A Dissertation
on

"SYNTHESIS OF CARBON NANOTUBES USING FERROCENE BY THERMAL CVD TECHNIQUE"

Submitted in partial fulfillment of the requirements for the award of degree of

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in
Nanoscience and Technology

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CERTIFICATE

This is to certify that the report entitled **“*Synthesis of Carbon Nanotubes using ferrocene by Thermal CVD technique*”** submitted by ***Surendra Pratap Yadav***, Roll. No. ***2K12/NST/21***, in partial fulfillment for the award of degree of Master of Technology in Nanoscience and Technology at ***Delhi Technological University, Delhi***, is a bonafide record of student’s own work carried out by him under my supervision and guidance in the academic session 2013-14. The matter embodied in dissertation has not been submitted for the award of any other degree or certificate in this or any other university or institute.

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Table of Contents

Certificate……………………………………………………………………i

Acknowledgment………………………………………………………ii

Table of Contents…………………………………………………..……..iii

List of Figures………………………………………………………….……iv

Abstract……………………………………………………………...……v

Chapter1 7

1.1 Introduction...**Error! Bookmark not defined.**

1.2 Types of Carbon Nanotubes...8

1.2.1 Single-Walled Carbon Nanotubes...8

1.2.2 Multi-Walled Carbon Nanotubes..9

1.2.3 Nanobud...10

1.3 Properties of Carbon Nanotubes..11

1.3.1 Strength...11

1.3.2 Hardness..11

1.3.3 Kinetic Properties...12

1.3.4 Electrical Properties..12

1.3.5 EM Wave absorption...12

1.3.6 Thermal Properties..13

1.3.7 Defects...13

1.3.8 Toxicity..14

1.4 Methods of Synthesis of Carbon Nanotubes 15

1.4.1 Arc Discharge 15

1.4.2 Laser Ablation..19

1.4.3 Chemical Vapour Deposition..20
1.4.4 Plasma Enhanced Chemical Vapour Deposition (PECVD)............................22
Chapter 2 24
Literature Review..24
2.1 Chemical Vapour Deposition (CVD)..24
2.1.1 History of CVD..25
2.1.2 Advantages of CVD...25
2.2.1 CNT Precursors..28
2.2.2 CNT Catalysts..30
2.2.3 Metal-Free CNT Growth...31
2.3 CNT Growth Control...32
2.3.1 Effect of catalyst material and concentration..................................33
2.3.2 Effect of Temperature...34
2.3.3 Effect of Vapour Pressure...35
Chapter 3……………………………………………………………………......................36
Experimental Details 36
3.1 The Experimental Setup…………………………………………………...……...36
3.2 Experiment No-1(750^{0}C,C_2H_2-100sccm)……………………….……………………..38
3.3 Experiment No-2(700^{0}C,C_2H_2-50 sccm)………………………………………....38
3.4 Experiment No-3(650^{0}C,C_2H_2-10 sccm)………………………………………....39
3.5 Experiment No-4(600^{0}C,C_2H_2-10 sccm)………………………………………....40
3.6 Experiment No-5(800C,C2H2-10 sccm)……….……………...…………………...41
Chapter 4: Result and discussion 42
4.1 Characterization of CNT using SEM...46
4.1.1 SEM image of CNT- (750˚C,C_2H_2-100sccm) 43
4.1.2 SEM images of CNT-2 (700˚C,C_2H_2-50sccm)...44
4.1.3 SEM image of CNT-3 (650˚C,C_2H_2-10sccm) 44
4.1.4 SEM image of CNT-4 (600˚C,C_2H_2-10sccm) 45
4.2 Characterization of CNT using HRTEM 46
4.2.1 Magnified image of CNT-1(750˚C,C_2H_2-100sccm).......................................46
4.2.2 Magnified image of CNT-1(600˚C,C_2H_2-100sccm).......................................47
Chapter 5 48
5.1 Conclusion………………………………………………………………......…48
5.1 Future Work……………………………………………………………..………48

List of Refrences..50

List of Figures

Chapter 1: Introduction………………..………………..………………………....….1

Figure.1.1Single walled carbon nano tube(SWCNT)..9

Figure.1.2 Multi-walled carbon nano tube(MWCNT)...10

Figure.1.3 Stable structure of nanobud...11

Chapter 2: Literature review…………….……….……..21

Figure.2.1 Schematic diagram of a CVD setup……..………………………………..........…23

Figure.2.2 Tip-growth model………………………………………………….……..…....24

Figure.2.3 Base-growth model……………..………………...25

Chapter 3: Experimental details…………..……………………………………….....31

Figure.3.1 CNT-1(750˚C,C_2H_2-100sccm)………………..……………….……………….32

Figure.3.2 CNT-2(700˚C,C_2H_2-50sccm)……………….……………………………………..33

Figure.3.3 CNT-3(650˚C,C_2H_2-10sccm)………..…………..………………………….…34

Figure.3.4 CNT-4(600˚C,C_2H_2-10sccm)……………………………………………...……35

Figure.3.5 CNT-5(800˚C,C_2H_2-10sccm)………………..……………………………….…35

Chapter 4: Result and discussion……………………………………………………..35

Figure.4.1 SEM micrograph of CNT-1..35

Figure.4.1 SEM micrograph of CNT-2..36

Figure.4.1 SEM micrograph of CNT-3..36

Figure.4.1 SEM micrograph of CNT-4..37

Figure.5.1 HRTEM micrograph of CNT-1……….……………………………..………….38

Figure.5.1 HRTEM micrograph of CNT-1……….………………………….....…………….39

Chapter 5 Conclusion and future work……………………………….…..…..40

Figure.5.1-CNTFET………………………………………………………………….…...…....41

Abstract

Carbon nanotubes (CNTs) are excellent materials in sense of their wide range of applications in hydrogen storage, biochemical applications, catalytic support, chemical sensor and field emission. Such extraordinarily applications are due to unique geometry, high mechanical strength, high chemical stability and excellent thermal and electrical conductivity. There are Various synthesis techniques such as laser ablation arc discharge, plasma enhanced chemical vapour deposition and Thermal chemical vapour deposition (CVD) is currently using throughout. Among these methods, Thermal CVD system is one of the most commonly used techniques for laboratory and commercially for large scale synthesis of CNTs. Thermal decomposition of ferrocene provides both catalytic particles and carbon sources for MWCNT growth using Ar as a carrier gas, and acetylene as a carbon source then We first turn to a local-scale analysis of the sample morphology and structure using both SEM and HRTEM.

1-Introduction

Nanotechnology involves the creation and manipulation of materials at the nanometer (nm) dimension by scaling up from small groups of atoms or by refming or reducing bulk materials. A nanometer can be represented as 1 x 10^{-9} m or one millionth part of a millimeter. We can have a sense of this scale as, a single red blood cell has a diameter of around 5000 nm, a human hair has diameter of the order of 10,000 to 50,000 nm, a DNA molecule has a diameter of 2 - 12 nm and viruses typically have a maximum dimension of 10 to 100 nm. Nanotechnology [1] is a combination of different fields like physical, chemical, electronic processes, materials, and biological applications and concepts in which one of the defining characteristic is size. Nanotechnology is a immerging area of research and development, and also applicable in industrial activity which has been growing rapidly world wide for the past decade.

1.1 Carbon Nanotubes

Carbon nanotubes (CNTs) are allotropes of carbon which have cylindrical nanostructure [2]. Nanotubes have length-to-diameter ratio of up to 132000000:1, significantly larger than for any other material in world. These formed cylindrical carbon molecules have extraordinary properties, which are precious for electronics, optics, nanotechnology and other fields of material science and technology. Carbon nano tubes having extra ordinary properties of mechanical strength electrical and thermal conductivity its application as additivesto various structural materials as baseball bats, golf clubs, car parts etc.

1.2 Types of Carbon Nanotubes

Carbon nanotubes are the members of fullerene structural family. The name of carbon nanotubes has been derived from their long and hollow cylindrical structure. The walls of CNT are formed by grapheme. Graphene is one-atom-thick sheet of carbon which are rolled at different angle called "chiral" [3]. Nanotube properties are decided by rolling angle and radius. Nanotube is metallic or semiconductor is determined by rolling angle and radius of nanotube. There are two types of Nanotubes

(i) Single walled nanotubes (SWNTs)

(ii) Multi-walled nanotubes(MWNTs)

1.2.1 Single-Walled Carbon Nanotubes

Most of single-walled nanotubes (SWNT) [4] have a diameter of about to 1 nanometer, with a tube length that can be 1000000 times longer than diameter. The SWNT is formed by wrapping a one-atom-thick layer of graphite. SWCNTs are seamless cylinder of Graphene sheet. The way the graphene sheet is wrapped is represented by indices (n, m). These whole numbers n and m denote the number of unit vectors along two directions in the honeycomb crystal structure of graphite. If $m = 0$, the nanotubes are called zigzag nanotubes, if $n = m$, the nanotubes are called armchair nanotubes else they are called chiral nanotubes.

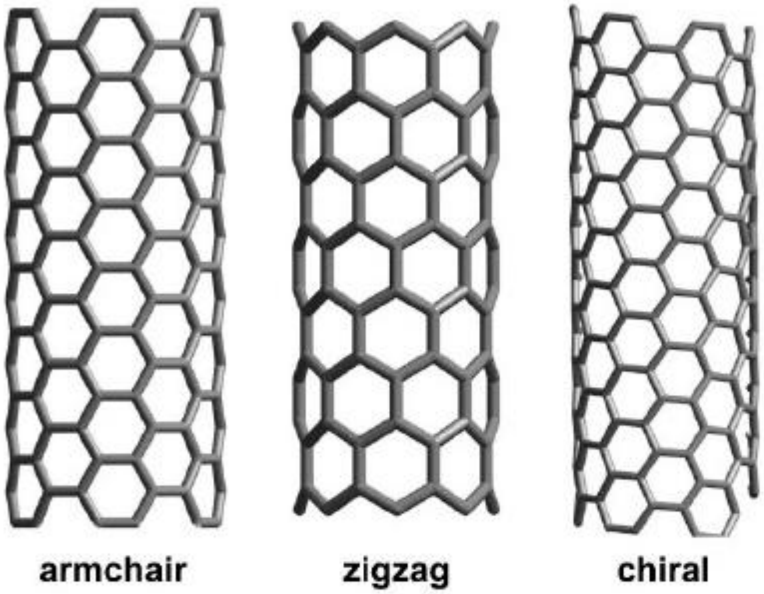

Figure 1.1 - Single walled carbon nano tube (SWCNT) [4]

1.2.2 Multi-Walled Carbon Nanotubes

As compare to SWNT Multi-walled nanotubes (MWNT) [5] consist of multiple rolled layers of graphene. By two examples we can identify the social systems of multi-walled nanotubes. Sheets of grapheme s are arranged in concentric cylinders as at (0,8) and the SWCNTs are put within a larger (0,17) this is informed by Russian Doll model. Second, in the Parchment model, a single sheet of graphite is known as graphene, like a rolled newspaper. The interlayer distances in multi-walled nanotubes are almost equal to the distance between graphene layers which is approximately 3.4 Å. The Russian Doll structure is found more commonly [6]. The individual shells of this structure can be described as SWNTs that can be metallic or semiconducting depending on unit vectors. There is restriction along the relative diameters of the individual tube, one of the shells so the whole MWNT is becomes a zero-gap metal.

