CHAPTER 1

INTRODUCTION

1.1 NANOTECHNOLOGY

Nanotechnology is defined as the study and use of structures between 1 nanometer and 100 nanometer in size. It deals with matter in atomic and molecular scale. It focuses on researches involving molecular self-assembly and developing new materials with dimensions in nanoscale to atomic scale. Nanotechnology involves applications in the field of surface science, organic chemistry, molecular biology, semiconductor physics, microfabrication, etc.

The origin of nanotechnology in the 1980s, had its initial step by the invention of the scanning tunneling microscope in 1981 and the discovery of fullerenes in 1985 (Kroto et al 1985). The concept and goal of nanotechnology were popularized in 1986 with the publication of the book “Engines of Creation”. In 1986, Gerd Binnig and Heinrich Rohrer at IBM Zurich Research Laboratory received the Nobel Prize in Physics for their invention of scanning tunneling microscope in 1981. In 1996, Harry Kroto, Richard Smalley, and Robert Curl, won the Nobel Prize in Chemistry for the discovery of Fullerenes in 1985.

One nanometer (nm) is $10^{-9}$ of a meter. For example, the spacing between these atoms in a molecule and carbon-carbon bond lengths are in the range of 0.12–0.15 nm. Nanotechnology has two main approaches,
"bottom-up" and "top-down" are shown in Figure 1.1. In "bottom-up" approach, materials and devices are built from molecular components. Whereas in "top-down" approach, nano-components are developed from larger unit (Rodgers 2006). Nanoelectronics, nanomechanics, nanophotonics and nanoionics comprise the foundation of nanotechnology.

![Figure 1.1 Schematic representation of bottom-up and top-down approaches](image)

The properties of materials at nanoscale are considered different from the bulk. Larger surface area of nanomaterials when compared to the same mass of material produced in a bulk. This transition makes nanomaterials to adapt superior mechanical, chemical and electrical properties. In addition, quantum effect plays a vital role in determining the behavior of matter at the nanoscale. This property affects the optical, electrical and magnetic behaviour of materials. In nanoscale, materials can be architectured into various dimensions, such as one dimension (eg: thin films),
two dimension (eg: nanowires and nanotubes) and three dimensions (eg: nanoparticles).

1.2 CARBON

The chemical element, carbon represented by symbol “C” have atomic number 6 and electronic configuration [He] 2s² 2p². It belongs to the sixth element of the periodic table. The hybridization of carbon can be sp (e.g. C₂H₂), sp² (e.g. graphite) or sp³ (e.g. CH₄) forms. Figure 1.2 shows the different hybridisations of carbon.

In sp³ hybridisation, two linear 2sp³ orbitals are formed and two 2p orbitals are left. Linear σ bonds are created by the overlap of the 2sp³ hydride orbitals of neighbouring atoms. Two π bonds are produced by the overlapping unhybridised π orbitals of the two C atoms. These bonds are represented as C=C.

![Figure 1.2 The different hybridisations of carbon a) sp, b) sp², c) sp³](image)

In sp² hybridisation, three equivalent 2sp² orbitals are produced and one unhybridised 2p orbital is left. They are coplanar and oriented at 120° to each other and form σ bonds by an overlap with orbitals of neighbouring atoms. The remaining p orbitals on each C atom form a π bond by the overlap.
with the $\pi$ orbital from the neighbouring C atom. The bonds produced between two C atoms are represented as C=C.

In sp$^3$ hybridisation, four equivalent 2sp$^3$ hybrid orbitals are tetrahedrally arranged around the atom. They form four equivalent $\sigma$ bonds by an overlap with orbitals of other atoms. For example, in ethane molecule ($\text{C}_2\text{H}_6$) a $\sigma$ bond (or C-C) is formed between two carbon atoms by the overlap of sp$^3$ orbitals, and three Csp$^3$-H1s $\sigma$ bonds are formed on each C atom.

