to 200% [74, 75] relative to the catalyst weight has been claimed as very high.

It is very important that the metal particles are not aggregated during the SWNT growth process [69, 76]. Li et al. [77] demonstrated an upper limit size of 8.5 nm to nucleate SWNT over Fe-Mo catalysts dispersed on $\text{Al}_2\text{O}_3$ film. Particle aggregation could be prevented by providing a nucleating agent such as Mo, Ru, and W, in addition to catalyst precursors, which would rapidly adsorb the precursor atoms (Fe, Co, Ni) [76]. Therefore, the catalysts consist of Fe-Mo [78-80] or Co-Mo [81-84] bimetallic species have been very frequently used. Other special catalyst precursors have also been studied, for example ferritin [85-87], nickel formate [88], or ferrocene [89]. Mo provides a synergistic effect to Fe in SWNT synthesis [90]. The interaction mechanism was studied by Hu et al. [91], and has been systematically investigated by Alvarez et al. [82-84]. It was concluded that the catalysts are effective when both metals are simultaneously present. When they are separated they are either inactive (Mo alone) or unselective (Co alone). The selectivity of the Co-Mo catalysts toward SWNTs depends on the
stabilization of Co species in a nonmetallic state before exposure to the carbon containing gases [92]. If Co-Mo interaction is disrupted, SWNT selectivity decreases sharply [93]. The Co-W synergism has been disclosed accordingly [94]. With respect to the catalyst support, MgO seems to be the preferable support for SWNT growth [95]. MgO is easier to be removed and provides higher yield with a smaller diameter compared with for example Al₂O₃ [96]. The gas sources used in the synthesis of SWNT are mostly methane, though CO, ethylene or acetylene have been frequently used. The most successful process up to now is the HiPCO process [76, 97], in which the production of SWNTs is induced by the decomposition of Fe(CO)₅ in flowing CO at high pressure and elevated temperature. Iijima et al. [98] very recently reported a breakthrough in the synthesis of SWNTs. By adding water to the standard SWNT synthesis scheme, the yields reached astonishingly 50000% relative to the starting metal. The results are so remarkable, suggesting that large scale synthesis of SWNTs is no longer a dream.

2.9 Critical and Comparative View for CNT Fabrication Methods

The above descriptions review many interesting and successful attempts to grow CNTs by Various methods. However, as the related publications in the literature reveal, the three most widely used techniques are: arc- discharge, laser ablation/laser furnace, and chemical vapor deposition (CVD) and its variant plasma enhanced CVD (PECVD). In the following a critical and comparative view is presented showing the merits/demerits of these three
methods.

The Table 2.1 summarizes some of significant feature for the arc-discharge, laser ablation and CVD methods. The content of the table are self evident for an easy and quick evaluations of the three methods also including the PECVD as a variant of CVD. In addition to the above summary, observations for some more specific features for the three methods under context will made in the following.

**Arc-discharge**
- The crystallinity and perfection of arc-produced CNTs are generally high, and the yield per unit time is also higher than other methods.
- Both MWCNT and single-wall CNT (SWCNT) can be produced. Industrial methods also have been developed (such as Plasma-jet Arc-discharge method)
- It is hard to grow aligned CNTs (SWCNTs or MWCNTs) by arc discharge, although partial alignment of SWNTs can be achieved by convection or directed arc plasma.
- The growth temperature of the arc-discharge method is higher than that of other CNT production methods.
- A major drawback of the method is a poor control of deposition of CNT in a desired area.
- The CNT products contain a large amount of other C particles or carbonous structures requiring extensive purification.
Laser Ablation

- High-quality SWCNTs with minimal defects and contaminants, such as amorphous carbon and catalytic metals, have been produced using the laser-furnace method.
- As high-quality SWCNT production method with easier diameter control, by controlling laser intensity for lesser contaminants, such as carbon and catalytic metals the purification processes are simpler.
- Highly crystalline and pure useful for scientific investigations and study of growth dynamics.
- The future research for SWCNT owing to their unique electronic properties, makes this approach preferred and even indispensible, at present, for preparing SWCNT.
- The drawback of this method, similar to arc-discharge, is a poor control of deposition of CNT in a desired area.
- The laser method for CNT is expensive requiring costly laser furnace set-up.

CVD-CNT

- CVD-CNT production is easy to scale up thus has industrial and commercial significance.
- It is versatile in that it harnesses a variety of hydrocarbons (precursors) in any state (solid, liquid, or gas), enables the use of various substrates, and allows CNT growth in a variety of forms, such as powder, thin or thick films.
- A significant advantage of CVD-CNT is ability to grow a desired architecture of nanotubes at predefined sites on a patterned substrate. CVD is ideally suited to growing aligned CNTs on desired substrates for specific applications, which is not feasible by arc or laser methods.
MWCNT are routinely prepared in laboratories as well as commercially. The Single wall CNT (SWCNT), though experimented, their CVD methods are not yet well established and this as present is a disadvantage of CVD method compared to arc and laser based methods.