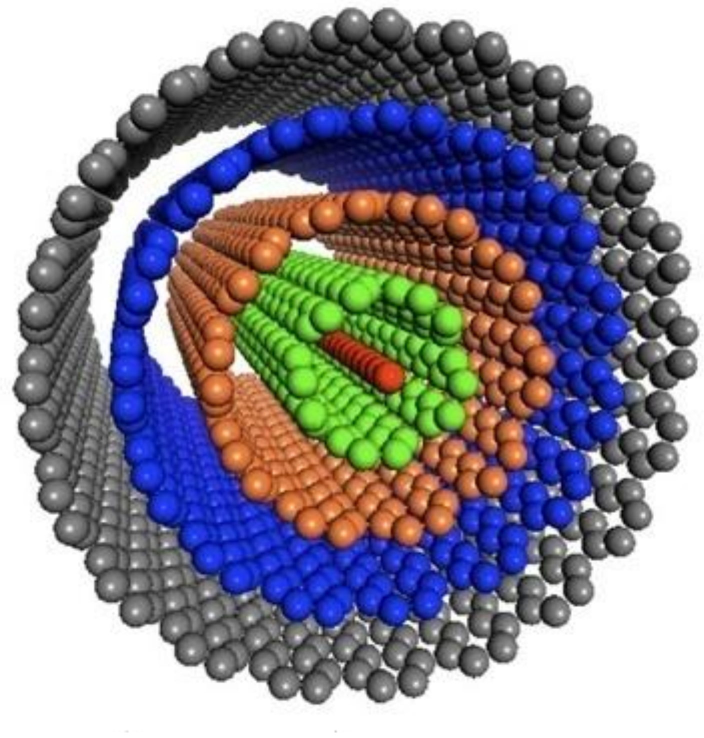

Figure 1. 2 - Multi-walled carbon nanotube (MWCNT)

1.2.3 Nanobud

Carbon Nanotubes are the modern days created materials, made by merging two pr allotropes of carbon: fullerenes and nanotubes. In this novel material, fullerene-like "buds" are covalently bound to the sidewalls of the carbon nanotube. So formed hybrid material has properties of both fullerenes and carbon nanotubes. CNTs particularly found to be exceptionally good emitters with excellent properties. Addition to this in composite materials, these buds functions as molecular anchors thus preventing slipping of the nanotubes so improving the composite’s mechanical properties.

Figure 1.3 - Stable structure of nanobud

1.3 Properties of Carbon Nanotubes

1.3.1 Strength

Carbon nanotubes are the toughest and strongest materials discovered in terms of elastic modulus and tensile strength. This strength comes from the covalent sp^2 bond formation between the individual carbon atoms. In the year 2000, a multi-walled carbon nanotube (MWNT) was tested which have a tensile strength of 63 gigapascals (GPa). Further studies, conducted in the year 2008, revealed that individual CNT shells have strengths of up to ~100 GPa, that is in agreement with quantum models. In spite of low density 1.3 to 1.4 g/cm^3 carbon nanotubes have specific strength of up to 48,000 $kN \cdot m \cdot kg^{-1}$ which is the best of known materials, compared with high-carbon steel's 154 $kN \cdot m \cdot kg^{-1}$[7].

1.3.2 Hardness

Carbon nanotubes have very high hardness that is why single-walled carbon nanotubes can withstand a pressure up to 24 GPa without deformation after that they undergo a transformation to super hard phase nanotubes. Current experimental techniques reports that Carbon nano tubes may sustain a maximum pressure are around 55 GPa. While, these new super hard phase of CNTs collapse at higher pressure.

1.3.3 Kinetic Properties

Multi-walled nanotubes are made from multiple concentric nanotubes nested within one another. These multi-walled nanotubes exhibit a property where an inner nanotube core may slide, within its outer nanotube shell, almost without friction, thus creating an atomically perfect linear or rotational bearing. This is one of the most appropriate examples of molecular nanotechnology, and without producing any mechanical losses the precise positioning of atoms to be created in useful machines. This property has already been utilized to create the world's smallest rotational motor. In future its applications can be seen in gigahertz mechanical oscillator.

1.3.4 Electrical Properties

Electrical properties a carbon nanotube are strongly affected by electronic structure and symmetry of graphene. For a given nanotube (n,m), nanotube can be classified as- if $n = m$, the nanotube is metallic; if $n - m$ is a multiple of 3, then the nanotube is semiconducting , otherwise the nanotube is a moderate semiconductor. Thus all metallic armchair nanotubes have ($n = m$), and semiconducting nanotubes are (6,4), (9,1), etc.

1.3.5 EM Wave absorption

Multiwalled carbon nanotubes (MWNTs) have one of the most recently researched property is their microwave absorption characteristics. This research can be used to better the stealth characteristics of aircraft and other military vehicles by utilizing microwave absorption characteristics for military push for radar absorbing materials (RAM). Research has been carried on filling metals such as Iron, Nickel, Cobalt, etc. within MWNTs, to increase the absorption effectiveness of MWNTs in the microwave regime. So far, this research has shown amelioration in both maximum absorption and bandwidth of absorption. The reason of absorptive properties change when filled is that the complex permeability (μ_r) and complex permitivity (ε_r), also changes. The direct relationship between μ_r, ε_r, and the other system parameters that affect the absorption sample thickness, d, and frequency, f, is shown in the equations below, where normalized input impedance are represented by Z_{in}. The equation shown below, these characteristics vary by frequency. Due to this, it is suitable to set a baseline reflection loss (R.L.) that is deemed effective and determine the bandwidth within a given frequency that produces the desired reflection loss.

1.3.6 Thermal Properties

All nanotubes have very good thermal conductions along the axis of the tube, and this property exhibiting a unique property known as "ballistic conduction"[8], CNT shows also a good insulator along tube axis at similar time. The various measurements conclude that a SWCNT has a room-temperature thermal conductivity along its axis of about 3500 $W\cdot m^{-1}\cdot K^{-1}$ which is almost 10 times compare this to copper, well known for its good thermal conductivity, which transmits 385 $W\cdot m^{-1}\cdot K^{-1}$. In the radial direction conductivity across SWNT axis is about 1.52

$W \cdot m^{-1} \cdot K^{-1}$ at room-temperature. The temperature stability of carbon nanotubes is almost up to 2800 °C in vacuum and about 750 °C in air.

1.3.7 Defects

In any material, the existence of a crystalline defect affects the material properties. It can occur in the form of atomic vacancies. Existence of such high level defects can lower the tensile strength by up to 85%. An important example of this is the creation of pentagon and heptagon pair in "stone wales defects"[9] by rearranging the bonds. Because of the very small structure of CNTs, the tensile strength of the tube depends on its weakest segment in a similar manner as chain, where the strength of the weakest link becomes the maximum strength of the chain.

1.3.8 Toxicity

The toxicity of carbon nanotubes has been a very important question since evolution of nanotechnology. Such research has just begun and need to analyse it precisely. The data obtained are still fragmentary and subject to criticism and further investigation. Preliminary results highlight the difficulties in evaluating the toxicity of this heterogeneous material. Following parameters such as structure, surface area, size distribution, surface chemistry, agglomeration state and surface charge, as well as purity of the samples, have a large impact on the reactivity of carbon nanotubes. However, from available data it can be clearly showed that, under some conditions, nanotubes can cross membrane barriers, thus it can be concluded that, if these materials may produce harmful effect if they reach the organs, they can be inflammatory and fibrotic reactions.

1.4 Methods of Synthesis of Carbon Nanotubes

1.4.1 Arc Discharge

Arc discharge is the method that uses very high temperatures (above 1700 ˚C) for CNT synthesis that is why there are fewer structural defects in comparison with other techniques used for formation of CNT.

1.4.1.1 MWNTs synthesis.

The arc discharge synthesis of MWNTs is very simple in the case when all growth conditions are ensured. The most common methods use DC arc discharge between two graphite plates which are usually water-cooled electrodes with diameters between 6 and 12 mm in a chamber filled with helium at sub atmospheric pressure. Nevertheless, some other scientist has used hydrogen or methane atmosphere. For example, Ebbesen and Ajayan [8] use a variant of the standard arc discharge technique which was also used by Iijima for synthesis of fullerene under He atmosphere to obtain CNTs at large-scale. Under certain physical conditions, a pure nanotube and nanoscale particles in a large quantity were obtained. The purity and yield of CNT depend sensitively on the gas pressure in the reaction vessel. Wang et al. showed that different atmospheric condition influence the final morphology of CNTs. They used DC arc discharge of graphite electrodes in the presence of He and methane gas. Then by evaporation of CH_4 gas under high pressure and high arc current, thick nanotubes embellished with many carbon nanoparticles were obtained. At the same time, thin and long MWNTs were obtained under a CH_4 gas pressure of 50 Torr and an arc current of 20 A for the anode with a diameter of 6 mm. However, Zhao *et al*. found that the variation of carbon nanotube morphology was more significant in case of evaporation of CH_4 gas as compared to that in He gas. And for that purpose in a different work, Zhao *et al* [10]. Hydrogen gas was used as atmosphere for preparation of fine and long MWNTs. He found by comparing with He and methane gases, a very big difference and that was little carbon smoke occurred in H_2 gas, but much more carbon smoke was observed for the evaporation in CH_4 and He gases. Further they showed that evaporation of graphite electrodes in presence of H_2 gas by DC arc discharge forms not only fine and long MWNTs but also graphene sheets deposited on the cathode. Another research group Shimotani *et al* [11] has reported synthesis of MWNTs using an arc discharge technique under He, acetone, ethanol and hexane atmosphere at various pressures (from 150 to 500 Torr). And by result of this experiment they concluded that arc discharges in the three organic atmospheres (ethanol, acetone and hexane) produce more MWNTs two times at least, than those in the He atmosphere. Explanation of this is as: contrary to helium which is known to be inactive, the acetone, ethanol and hexane can be ionized and the molecules can be decomposed into hydrogen and carbon atoms. Now these ionized species may contribute the synthesis of MWNTs, so helping in higher yield of CNTs production. It can also be showed that in all the cases of organic molecular atmospheres, yields of MWNTs increase as the pressure increases up to 400 Tore. Jiang et al. studied the presence of NH_3 atmosphere on the arc-discharge growth of CNTs and demonstrated that the arc-discharge method in NH_3 atmosphere is highly efficient method for preparation of CNTs. They observed that there was no significant difference in the shapes and the structures between NH_3 atmosphere and other atmospheres such as He, H_2, etc. But it was found that consumption of anode during the process was faster than the growth of MWNTs layer on the cathode. Therefore the gap between the electrodes of 30 to 110 mm^2 surface area has to be held in the desired distance during the growth process. This is ensured by one electrode constant feed to prevent the gap formation that leads to a high yield and stable arc discharge growth process.