Solid carbon has two main allotropic forms that are stable at room temperature, Diamond and graphite. Fullerenes (Guo et al 1991), carbon nanotubes (Iijima et al 1993) and graphene (Novoselov et al 2004) are reported as very stable nanometer size sp$^2$ carbon bonded materials.

1.2.1 Allotropes of carbon

The ability of carbon to exist in different forms in the same physical state is known as ‘Allotropy’. The allotropic form of solid phase carbon exist mainly as follows: diamond, graphite, buckminsterfullerene, carbon nanotubes and graphene (Figure 1.3).

**Diamond**: An electrical insulator with 3D-lattice crystal structure. Diamond consists of carbon atoms that are tetrahedrally bonded to each other through sp$^3$ hybrid bonds that form a three dimensional network. Each carbon atom has four nearest-neighbour carbon atoms. This is the hardest known substance, due to very strong C-C covalent bonds.
Graphite: An electrical conductor having layered lattice crystal structure with 2D structure. The layered structure with each layer called graphene sheet are formed from hexagons of carbon atom. Each carbon atom forms three covalent σ-bonds with C atoms. These σ-bonds are made up of sp² hybrid orbital. The p-orbitals, perpendicular to the plane of the σ-bonds, overlap to form a delocalized π-system. The hexagonal sheets are held together by weaker Van der Waals force. Due to this weak force, graphite is slippery and used as a lubricant.

Amorphous carbon: The carbon that does not have any crystalline structure is termed amorphous carbon. Similar to glassy materials, they possess some short-range order rather than long-range pattern of atomic positions. Materials with more sp³ hybridized bonds are referred to as tetrahedral amorphous carbon (due to the tetrahedral shape formed by sp³ hybridized bonds). Most of
the material classified as “amorphous” include crystallites of graphite or diamond with varying amounts of amorphous carbon binded together to form polycrystalline or nanocrystalline materials. Commercially available carbon consists of significant quantities of other elements, which may form crystalline impurities. The examples of amorphous carbon include coal and soot. These products are obtained by pyrolysis, other than normal conditions.

**Fullerenes**: A new class of carbon material with 0 D called $C_{60}$ was discovered in 1980s. It was named “buckminsterfullerene” after the architect and inventor Buckminster Fuller, well-known for building geodesic domes that resembles the structure of $C_{60}$. It has spherical molecules about 1nm in diameter, comprising 60 carbon atoms arranged as 20 hexagons and 12 pentagons. In fact the configuration was similar to a football. Each carbon atom is trigonally bonded to three other carbon atom in $sp^2$ derived bonding configuration. The curvature of the trigonal bonds in $C_{60}$ leads to some mixture of $sp^3$ bonding, characteristic for tetrahedrally bonded diamond, but absent in graphite. Larger quantities of $C_{60}$ can be produced by resistively heating graphite rods in a helium atmosphere. Since $C_{60}$ is soluble in benzene, single crystal of it can be grown by slow evaporation from benzene solution. Fullerenes find application in various fields such as miniature ‘ball bearings’ to lubricate surfaces, drug delivery vehicles and in electronic circuits.

**Graphene**: Graphene is atomically two dimensional material. It is single one-atom-thick planar sheet made of $sp^2$-bonded carbon atoms densely packed in a honeycomb crystal lattice (Novoselov et al 2005). Bulk graphite comprises of several loosely bonded graphene layer stacked over each other. Hence these layers slip freely to make the extraction of graphene possible from graphite crystal through mechanical or chemical exfoliation (Zhang et al 2005). Graphene have exciting electronic properties, such as room temperature anomalous quantum Hall effect (Novoselov et al 2007) and
electrons behaving like massless Dirac fermions (Novoselov et al 2005). The outstanding electronic property of graphene with high mobility and tunable electronic conduction make them capable material for future electronics.