Another disadvantage of CVD-CNT is that the structural order/crystallinity is poor and hence also of inferior mechanical and electrical properties.

### 2.10 The CVD method as adopted in the Present Thesis

In accordance with the object as stated in chapter 1, the required specimen of MWCNT for investigations in the present thesis, were fabricated by the catalytic CVD method. The CVD set-up used for growing MWCNT is shown schematically in Fig. 2.4.

The CVD reactor (Fig. 2.4) consists of a horizontal quartz tube (100 cm long, 4.2 cm in diameter) housed in a cylindrical electrical furnace of length (60 cm) such that quartz tube extends out as shown in the figure. The set-up also comprises an arrangement for laminar gas flow such as $\text{N}_2$ as a carrier gas. Inside the quartz tube, a constant nitrogen gas flow is required to be maintained at pressures slightly above the atmospheric, in order to provide the condition for a laminar gas flow. A Pyrex flask containing the reagent mixture composed of precursors for the carbon source and the catalyst precursor in a 20:1 mass ratio was connected, via a T joint, to the tube close to the nitrogen inlet. A heater plate was located below the flask.

The choice for the precursors, both for the carbon source and the catalyst has been influenced by several studies reporting encouraging results fo MWCNT. It is found that, ferrocene (98%

In the first step of the process, the residual air in the Quartz reactor tube is purged-of by means of a pure nitrogen flow. The furnace is then heated to the growth temperature in a range between 700° and 900°C. Subsequently, the pyrex flask containing the camphor/ferrocene mixture is heated up to 220°C leading to the vaporization of reagents, and the gases are carried into the furnace by the nitrogen gas flow. The high temperature in the reactor tube causes the pyrolysis of the gaseous form of precursors and the carbon species are deposited on the substrates placed in the hot zone region that is approximately 30 cm. After allowing a suitable growth time the furnace is switched off. Upon cooling down to room temperature, a deposit of carbon is found on the inner tube wall and the substrates. The method used is typical of some of CVD-MWCNT studies in literature with certain incidental modifications as suitable to the present study. The following range of process parameters have been experimented to arrive at the most suitable growth/deposition process parameters.
for the MWCNT specimen-
- furnace temperature (700, 800 and 900 °C),
- carrier gas flow rate (100, 500, 1500 ml/min),
- substrate tilt with respect to gas flow (0°, 45° and 80°).
- metal catalyst (ferrocene) concentration (2.5, 3.3 and 5.0 wt%)
- substrates: Quartz and Silicon placed at a tilt (0° 30°, 45°) with respect to gas flow.

Among the above range of growth parameters, it has been found that the growth temperature is the most influential in controlling the CNT diameter. A low catalyst concentration (3.3 wt%) led to the growth of CNTs of diameter ~20 nm. The only parameter entirely not correlated to the others was the substrate tilt with respect to gas flow. CNTs with better physical and structural characteristics were obtained at a growth temperature of 800°C, 420ml/min carrier gas flow, 3.3% catalyst concentration with the silicon substrate being preferred. The tilt of substrate made little difference to the properties of the grown MWCNT.

Fig 2.4 The CVD set-up used in the present study for the growth of MWCNT using ferrocene as precursor for Fe catalyst and camphor as source for Carbon
Table 2.1 Summarized features of Arc-discharge, Laser ablation/furnace, CVD /Plasma enhanced CVD methods for growing MWCNT

<table>
<thead>
<tr>
<th>CNTs production methods</th>
<th>Arc Discharge</th>
<th>Laser Ablation</th>
<th>Thermal Chemical Vapor Deposition</th>
<th>Plasma-Enhanced CVD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Summary</td>
<td>Graphite evaporated by a plasma via high currents</td>
<td>Graphite blasted with intense laser pulses</td>
<td>Decomposition of hydrocarbon gases at high temperature</td>
<td>Metal catalysts nucleate growth of CNTs with help of plasma effects</td>
</tr>
<tr>
<td>Yield</td>
<td>30%</td>
<td>Up to 70%</td>
<td>20 to ~100%</td>
<td>Up to 90%</td>
</tr>
<tr>
<td>Fabrication Temperature</td>
<td>5,000-8,000 °C</td>
<td>1,000-3,000 °C</td>
<td>800-1,500 °C</td>
<td>500-800 °C</td>
</tr>
<tr>
<td>Advantages</td>
<td>Less structural defects of CNTs</td>
<td>Produces SWNTs; diameter control via reaction temperature</td>
<td>Easiest to scale to industrial production</td>
<td>Excellent structures; great uniformities and alignments</td>
</tr>
<tr>
<td>Disadvantages</td>
<td>Tubes tend to be short and highly entangled</td>
<td>More expensive than the other methods</td>
<td>Typically MWNTs with a high density of defects</td>
<td>Production rates still relatively low</td>
</tr>
</tbody>
</table>