For arc discharge deposition usually DC arc discharge is used, but pulsed techniques are also reported. For example Parkansky *et al* [12]. Reported the use of single-pulse arc production to form near vertically oriented MWNTs deposited on the Nickel/glass samples using a graphite counter electrode in ambient air. By this method MWNTs (typically 5–15 walls) with a diameter of almost 10 nm and lengths of about 3 mm were produced on the samples.

1.4.1.2 SWNTs Synthesis.

The arc discharge deposition of CNTs could be done with or without use of different catalyst. MWNTs are produced when catalyst is not used. On contrary, the SWNTs are produced when the transition metal is used as catalyst. A composite anode is utilized in the process of SWNTs growth usually in hydrogen or argon atmosphere. The anode is made up of composition of graphite and a metal. These metals are Pd, Ag, Pt, Ni, Fe, Co, etc. or mixtures of Co, Fe, Ni with other elements like Co–Cu, Ni–Cu, Ni–Ti, Co–Ni, Fe–Ni, Fe–No, etc[13]. The metal catalyst plays a significant role in the process yield. For getting high efficiency, this process is held on a constant gap distance between the electrodes that provide stable current density and anode consumption rate. In this process, extra unwanted products such as MWNTs or fullerenes are also produced. For the first time, the SWNTs growth process was explained in two separate works by Iijima and Ichihashi [14] who described SWNTs of 1 nm and Bethune *et al*. who presented Cobalt catalyzed growth of SWNTs. Bethune *et al*. reported that cobalt-evaporation of carbon and cobalt in an arc generator leads it to the formation of carbon nanotubes (CNT) with very small diameters of about 1.2 nm and walls of it made up of a single atomic layer thick only. Ajayan *et al*. also used Cobalt as catalyst for synthesis of SWNTs of 1–2 nm diameter using arc discharge method in He atmosphere. The other catalyst which is also used very commonly for SWNTs synthesis is nickel. Seraphin et al [15]. Studied the catalytic role of different metals like

Nickel, Platinum and Palladium, in the formation of carbon nanoclusters using DC arc discharge method at operating voltage of 28 V and current of 70 A, and under a 550 torr. He atmosphere pressure. It was found out that nickel-filled anode stimulated the growth of SWNTs. A similar method was used by Saito *et al*. who reported SWNTs growing radically from Nickel fine particles i.e. Ni being used as catalyst. Zhou *et al* [16]. Reported radically nanotubes produced with high atomic number metal i.e. platinum-group metals (Ru, Rh, Pd, Os, Ir, Pt) using arc discharge method. From the analysis it was observed that Rh, Pd, and Pt showed catalytic activity which can be used for growing SWNTs, but the other metals did not such bundles of dense SWNTs with diameter range 1.3–1.7 nm were extruding in radial direction from metal particles of Rh and Pd. In this the sizes of core particles were 50–200 nm for Pd and 20–30 nm for Rh. In the case of Pt SWNTs of dimension 1.3–2.0 nm in diameter and sometimes similar to 3 nm grew from a tiny particle of about 10 nm. In another work, Saito et al. reported SWCNTs synthesis by the arc discharge method with the help of Fe, Co, Ni, F/Ni, La, and Cu catalysts. According to growth patterns and morphology of SWNTs, it was divided into three groups: first was the tubes tangled with each other to form ‘‘highway junction’’ pattern for Co and Fe/Ni, second long and thin tubes radically growing from Ni particles, and third and last short and thick tubes growing from lanthanide compound particles.

1.4.1.3 DWNTs Synthesis

It has been reported the process of DWNTs formation is more complicated than the production of SWNTs. Hutchison *et al*. first reported the technique to form DWNTs by arc discharge technique in a mixture atmosphere of argon and hydrogen. The anode used for this was a graphite rod of 8.2 mm diameter filled with catalyst. Catalyst used was a mixture of Nickel, Cobalt, Fe and Sulphur. The obtained DWNTs formed into bundles and SWNTs were observed as a by-product. Further Sugai *et al* [17]. Reported a new synthesis technique to form high-quality DWNTs using high-temperature pulsed arc discharge method using Y/Ni alloy catalysts.

1.4.2 LASER Ablation

Laser ablation, is one of the best methods to grow SWNTs with a very high-quality and high-purity. This method was first demonstrated by Smalley's group in 1995. The principles and mechanisms of this method are similar to the arc discharge with only difference that the energy is provided by a laser that hits a graphite pellet containing catalyst materials usually nickel or cobalt. The properties of CNTs prepared by this pulsed laser deposition method are strongly dependent on many parameters such as: the laser energy affluence, laser peak power, laser versus pulse, laser repetition rate and laser oscillation wavelength, the chamber pressure and the chemical composition, the structural and chemical composition of the target material, flow of the buffer gas and pressure of the buffer gas, the temperature of substrate and ambient and the distance between the target and the substrates. The lasers used for the ablation are Nd: YAG and CO_2. For example, Zhang et al [18]. Prepared SWNTs by continuous wave of CO_2 laser ablation without applying additional heat to the target. It was observed that the average diameter of SWNTs formed by this technique increases with increase in laser power. So we can conclude now the relationship between the excitation wavelength and the growth mechanisms of SWNTs. The UV laser [19] is superior in photochemical ablation to the infrared laser which is effective for photo thermal ablation. So it may be expected that a UV laser creates a new species of nanoparticles and suggests a new generation mechanism of CNTs. Lebel et al. used the UV-laser doped with Cobalt/ Nickel metal catalyst to synthesized SWNTs by ablation of a graphite target appropriately. In his work, he used SWNTs as a reinforcing agent of polyurethane. Kusaba and Tsunawaki [20] used XeCl excimer laser which produced the highest yield of SWNTs with the diameter between 1.2 and 1.7 nm and the length of 2 mm or above. This laser has oscillation wavelength of 308 nm which irradiate a graphite containing Cobalt and Nickel at various temperatures and they found that laser ablation yield was maximum at temperature 1623 K. Recently, Stramel *et al* [21]. have used Tm:Ho:LuLf laser which a laser host material LuLF (LuLiF4) that is doped with holmium and thulium in order to reach a laser light production in the vicinity of 2 mm. By using this laser he successfully applied MWNTS and MWNTs–polystyrene targets for deposition of composite thin films onto silicon (Si) substrates using Pulse Laser Deposition with a pulsed, diode pumped. It was found that usage of pure MWNTs targets increases the thin film which has higher quality MWNTs as compared to PSNTs targets. Similarly, Bonaccorso *et al* [22]. used PLD techniques with Nd: YAG laser ablation for preparation of MWNTs thin films of commercially polystyrene-nanotubes pellets on alumina substrates.

1.4.3 Chemical Vapor Deposition

Catalytic chemical vapor deposition (CCVD) is done by either thermal or plasma enhanced (PE) which has now became the standard method for the production of CNTs. However, there are other CVD techniques too, such as hot-filament (HFCVD), water assisted CVD, microwave plasma (MPECVD) or radiofrequency CVD (RF-CVD), oxygen assisted CVD. CCVD is economically better process for large scale production and also viable for quite pure CNTs production compared to laser ablation. We can easily control the reaction course of CVD and can obtain high purity of the material. There is no consensus in CNT growth model so it is still under discussion. Recently, Fotopoulos and Xanthakis gave the model to explain the CNT growth which are generally accepted models that are based on growth and tip growth. For this they took a hypothesis that SWNTs are produced by base growth only, i.e. the cap is formed first creating SWNTs and then by a lift off process the CNT is created by addition of carbon atoms at the base forming MWNTs. By TEM studies it has been found that the base growth of SWNT in thermal CVD is assisted by a considerable deformation of the Nickel catalyst nano particles and the creation of a subsurface carbon layer. These effects may be produced by the adsorption on the catalyst nanoparticle during pyrolysis. In order to produce SWNTs, the size of the nanoparticle catalyst must be smaller than about 3 nm. The function of the catalyst in the CVD process is the decomposition of carbon source via either plasma irradiation (plasma-enhanced CVD, PECVD) or heat (thermal CVD) and its new nucleation to form CNTs. Transition metals are most frequent used catalyst in this method, primarily Fe, Co, or Ni. Sometimes, the traditionally used catalysts are further doped with other metals, e.g. with Au. Concerning the carbon source, the most preferred in CVD are hydrocarbons such as methane, ethane, ethylene, acetylene, xylene, eventually their mixture, iso-butane or ethanol. In the case of gaseous carbon source, the growth of carbon nanotubes efficiency strongly depends on the reactivity and concentration of gas phase intermediates produced together with reactive species and free radicals as a result of hydrocarbon decomposition. The potential chemisorptions and physiosorption on the catalyst surface to initiating growth of CNTs is expected that the most efficient should be produced in gaseous phase. Commonly used substrates are Cu (copper) Si (silicon), Ni (nickel), SiO_2 (silicon di-oxide), Cu/Ti/Si, stainless steel or glass, rarely we may use $CaCO_3$; tungsten foil and graphite or other substrates were also tested. A special type of substrate, mesoporous silica another tested substrate is, since it might play a templating role in guiding the initial CNT growth. For anexample, Zhu *et al* [23]. Reported a CCVD synthesis of DWNTs over supported metal catalysts decomposed from Fe and Co on mesoporous silica. They obtained bundles of tubes with a relatively high percentage of DWNTs in areas where tubular layered structures could be clearly determined. Furthermore, the crystal-like alignment of very uniform DWNTs was observed. Similarly, Ramesh *et al* [24]. succeeded in high-yield selective CVD synthesis of DWNTs over Fe/Co loaded high-temperature stable mesoporous silica. Another substrate, zealots, was studied by Hiraoka *et al*. They used CCVD of acetylene over well-dispersed metal particles (typically Co/Fe binary system) embedded in heat-resistant zeolites at temperatures above 900 ^{0}C for selective synthesis of DWNTs.