**Carbon nanotube:** A Carbon nanotube (CNT) is made up of carbon atoms in a tubular morphology. CNTs bonding structure have \( sp^2 \) hybridization. They have a 2D structure with diameter in the range of few nanometer and length in micrometers. Since the landmark publication of Iijima (1991) the CNTs are widely used in many applications due to their unique electrical, mechanical, optical and thermal properties. The application of CNTs normally depends on CNTs structure (number of walls, diameter, length, chiral angle, etc.).

### 1.3 CARBON NANOTUBES

Radushkevich et al (1952) initially observed and described CNTs. In 1976, Oberlin et al observed the single or double walled carbon nanotubes. Later in 1991, the discovery of CNTs is accredited to Iijima as the first scientist who described the MWNTs preparation process (Iijima 1991). In 1993, Iijima et al and Bethune et al (1993) reported the growth process of SWNTs. The focus of research on CNT made them an exciting material after ever. The outstanding properties of CNT include: many-fold stronger than steel, electrical conductivity higher than copper, thermal conductivity higher than diamond, etc.

### 1.3.1 Types of CNT and structures

CNTs can be classified into two basic forms, single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs). SWCNTs are composed of a single tube of graphene, whereas MWCNTs
consists of several concentric tubes of graphene fitted one inside the other. The diameter of SWCNTs exists in few nanometres and several tens of nanometres in the case of MWCNTs. SWCNT was discovered in 1993 (Iijima & Ichihashi), 2 years after the discovery of MWCNTs (Iijima 1991). They are often seen as straight or elastic bending structures individually or in ropes by Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM). The exceptional properties of CNTs are exploited in the field of solar cells, fuel cells, supercapacitors, transistors, memories, displays, separation membranes and filters, purification systems, sensors, etc.

A nanotube is generally characterized by its diameter \( D \) and the chiral angle \( \theta \) \((0 \leq \theta \leq 30^\circ)\). The chiral vector \( C_h \) is defined with the two integers \((n, m)\) and the basis vectors of the graphene sheet.

\[
C_h = na_1 + ma_2 \equiv (n, m) \quad (1.1)
\]

where \( a_1 \) and \( a_2 \) are the graphene lattice vectors and \( n \) and \( m \) are integers. The integers \((n, m)\) determine \( D \) and \( \theta \):

\[
D = \frac{|C|}{\pi} = a \left( n^2 + nm + m^2 \right)^{1/2} / \pi \quad (1.2)
\]

\[
\theta = \tan^{-1} \left[ 3^{1/2} m / (m + 2n) \right] \quad (1.3)
\]

where \( a = |a_1| = |a_2| \) is lattice constant of graphite.
By rolling a graphite sheet in different directions, three typical NTs can be obtained: zig-zag \((n, 0)\), armchair \((m, m \text{ or } n = m)\) and chiral \((n, m)\) where \(n > m > 0\) by definition. \(\theta\) ranges from 0 for zig-zag \((m = 0)\) and 30° for armchair \((m = n)\) tubes. Figure 1.4 shows the schematic representation of types of NTs with various chirality and \((n,m)\) indices determine the metallic or semiconducting SWCNT by electronic band structure calculations (Mintmire et al 1992). Zigzag \((n, 0)\) SWCNTs exhibit two types of behavior: Metallic (if \(n/3\) is an integer) and otherwise semiconductors (Saito et al 1992). In the case of chiral \((n,m)\) SWNTs, when \((2n+m)/3\) is an integer the tubes are metallic, and otherwise semiconducting. The gaps of the semiconducting \((n,0)\) and \((n,m)\) tubes depend inversely on diameter. When \(n = m\), armchair \((n,n)\) tubes are expected to be truly metallic with band crossings at \(k = \pm 2/3\) of the one-dimensional Brillouin zone.
The metallic nature of armchair (n = m) tubes occur due to the bands crossing the Fermi level (Dresselhaus et al 1996). In contrast, chiral and zigzag have two possibilities. When n - m = 3 l (where l is an integer), tubes are estimated to be metallic. In the case n - m ≠ 3 l, tubes are expected to be semiconducting with an energy gap of 0.5 eV. This energy gap depend on the diameter (ie, \( E_{\text{gap}} = 2\gamma_0 a_{\text{C-C}}/d \), where \( \gamma_0 \) is the C–C tight-binding overlap energy, \( a_{\text{C-C}} \) the nearest neighbour C–C distance (0.142 nm) and ‘d’ the diameter).