1.4.4 Plasma Enhanced Chemical Vapour Deposition (PECVD)

Plasma enhanced chemical vapour deposition (PECVD) is a suitable method for synthesis of CNTs hybrid materials and modification of their surface properties. Lim *et al*. reviewed the application of PECVD in the production and modification of CNTs. They emphasize the usage of the PECVD method for SWCNTs growing at low temperatures and make an effort to better understand plasma chemistry and modelling. An example of the MWNTs forest-like structure deposited on solid substrate using PECVD is shown in Fig. PECVD can be also used in several different modes: radio frequency (RF-PECVD), direct current (DC-PECVD), diffusion (DPECVD) or microwave (MWPECVD). Kim and Gangloff [25] demonstrated the low-temperature (480–612 ^{0}C) synthesis of CNTs on different metallic underlayers (i.e. NiV, Ir, Ag, Pt, W, and Ta) using DPECVD. They used an Fe/Al bilayer as the catalyst. Wang and Moore prepared vertically aligned CNTs using FeNi or Fe sputtered catalyst layers on glass substrates by RF- or DC-PECVD. They compared the CNTs growth mechanisms using both methods with respect to flow rate of gas, power of catalysts and plasma. They explained region of RF-PECVD provided more efficient decomposition of gas molecules than DC-PECVD by plasma theory. The major difference between RF- and DCPECVD was the higher concentration of reactive radicals in the former. However, a well aligned vertical CNT growth in DC-PECVD occurs. Fe, Ni thin film catalysts exhibited higher activity and better wetting ability than the Fe island thin film catalysts. Like in thermal CVD, numerous catalyst types to improve the yield and the quality of CNTs production are also applied using PECVD system. For example, Luais *et al* [26] prepared spherical Ni nanoparticles film $Ni(NO_3)_2$ as a preliminary material was used as a catalyst. The diameter of Ni nanoparticles was about 50 nm. This catalyst was further used for synthesis of vertically aligned CNTs by PECVD in an electron cyclotron resonance chamber using a gas mixture of C_2H_2/NH_3 at 520 ^{0}C. The average thickness of the CNTs film was about 1 mm and the CNTs diameter was around 50 nm. After CNTs preparation, their surface was functionalized with oxygenated and aminated groups using microwave plasma to make them suitable for future biosensing applications. Moreover, they found that the plasma treatment was a very effective way to retain the CNTs aligned forest structure of electrode surface. He focused their study on a TEM investigation of the crystallography of Ni catalysts for the vertical growth of carbon nanofibers (CNFs), which were synthesized by DC PECVD in an atmosphere composed of isopropylic alcohol and water. Yung and colleagues tested the influence of four types of substrates, namely Si, n++ Si, p++ Si and SiO_2, on CNTs growth on the Ni catalyst layer using PECVD [27]. According to the report type of Si substrate has significant effects on CNT growth characteristics. Sun *et al*. studied the effect of catalyst film (Ni or Fe) thickness on vertically aligned CNTs growth by PECVD on different metal underlayers (Ti, Cr or Al) deposited on Si wafers. They found a critical thickness of about 10 nm of Fe or Ni catalyst film is needed to grow CNTs on various underlayer metals. The observed result is that density, growth rate average diameter, diameter distribution, and contact resistance exhibited strong correlation with the choice of catalyst/underlayer combination.

2.1 Chemical Vapour Deposition (CVD)

The most popular method of producing CNTs now a day is Chemical vapour deposition (CVD). This process comprises the thermal decomposition of a hydrocarbon vapour which is achieved in presence of a catalyst (i.e. metal catalyst). Thus, it is also called as thermal CVD or the catalytic CVD method/process.

2.1.1 History of CVD

History of synthesis of carbon filaments by CVD method dates back to the nineteenth century. Early in 1890, the French scientists noticed that the creation of carbon filaments during experiments which comprised the passage of cyanogens over the red-hot porcelain. By the mid of twentieth century, the CVD had been an established method for the production of carbon microfibers by utilizing thermal decomposition of hydrocarbons in presence of catalysts (i.e. metal catalysts).

2.1.2 Advantages of CVD

It uses a patterned substrate. It also provides the better control of the growth parameters as compared to the arc-discharge and the laser-ablation method, the CVD is a economic and simple technique to synthesize CNTs at low temperature and pressure. In crystalline, the arc-discharge and laser-ablation grown CNTs are found superior to the CVD-grown CNTs (though CVD-grown MWCNTs consists the inferior crystalline, but the crystallinity of SWCNT grown by CVD method is similar to that grown by arc-discharge or laser ablation methods).However, in comes to the control of structure or architecture of CNT, CVD is the only answer for this. The CVD is versatile in the sense that it provides harnessing of plenty of hydrocarbons in different states (i.e. solid, liquid or gas), and also enables the use of various substrates, and allows the growth of CNT in a variety of forms, such as powder, aligned or entangled, thin or thick films, coiled orstraight the yield and purity, CVD beats the arc-discharge and laser-ablation methods. And, when it nanotubes or a desired architecture of nanotubes on the predefined sites.

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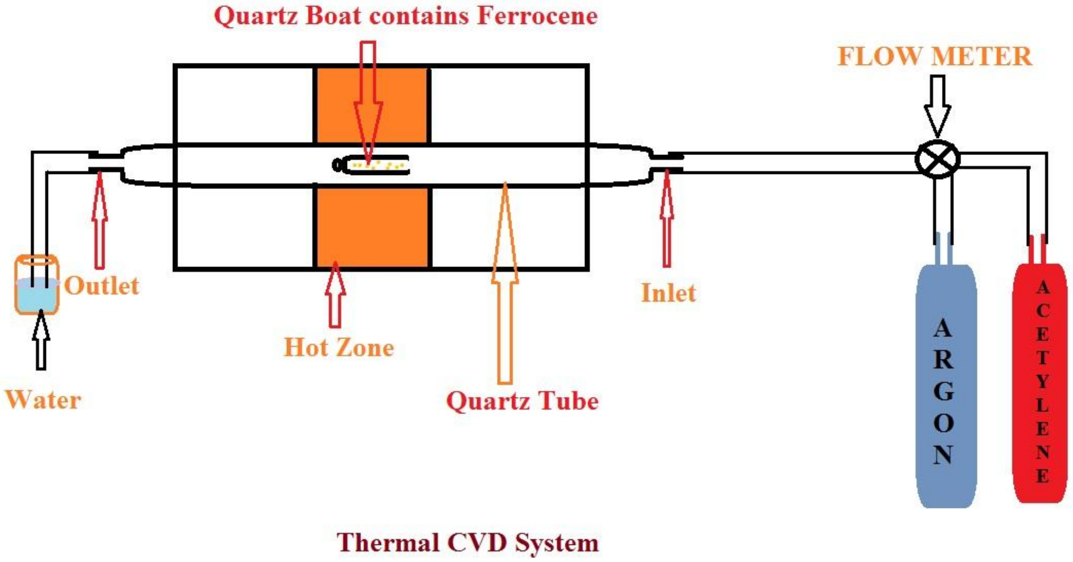

Figure-2.1- Schematic diagram of a CVD setup.

Keep the process continued on. Now there are available two different general cases. Whenever the catalyst–substrate interaction becomes weak (the metal has an acute contact angle with the down through the metal, and the CNT precipitates out across themetal bottom, pushes the surface of whole substrate), the decomposition of hydrocarbon at the top surface of the metal, the carbon diffuses metal particle off the substrate (as depicted in step (i)). As long as the top of metal's is open for fresh hydrocarbon decomposition (the concentration gradient exists in the metal which allows the diffusion carbon), The CNT is continued to grow longer and longer (ii). Once the metal has been fully covered with the excess a carbon, its catalytic activity ceases and the CNT growth has been stopped (iii). This method is known as "tip-growth model."

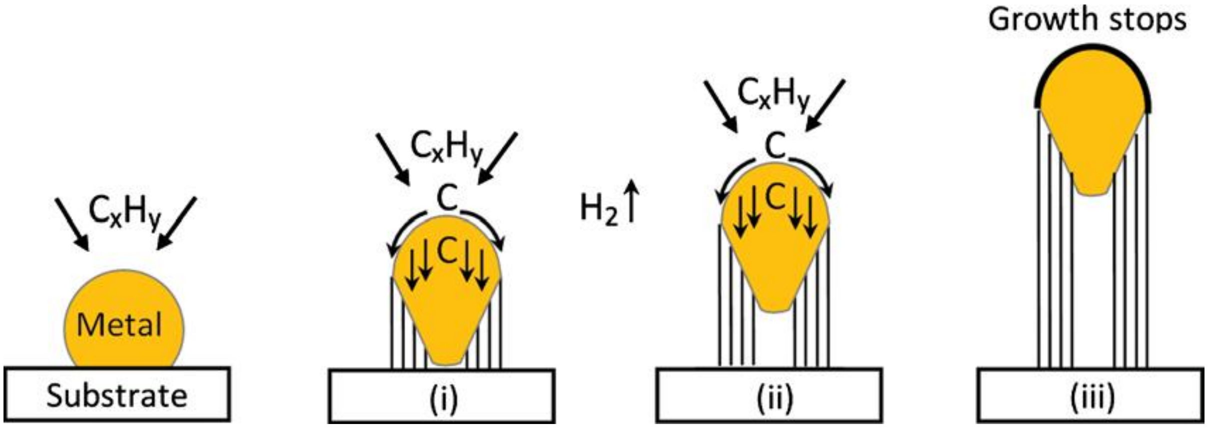

Figure-2.2 Tip-growth model [28]

In another case, whenever there is strong catalyst–substrate interaction (the metal makes an obtuse contact angle with the substrate), the initial decomposition of hydrocarbon and diffusion of carbon takes place in the same way as that in the case of tip-growth, but the precipitation of CNT failed to push the particle of metal up; so the precipitation may be compelled for emerging out from the apex of metal (the farthest from the substrate, having least interaction with the substrate). Firstly, the carbon crystallizes out in the form of a hemispherical dome (the most favoured closed-carbon network on a nano particle with spherical shape) which may be then extended up to the shape of a seamless graphitic cylinder. The Subsequent deposition of hydrocarbon takes place on the lower periphery of the metal, and as a dissolved carbon which diffuses upward. Thus CNT then grows up with the catalyst rooted on its base; thus, this is known as “base-growth model.”