1.3.2 Morphologies of CNT

Theoretically it was reported that CNTs can exists in different shapes such as: toroidal (Ihara & Itoh 1993), coiled (Dunlap 1994) and branched (Macky & Terrones 1991) other than the straight. All these structures depend on the introduction of non-hexagonal defects in seamless hexagonal networks. Especially, the models of the regular helical coils of CNT’s are derived from a very definite packing of pentagons and heptagons in a perfect hexagonal lattice. The architecture may lose its coil structure, if the regular arrangement is disturbed by misplacing one single non-hexagonal ring (Dunlap 1994). The model describes the architecture of the regular helically coiled nanotubes with non-hexagonal/hexagonal ratio higher than unity (Lambin et al 2003).

1.3.2.1 Coiled carbon nanotubes

In the early 1990s, Coiled CNTs were predicted (Itoh & Ihara 1993). These CNTs are produced when paired pentagon-heptagon atomic rings assemble themselves periodically within the hexagonal carbon network (Gao et al 2000). Theoretical calculations have proved that different forms of helically coiled structures can exists with structures that are energetically and
thermodynamically stable (Ihara & Itoh 1993). Figure 1.5 represent a schematic model of coiled CNTs. In 1950s, the helical structures of carbon have been observed (Davis et al 1953). In 1994, Coiled CNTs were observed experimentally (Amelinckx et al 1994).

![Figure 1.5 Morphology of coiled CNT (Wu et al 2013)](image)

Various mechanisms were proposed for the formation of coiled CNTs. Theoretically it was predicted, regular insertion of pentagon-heptagon pairs at the junction result in CNTs without other crystallographic defects. The most widely accepted model describes the localized stresses and anisotropic rates of carbon deposition (Ivanov et al 1994) on catalyst particles. A thermodynamic model (Bandaru et al 2007) was postulated, where helix/coil formation depends on the interactions between catalyst particles and growing nanostructures. In general coiled CNTs can be produced in large quantity by catalytic CVD (Ivanov et al 1994).

The attraction of their special morphology enables them to be used as high-performance electromagnetic wave absorbers, sensors, resonators, nanoscale mechanical springs, electrical inductors, and generators of magnetic
beams. For applications, it is advantageous to have control over the geometry (diameter, pitch, length, and turning direction) and coil morphology.

1.3.2.2 Branched carbon nanotubes

The initial models on the structure (Scuseria 1992) of CNT Y-junctions are based on the insertion of non-hexagonal rings in the hexagonal network, where the three branches of the Y are connected. Most of the structural models (Menon & Srivastava 1997) follow the same construction principle of conserving the sp$^2$ hybridization of the carbon network. They vary only in the kind, number, and position of the non-hexagonal rings. These changes enable the possibility of the constructions of various symmetric and asymmetric model junctions (Andriotis et al. 2002). The dependence of electrical properties on CNTs structure (chirality and diameter), enables various combinations of metallic and semiconducting tubes to build CNT junctions for nanoscale integrated circuits (Popov 2004).