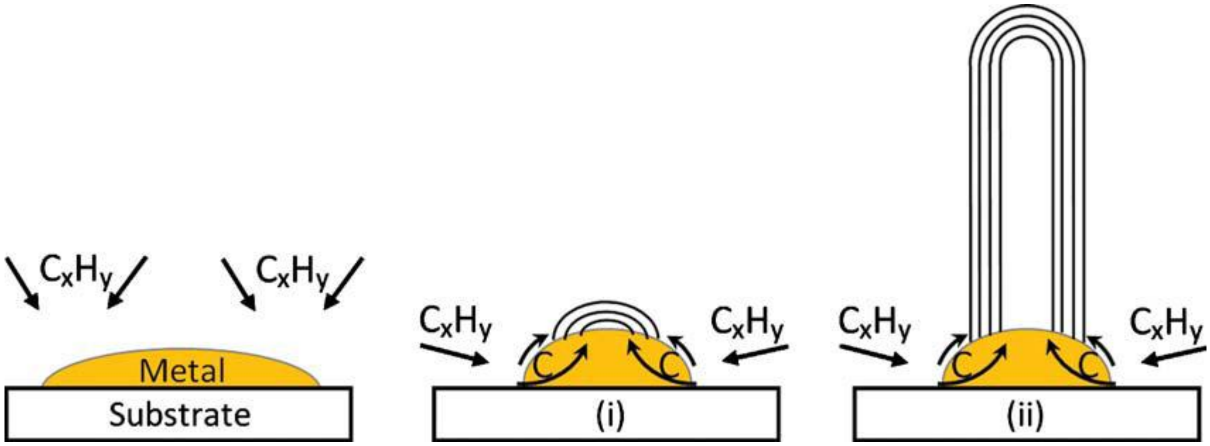

Figure 2.3- Base growth model [29]

2.2.1 CNT Precursors

The Most commonly used CNT precursors are ethylene, methane, benzene, xylene, acetylene and carbon monoxide. The lab Endo *et al* reported the growth of CNT by the pyrolysis of benzene at a temperature of 1100 ˚C, whereas the lab. Jose-Yacaman *et al* [30] got clear helical MWCNTs at a temperature of around 700 ˚C from the acetylene. In those cases the nano particles of iron were mainly used as the catalyst. Later on, the MWCNTs were also grown from many other precursors including the fullerene and cyclohexane. Whereas on the other hand,the SWCNTs were firstly produced at the lab Dai *et al* [31].by disproportionation of carbon monoxide at the temperature of 1200˚C, in the presence of nanoparticles of molybdenum. Later, the SWCNTs were also produced from acetylene, benzene, methane, ethylene, fullerene, cyclohexane etc. by using various catalysts. In 2002 the laboratory Maruyama *et al*. reported the low-temperature synthesis of high-purity SWCNTs from the alcohol on Fe–Co-impregnated zeolite support method and since then the ethanol has become the most popular precursor for CNT in the method of CVD all over the world. The Special feature of ethanol is that the ethanol-grown CNTs are mostly free from the amorphous carbon, owing to the effect of etching OH radical. Later on, the SWCNTs with vertically-aligned were also grown on Mo-Co-coated quartz and silicon substrates. Recently, Maruyama’s group has shown that intermittent supply of acetylene in ethanol CVD significantly assists ethanol in preserving the catalyst’s activity and thus enhances the CNT growth rate. The molecular structure of the precursor has a detrimental effect on the morphology of the CNTs grown. Linear hydrocarbons such as the thermal decomposition of methane, ethylene, acetylene, into atomic carbons or linear dimers/trimers 750˚C, C_2H_2-100sccm of carbon, and generally produce straight hollow CNTs. On the other hand, cyclic hydrocarbons such as benzene, xylene, cyclo hexane, fullerene, produce relatively curved/hunched CNTs with the tube walls often bridged inside. General experience is that low-temperature CVD (600–900 ˚C) yields MWCNTs, whereas high-temperature (900-1200 ˚C) reaction favours SWCNT growth. This indicates that SWCNTs have a higher energy of formation (presumably owing to small diameters; high curvature bears high strain energy). Perhaps that is why MWCNTs are easier to grow (than SWCNTs) from most of the hydrocarbons, while growth of SWCNTs from selected hydrocarbons (viz. CH_4 (methane), CO (carbon mono oxide) etc. which have a reasonable stability in the temperature range of 900–1200 ˚C).Commonly efficient precursors of MWCNTs (viz. acetylene, benzene, etc.) are unstable at higher temperature and lead to the deposition of large amounts of carbonaceous compounds other than the nanotubes. In 2004, using ethylene in CVD, Hata *et al* [32] Reported water-assisted highly-efficient synthesis of impurity-free SWCNTs on Si substrates. They proposed that controlled supply of steam into the CVD reactor acted as a weak oxidizer and selectively removed amorphous carbon without damaging the growing CNTs. Balancing the relative levels of ethylene and water was crucial to maximize the catalyst's lifetime. However, very recently, Zhonget *al el* [33]. have shown that a reactive etchant such as water or hydroxyl radical is not required at all in cold-wall CVD reactors if the hydrocarbon activity is low. These studies emphatically prove that the carbon precursor plays a crucial role in CNT growth.

2.2.2 CNT Catalysts

For synthesizing CNTs, usually, metal nanostructure (particles or rods) are required for the deposition of hydrocarbon at a lower temperature required for spontaneous deposition.Most commonly-used metals for catalyst used in synthesis of CNTs are Fe(iron), Co(cobalt), Ni(nickel), because of two main reasons: (i) high solubility of carbon in these metals at high temperatures; and (ii) high carbon diffusion rate in these metals. Above and beyond that high melting point as well as low equilibrium-vapour pressure of these metals offers a wide temperature window of CVD for a wide range of carbon precursors. Recently Fe (iron), Co (cobalt), and Ni (nickel) are considered as stronger adhesion with the growing CNTs (than other transition metals do) and hence they are more efficient in forming high-curvature (low-diameter) CNTs such as SWCNTs. Solid organometallocenes (ferrocene, cobaltocene, nickelocene) are also widely used as a CNT catalyst, because they form metal nanostructures *in-situ* which catalyze the hydrocarbon decomposition more efficiently. It is a general experience from the synthesis of CNTs is that the catalyst-particle structures (rods or particle) size dictates the tube diameter. Campbell's group has reported the particle size dependence and a model for iron-catalyzed growth of CNTs. Hence, metal nanoparticles of controlled size may pre-synthesized by other trustworthy techniques, can be used to grow CNTs of controlled diameter. Catalysts coated on various substrates in the form of thin film are also proven good in getting uniform CNT deposits. The key factor to get pure CNTs is achieving hydrocarbon decomposition on the catalyst surface alone, and prohibiting the aerial pyrolysis. Apart from the popular transition metals (Fe, Co, Ni),other metals of this group, such as Cu, Au, Ag, Pt, Pd were also found to catalyze various hydrocarbons for CNT growth. A comprehensive review of the role of metal particles in the catalytic growth of CNTs has been published by Kauppinen's group [34]. On the role of CNT catalysts, it is worth mentioning that transition metals are proven to be efficient catalysts not only in CVD but also in arc-discharge and laser-vaporization methods. Therefore, it is likely that these apparently different methods might inherit a common growth mechanism of carbon nanotubes and is not yet clear. Hence we can say that open field of research to correlate different CNT techniques in terms of the catalyst's role inentirely different temperature and pressure range.

2.2.3 Metal-Free CNT Growth

Very recently nanodiamond particles (5 nm) were successfully used as a CNT catalyst. Ethanol suspension of nanodiamond particles was spread on graphite plates and dried in air at 600 ˚C. This resulted in isolated diamond particles, monolayers of diamond, and multilayered diamond stacks on the substrate, depending upon the diamond concentration (0.01–1.0 wt %). Ethanol CVD over these diamond-loaded substrates at 850 ˚C and diamond particles do not fuse even after high-temperature thermal CVD process, implying that they stay on in solid state during CVD. Nano diamond is therefore said to act as a CNT growth seed. This result proves that CNT growth is possible without metal catalyst. Does nanodiamond act as a catalyst? If it does, how? These are open questions .In many studies, oxygen was noticed to activate the CNT growth. Recent studies have revealed that many metals do not exhibit catalytic activity in pure-metal form, do well in oxide form. Does metal oxide act as a catalyst? Growth of CNTs as in temperature free directional form has been achieved on sapphire. CNTs have also been grown on semiconductors such as Si and Ge nanoparticles (though C has little solubility in bulk Si or Ge), provided that then a noparticles are heated in air just before CVD. Similarly, CNT growth on SiC substrates takes place only when some oxygen is present in the chamber. Porous $Al2O_3$has already been shown to facilitate CNT growth without any catalyst. Catalyst-free CNT growth is also possible in oxy-fuel flames. And oxide, typically used as a catalyst support in CVD, is itself capable of forming grapheme layers. All these examples resoundingly indicate that oxygen plays a key role in CNT growth. The question is: is it a catalyst? HRTEM investigation of the CNTs grown by cyclohexane pyrolysis over iron nanoparticles supportedon thin Al_2O_3 layers show that CNT keeps on growingeven when the metal is completely encapsulated in the tube center. The authors propose that the metal only helps toinitiate the CNT precipitation at the nucleation stage.

Once the head of Carbon nanotubes is created, thus non functionalization of metal becomes; subsequent carbon addition to the CNT base periphery is facilitated by the substrate's oxide layer. This concept is radically different to the existing concept that the metal must remain exposed (either on the CNT tip or base) to keep the growth on.

2.3 CNT Growth Control

It is well known that hydrocarbons are easily broken at high temperatures. Such a thermal decomposition is called Pyrolysis. However, in the presence of suitable metal catalysts, a hydrocarbon can be decomposed at lower temperatures (catalytic pyrolysis). The key of CNT growth by CVD is to achieve the hydrocarbon decomposition on the metal surface alone and prohibit spontaneous aerial pyrolysis (do not allow the hydrocarbon to break uncatalyzed, beyond the catalyst surface). Restriction of pyrolysis to the catalyst surface is controlled through proper selection of hydrocarbon and catalyst materials, vapor pressure of the hydrocarbon, concentration of the catalyst, and the CVD reaction temperature. Choosing camphor as the carbon source, the rest three key parameters were categorically optimized in our laboratory.

2.3.1 Effect of catalyst material and concentration

Early experiments of CNTs were carried out with different metal catalysts (Fe, Co, Ni) separately. Iron was found to have high catalytic effect in hydrocarbon decomposition on leading to higher CNT deposits, but those CNTs were poorly graphitized. On the other hand, cobalt catalyst resulted in better-graphitized CNTs but the yield went down. Hence a mixture of the two metals were tried to combine their individual advantages, and it was successful. Large volumes of well-graphitized MWCNTs were obtained. Additional advantage of using the bimetallic catalyst was that CNTs could be grown at much lower temperature viz. 550 ˚C. It is because 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 result would be more complicated. No much effort is known in this direction. Besides the catalyst material, the catalyst concentrates on also plays an important role in the CNT growth. In our lab, catalyst concentration in zeolite was varied in a wide range (1–50 wt %). No CNT formed for a catalyst concentration less than 2.4 wt% in zeolite. Lower catalyst concentrations(2.4–5%) exhibited SWCNT growth (at 850 ˚C and above), whereas higher concentrations favored MWCNT growth.A combined Fe + Co concentration of 40% accounted for the highest yield of MWCNTs with negligible metal contamination. These studies confirm that SWCNTs or MWCNTs can be selectively grown by proper selection of catalyst materials and their concentration.

2.3.2Effect of Temperature

The authors investigated the effect of temperature on camph or CVD in a wide range of 500–1000 ˚C. It was noticed that camphor did not decompose below 500 ˚C. At 550 ˚C very short-length tubes emerged from the zeolite poressuggesting 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 belocated amid nanotubes. TEM investigations revealed that the CNT diameter increased with the increasing growth temperature. Very clean CNTs, almost free from metallic impurity, were produced up to 750 ˚C. This, at low temperatures, the catalyst–support interaction is strong enough not to let the metal particles leave the zeolite (a) (matrix. So, the CNTs grow via base-growth process. However, at higher temperatures, the metal particles were gradually pronounced in the samples, preferably encapsulated at the CNT tips. This suggests that, at critical temperatures, tip-growth process coexists with base-growth process, dueto inhomogenity of metal dispersion. Bigger metal clusters may leave a part of it to be lifted up with the growing CNTs. From 750 ˚C onward, both the diameter and distribution range increased drastically. It issupposed that, at high temperature, the metal atoms agglomerate into bigger clusters leading to thick CNTs. Simultaneously; high temperature promotes camphor decomposition leading to more carbon generation and hence more wall formation. At 850 ˚C and above, SWCNTs began to form besides MWCNTs and the volume of SWCNTs increased with the increasing temperature.For instance, in 900 ˚C sample large bundles of SWNTs can be seen (in low contrast) underneath thick fibres (in high contrast). It is noteworthy that, while MWCNTs and fibres have a lot of metal contamination, there is no trace of metal associated with the SWCNT bundles. Thus, the best temperature for a gigantic growth of MWCNTs, was found to be 650 ˚C, as optimized for Fe–Co-impregnated zeolite

2.3.3 Effect of Vapour Pressure

For controlled growth of CNTs by CVD, the vapor 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 limited gas-flow rate and controlled suction with a rotary pump. In the case of a liquid hydrocarbon, its vapour pressure is controlled by its heating temperature before it enters the reactor. However, for a solid hydrocarbon such as camphor, it is quite tricky to control its vapour pressure. It becomes a function of three parameters: camphor mass, its vaporization temperature, and the flow rate of argon—the carrier gas. By proper optimization of these three parameters, the influx of camphor vapor 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 CVD. On the other hand, pure SWCNTs (free from MWCNTs) were selectively obtained from camphor CVD at low pressures (10–40 torr) where the camphor vapor pressure is quite in tune with the low metal concentration. Unfortunately, however, the quantity of such pure SWCNTs is still in milligram order. Gram-order SWCNT synthesis from camphor is still an open field of research.

Chapter-3 Experimental Details

3.1 The Experimental Setup

- The experimental setup consists of
  - A horizontal tube furnace
  - Quartz tube
  - Mass flow controller
  - Gas sources
  - Thermocouple
- **Horizontal reaction furnace:-** CVD apparatus consists of horizontal reaction furnace with a heating capacity of up to 1200 °C. The length of the furnace is 1 m and has an inner diameter of 10 cm.
- **Quartz tube: -** The quartz tube used to carry out the deposition has a length of 1.2 m with outer diameter of 8 cm and inner diameter of 7.5 cm. The quartz tube is placed inside the horizontal reaction furnace.
- **Mass flow controller:-** A mass flow controller is provided in the furnace to control the temperature, time and heating rate of the reaction. The controller

displays the set and current temperature and the current is automatically adjusted by the controller to maintain the set temperature.

- **Gas sources:-** Control valves are used to control the flow rate of gases passed in to the furnace.
- **Thermocouple: -** Thermocouple is a temperature-measuring device consisting of two dissimilar conductors that contact each other at one or more spots.

3.2 Experiment No-1(750 ^{0}C, C_2H_2-50sccm)

- 0.5 gm of ferrocene kept outside of the quartz tube.
- Flow the argon at 200 sccm.
- When temperature reached up to 750 ˚C slide the ferrocene boat inside the middle of quartz tube.
- Turn on the acetylene flow at 50 sccm for 10 minutes and argon flow also kept on.
- After 10 minutes close the acetylene flow.
- When temperature cool down up to 100 ˚C take out boat outside the quartz tube.

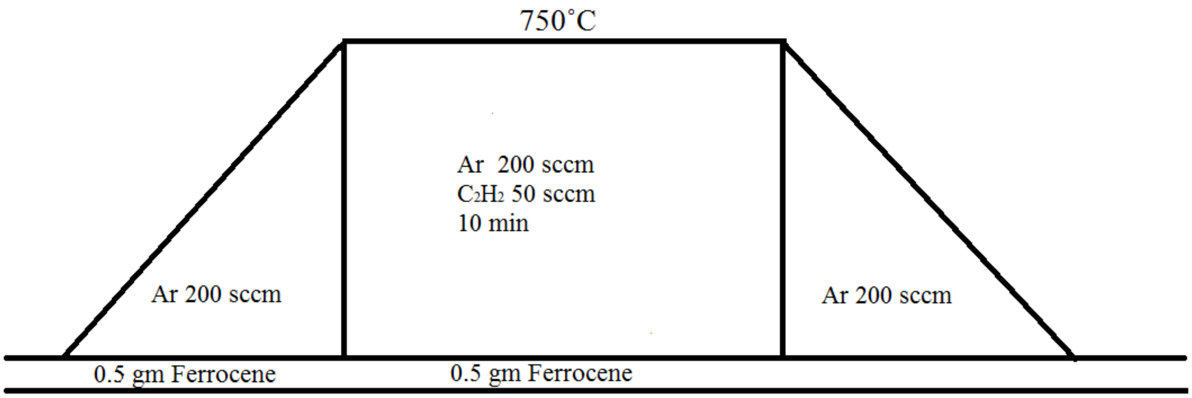

Figure-3.1 CNT-1(750 ^{0}C, C_2H_2-50 sccm)

3.3 Experiment No-2(700 ^{0}C, C_2H_2-50 sccm)

- 0.5 gm of ferrocene kept outside of the quartz tube.
- Flow the argon at 200 sccm.
- When temperature reached up to 700 ˚C slide the ferrocene boat inside the middle of quartz tube.
- Turn on the acetylene flow at 50 sccm for 5 minutes and argon flow also kept on.
- After 5 minutes close the acetylene flow.
- When temperature cool down up to 100 ˚C take out boat outside the quartz tube.

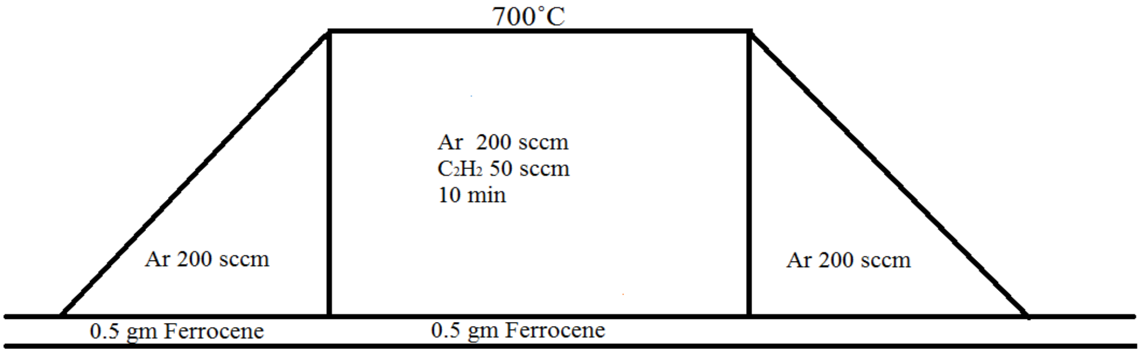

Figure- 3.2 CNT-2(700 ^{0}C, C_2H_2-50 sccm)

3.4 Experiment No-3(650 ^{0}C, C_2H_2-50 sccm)

- 0.5 gm of ferrocene kept outside of the quartz tube.
- Flow the argon at 200 sccm.
- When temperature reached up to 650 ˚C slide the ferrocene boat inside the middle of quartz tube.
- turn on the acetylene flow at 50 sccm for 10 minutes and argon flow also kept on.
- After 10 minutes close the acetylene flow.
- When temperature cool down up to 100 ˚C take out boat outside the quartz tube.

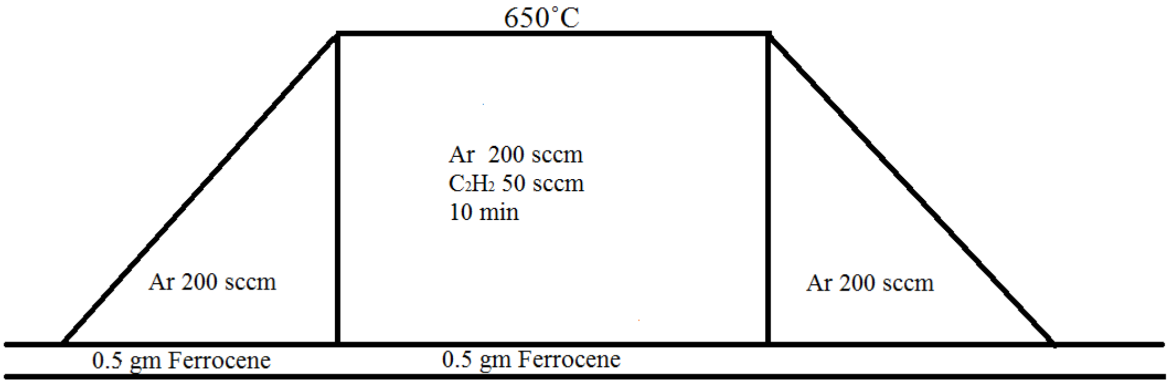

Figure-3.3 CNT-3(650 ^{0}C, C_2H_2-50 sccm)

3.5 Experiment No-4(600 ^{0}C, C_2H_2-50 sccm)

- 0.5 gm of ferrocene kept outside of the quartz tube.
- Flow the argon at 200 sccm.
- When temperature reached up to 600 ˚C slide the ferrocene boat inside the middle of quartz tube.
- Turn on the acetylene flow at 50 sccm for 10 minutes and argon flow also kept on.
- After 10 minutes close the acetylene flow.
- When temperature cool down up to 100 ˚C take out boat outside the quartz tube.