In 1999, the first report demonstrated their synthesis by pyrolysis of acetylene in Y-shaped templates (Li et al 1999). After then, various works has focused on catalytic CVD (Wei et al 2006). Various processes and mechanisms were also reported. A single-particle process (Heyning et al 2005) was performed for the synthesis of branched CNTs by altering the temperature, gas flow, or carbon source feeding. These changes vary the distribution of carbon atoms over the catalyst particles and modify the growth direction to obtain a multi-stem CNT. In a process (Ding et al 2005), the liquid-phase metal-carbon solution is to made encapsulated in a CNT. This splits into smaller particles and result in the growth of branched CNTs. Figure 1.6 illustrates a schematic representation of a branched CNT.
In a promising process (Wei et al 2006), the catalyst species encapsulated in two neighbouring CNTs fuse together to form a larger catalyst particle, that catalyzes the growth of a third CNT branch. The doping metals (Ti (Gothard et al 2004) or Mo (Choi & Choi 2005)) have major roles in the attachment process. There are also reports on multi-branching CNT structure synthesized by dc plasma enhanced CVD (AuBuchon et al 2006). The structure has aligned CNTs with branches of smaller diameters, grown along a direction perpendicular to the parent CNT. It was observed that these processes mostly produced branched MWCNTs, with some poor crystallographic structures.

![Figure 1.6 Morphology of branched CNT](image)

Choi & Choi (2005) reported the successful synthesizes of Y-junction SWCNTs controlled catalysts by thermal CVD. Here, Mo-doped Fe nanoparticles supported by aluminum oxide particles were used as catalysts. It was observed that distribution of Mo-doped Fe particles have a major role in Y-junction formation.
1.4 CARBON NANOTUBES SYNTHESIS

Carbon nanotubes are generally produced by three main techniques, arc discharge, laser ablation and chemical vapour deposition.

1.4.1 Arc Discharge

The arc discharge synthesis of MWCNTs is considered very simple technique. This method use DC arc discharge between two graphite electrodes placed in a chamber filled with helium at sub atmospheric pressure. Figure 1.7 demonstrates a diagram of typical arc-evaporation apparatus for the production of nanotubes. In addition to helium, there are reports on the use of hydrogen or methane atmosphere (Wang et al 1996). Ebbesen and Ajayan followed the arc discharge technique used by Iijima (1991) under He atmosphere to obtain first large-scale synthesis of CNTs. The gas pressure in the reactor decides the purity and yield of CNTs (Ebbesen & Ajayan 1992).

Figure 1.7 Diagram of typical arc-evaporation apparatus for the production of nanotubes (Ando & Iijima 1992)
Shimotani et al (2001) reported synthesis of MWCNTs using an arc discharge technique under He, ethanol, acetone and hexane atmosphere. It was observed that the organic atmospheres produce more MWCNTs than in the He atmosphere. In contrary to helium, the acetone, ethanol and hexane get ionized and decomposed into hydrogen and carbon atoms. These ionized species may contribute the yield synthesis of MWNTs.

Bethune et al (1993) reported Co catalyzed growth of SWCNTs. The co-evaporation of carbon and cobalt in an arc generator are responsible for the growth of CNTs with diameters (1.2 nm) and single atomic layer thick wall. A modified version of arc discharge method is also utilized for the SWCNTs synthesis. Chen et al (2010) reported the FH (ferrum–hydrogen) arc discharge method. This method uses a hydrogen DC arc discharge and carbon anode containing 1% Fe catalyst in $\text{H}_2$–Ar mixture gas. The SWCNTs obtained by this technique have high crystallinity with purity higher than 90%.

1.4.2 Laser Abalation

Laser ablation works act as crucial step for pulsed laser deposition process (PLD). This technique is one of the superior methods to grow SWCNTs with high-quality and high-purity. The first demonstration of this technique was performed by Smalley’s group in 1995 (Guo et al 1995). The mechanisms and principles are analogous to the arc discharge with the differentiation that the energy is provided by a laser hitting a graphite pellet containing catalyst materials (Ikegami et al 2004).

A schematic diagram of a laser-vaporisation apparatus for the synthesis of CNT is shown in Figure 1.8. The properties of CNTs prepared by PLD dependents on various parameters such as: the laser properties, the target
material, the chamber pressure and the chemical composition, the substrate and ambient temperature and the distance between the target and the substrates.