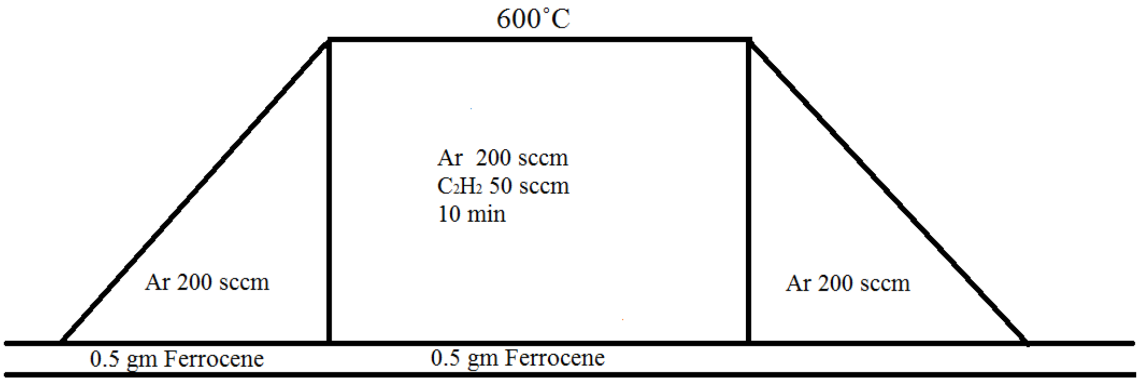

Figure-3.4 CNT-4(600 ^{0}C, C_2H_2-50 sccm)

3.6 Experiment No-5(800 ^{0}C, C_2H_2-50 sccm)

- 0.5 gm of ferrocene kept outside of the quartz tube.
- Flow the argon at 200 sccm.
- When temperature reached up to 800 ˚C slide the ferrocene boat inside the middle of quartz tube.
- turn on the acetylene flow at 50 sccm for 10 minutes and argon flow also kept on.
- After 10 minutes close the acetylene flow.
- When temperature cool down up to 100 ˚C take out boat outside the quartz tube.

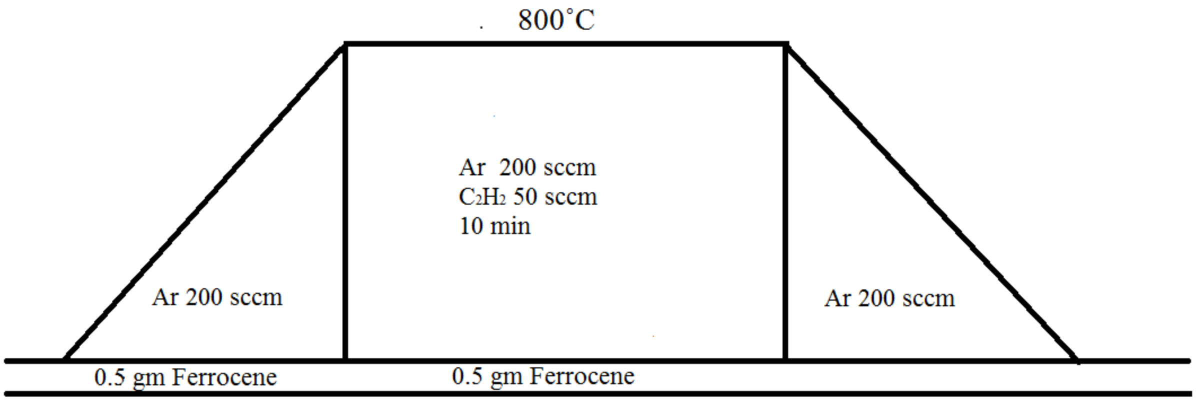

Figure-3.5 CNT-5 (800 ^{0}C, C_2H_2-50 sccm)

At a temperature higher than 500 °C, ferrocene decomposes completely spontaneously following the chemical reaction Fe- $(C_5H_5)_2$ f Fe + H_2 + CH_4 + C_5H_6 + ... as well as reactive hydrocarbons. Thus, when ferrocene enters the reaction zone, iron clusters and reactive carbon in the gas phase are produced. Upon these clusters, acting as catalyst nuclei, the SWCNTs nucleate and grow with the carbon atoms provided only from the ferrocene.

4.1 Characterization of sample using SEM

4.1.1 SEM image of CNT-1(750 ˚C, C_2H_2-50sccm)

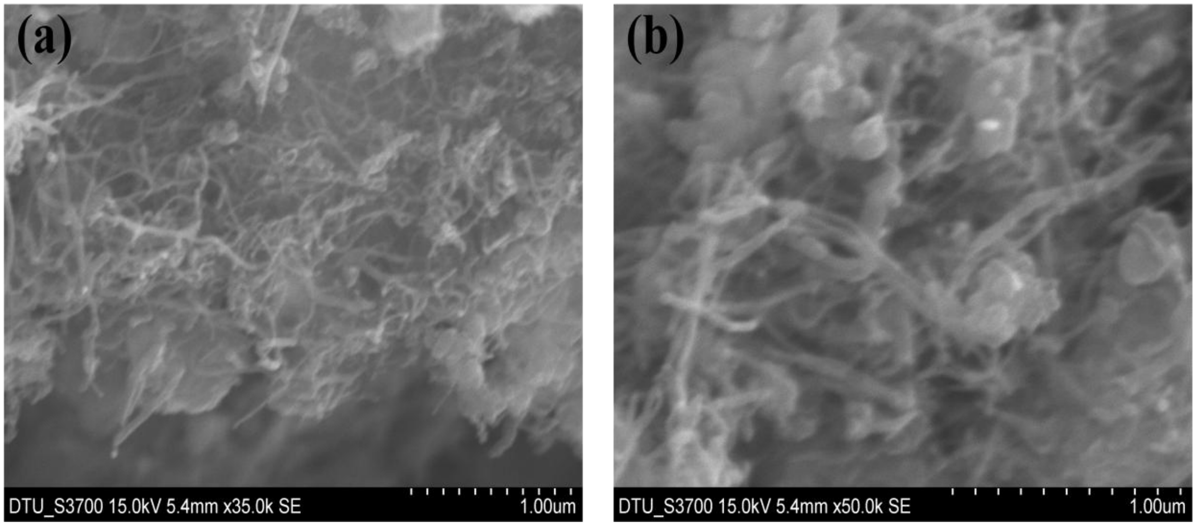

Figure- 4.1 SEM micrograph of CNT-1(a&b)(750 ˚C,C_2H_2-50sccm)

4.1.2 SEM images of CNT-2(700 ˚C, C_2H_2-50sccm)

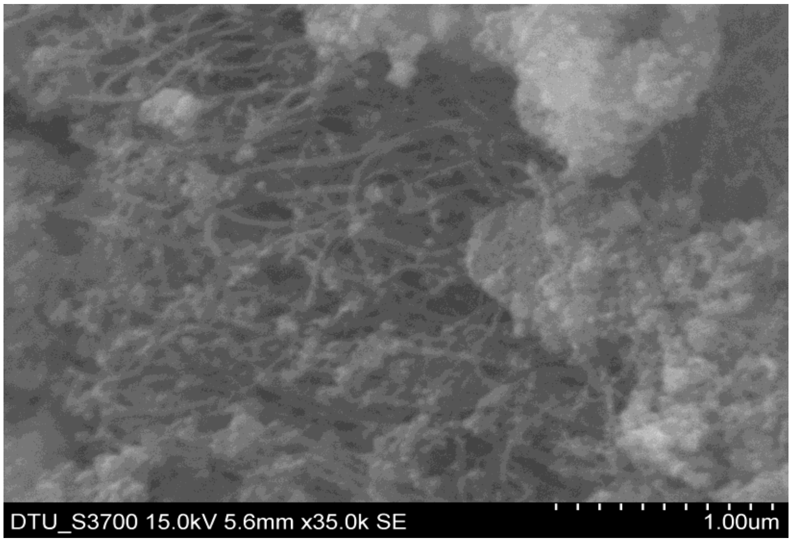

Figure-4.2 SEM micrograph of CNT-2(700 ˚C, C_2H_2-50sccm)

4.1.3 SEM image of CNT-3(650 ˚C, C_2H_2-50sccm)

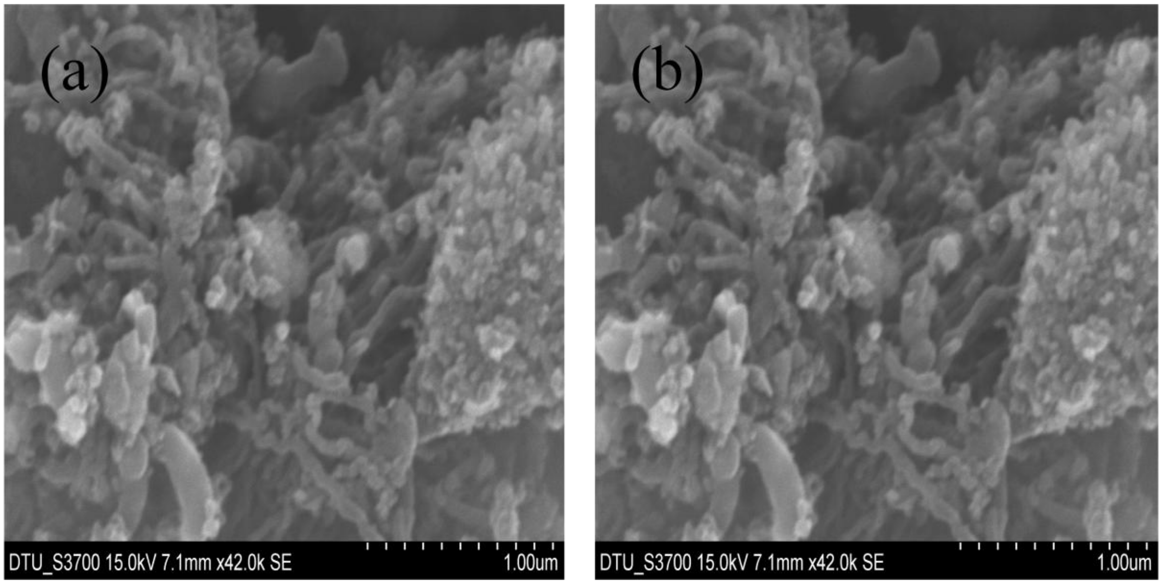

Figure 4.3 SEM micrograph of CNT-3 (a&b) (650 ˚C,C_2H_2-10sccm)

4.1.4 SEM image of CNT-4(600 ˚C, C_2H_2-10sccm)

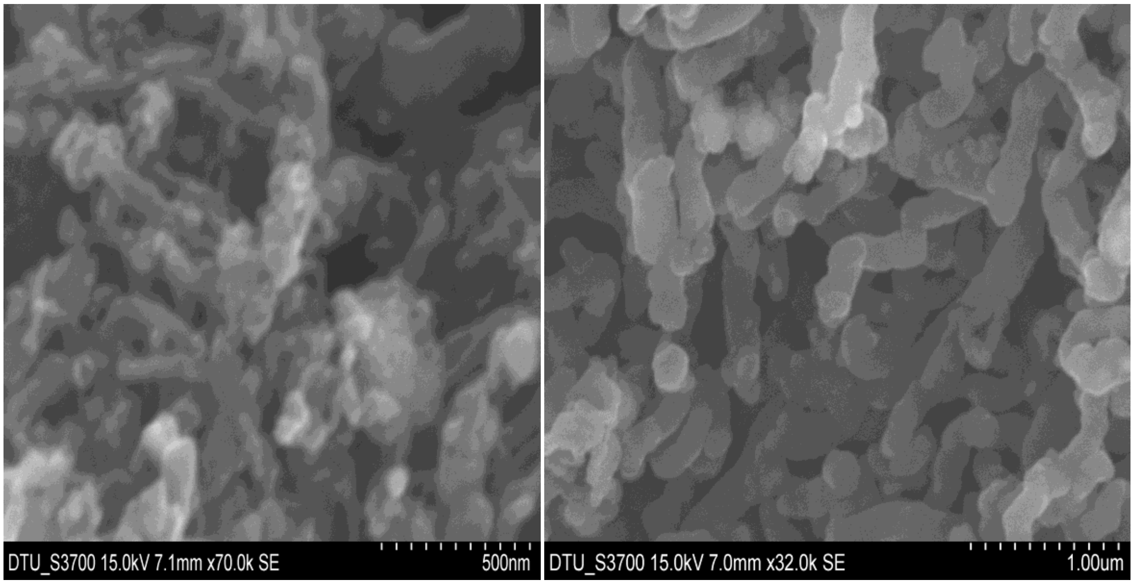

Figure-4.4 SEM micrograph of CNT-4 (a&b) (600 ˚C,C_2H_2-10sccm)

4.2 Characterization of sample using HRTEM

4.2.1 Magnified TEM image of CNT-1(750 ˚C, C_2H_2-100sccm)

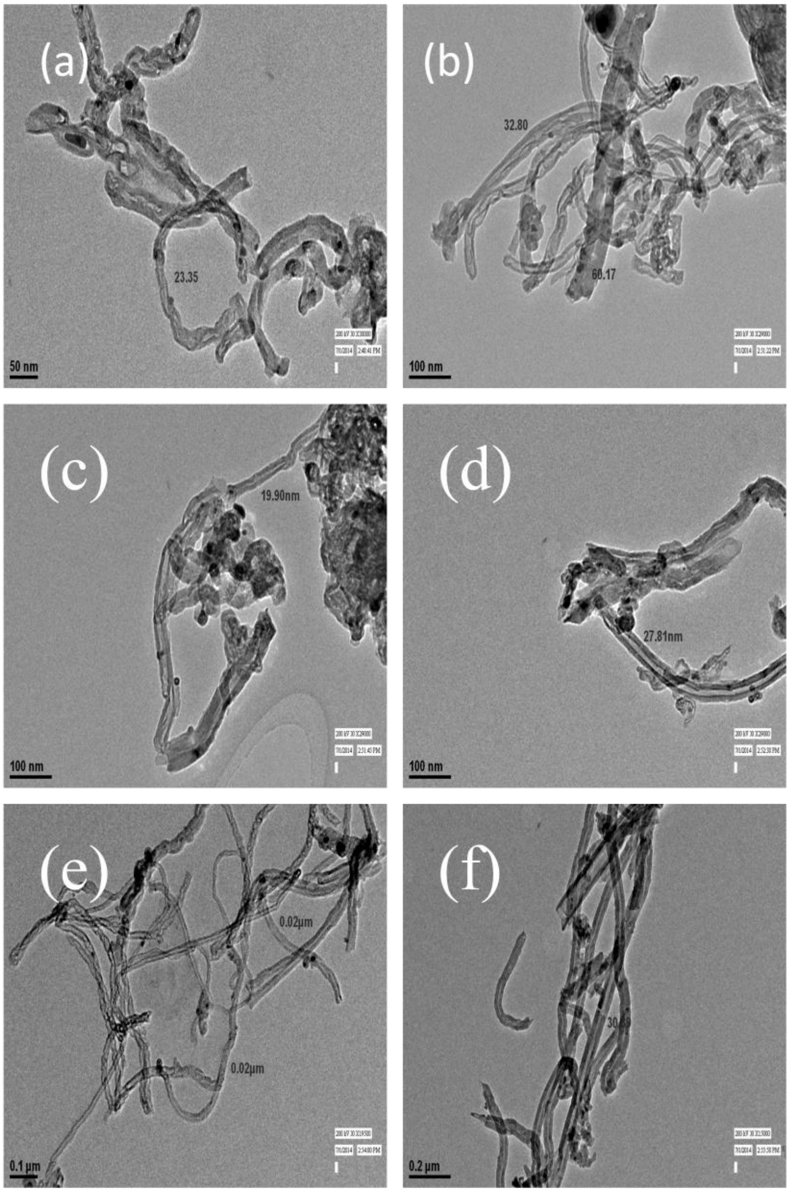

Figure 4.5 Micrograph of CNT-1(a,b,c,d,e&f)(750 ˚C,C_2H_2-100sccm)

4.2.2 Magnified TEM image of CNT-1(600˚C, C_2H_2-100sccm)

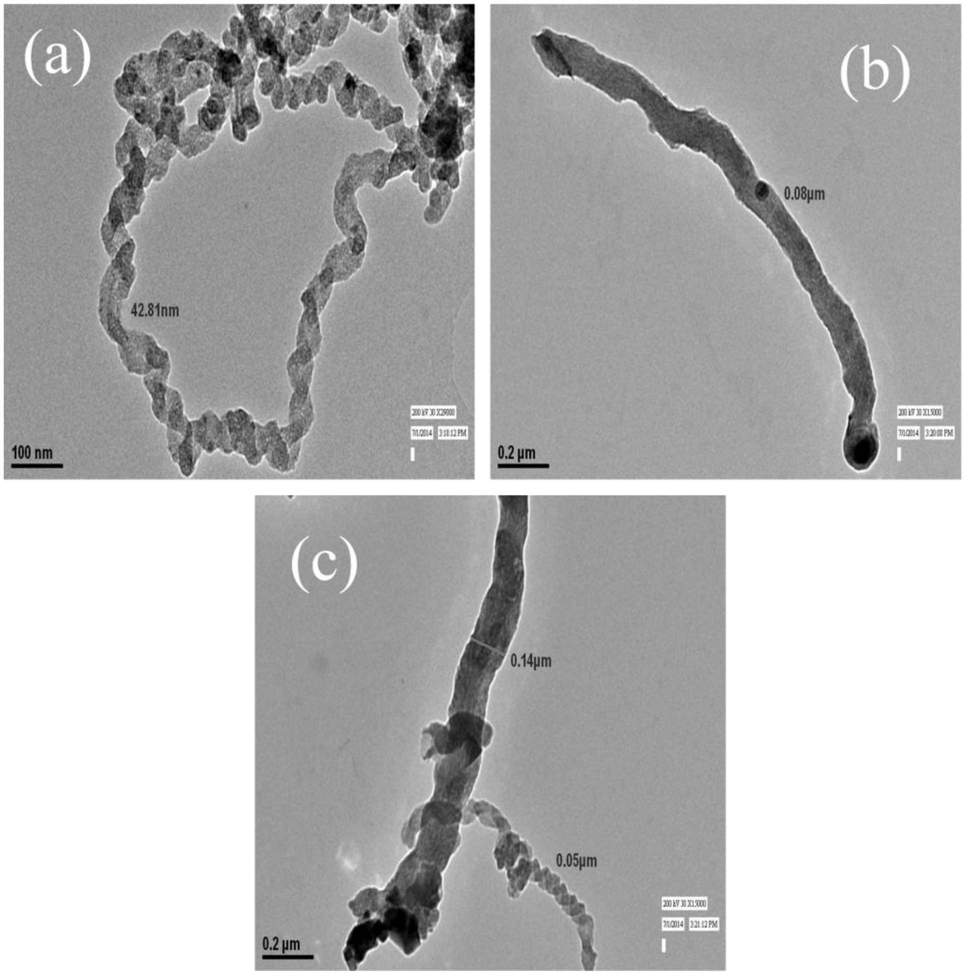

Figure 5.6 Magnified micrograph of CNT-4(a,b&c)(600 ˚C,C_2H_2-100sccm)

Chapter-5

5.1CONCLUSION

The high-temperature ferrocene method is suitable for the large scale synthesis of high quality and extremely narrow MWCNTs. The majority of the obtained diameters are in the range of 0.7-1.1 nm. The mean diameter can be tailored by varying the furnace temperature. Higher temperature lead to smaller diameters. The diameters are strictly limited by the isolated pentagon rule, which is needed to form a stable cap for MWCNT nucleation.

5.2 FUTURE WORK

Carbon Nanotubes (CNTs) and their compounds exhibit extraordinary electrical properties for organic materials, and have a huge potential in electrical and electronic applications such as photovoltaics, sensors, semiconductor devices, displays, conductors, smart textiles and energy conversion devices (e.g., fuel cells, harvesters and batteries).

5.2.1 CNTFET

As one of the promising new devices, CNFET avoid most of the fundamental limitations for traditional silicon devices. every the carbon atoms in carbon nanotubes(CNT) are bonded to each other with sp^2 hybridization and there is no dangling bond which enables the integration with high-k dielectric materials. The operation principle of carbon nanotube field-effect transistor (CNFET) is similar to that of traditional silicon devices. This three (or four) terminal device consists of a semiconducting nanotube, act as conducting channel, bridging the drain and source contacts. The CNTFET device is turned on or off electrostatically via the gate. The quasi-1D device structure provides better gate electrostatic control over the channel region than 3D device (e.g. bulk CMOS) and 2D device (e.g. fully depleted SOI) structures [4]

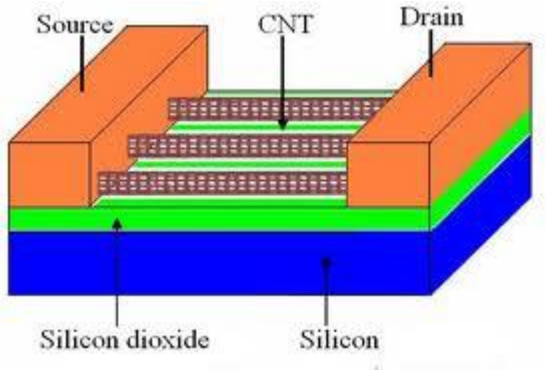

Figure 5.1-CNTFET [34]

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