Figure 1.8 Oven laser-vaporisation apparatus for the synthesis of single-walled carbon nanotubes (Yakobson & Smalley 1997)

Nd:YAG and CO$_2$ are the common lasers used for the ablation. For example, Zhang et al (2003) used CO$_2$ laser ablation for the preparation of SWCNTs. To date, the growth mechanisms of SWCNTs in connection to the excitation wavelength is yet to be clarified. UV laser is considered to create a new species of nanoparticles and suggests a new generation mechanism of CNTs. UV-laser (KrF excimer) ablation of a graphite target doped with Co/Ni metal catalyst was utilized for the synthesis of SWCNTs by Lebel et al (2010). XeCl excimer laser was used by Kusaba & Tsunawaki (2006) to irradiate graphite containing Co and Ni to produce SWCNTs.

1.4.3 Chemical Vapour Deposition

Figure 1.9 illustrates a schematic diagram of CVD set up used for CNT growth. In CVD process, hydrocarbon sources (gas/liquid) are passed through a tubular reactor made of quartz. The catalyst is placed at centre of the tube having suitable temperature (600–800°C) to decompose the hydrocarbon. The final black product (CNTs) grown on the catalyst are collected upon cooling the reactor to room temperature.

![Diagram of typical chemical vapor deposition apparatus for the production of nanotubes](image)

While using liquid hydrocarbon (benzene, alcohol, etc.), the liquid is pre-heated in a flask at lower temperature. The hydrocarbon vapor is carried into the reaction zone from the flask with the help of an inert gas. In the case of a solid hydrocarbon precursor (eg: camphor, naphthalene, ferrocence etc.),
it is placed in the low-temperature zone of the reaction tube. These volatile precursors get converted from solid to vapor and undergo CVD reaction while passing over the catalyst kept in the high-temperature zone. Similar to CNT precursors, catalyst precursors can also be used in different form: solid, liquid or gas. These precursors can be placed inside the reactor or injected from the inlet of reaction tube. The process in which metal nanoparticles are liberated by the pyrolysis of the catalyst vapor at a suitable temperature is known as floating catalyst method. On the other hand, catalyst coated substrates can also be placed in the high temperature zone of the furnace for the growth of CNT.

Catalyst plays a vital role in the CVD growth of CNT. In CVD the key purpose of the catalyst includes, the decomposition of carbon source via plasma irradiation or heat and its nucleation to form CNTs. The commonly used catalysts are transition metals (e.g., Fe, Co, or Ni.) (Lee et al 2010). The most frequently used carbon sources in CVD are methane, ethane, ethylene, acetylene, xylene, isobutene or ethanol. Generally Ni, Si, SiO₂, Cu, Cu/Ti/Si, stainless steel, glass, CaCO₃, graphite and tungsten foil are used as common substrates (Afolabi et al 2011 and Dumpala et al 2011).

Mesoporous silica comes under a special category of substrates, due its templating role in promoting the initial nanotube growth. Zhu et al (2003) reported a CVD synthesis of CNTs over Fe and Co loaded mesoporous silica. In addition Hiraoka et al (2003) succeeded in using another substrate, zeolites. They reported CVD of acetylene over Co/Fe embedded zeolites at 900°C for selective synthesis of CNTs. The choice and preparation of catalyst is a crucial step in CNTs synthesis. Hence the composition and morphology of the catalyst species hold the main role for the CNTs growth by CVD. For example, Flahaut et al (2005) reported the preparation of catalysts by the combustion using urea or citric acid. They observed that using citric acid can
either limit the CNT growth or increase its selectivity with fewer walls, depending on the catalyst composition. Xiang et al (2009) also reported the growth of CVD growth of CNTs using Co/Fe/Al layered double hydroxides catalysts. It was observed that enhancing the Co content increased the carbon yield as a result of fine dispersion of excess active Co species.

Li (2010) reported the growth MWCNTs over Ni deposited SiO$_2$/Si substrates using CVD of C$_2$H$_2$ at 900°C. Using different iron-containing proteins (hemoglobin, myoglobin and cytochrome) as catalysts, Kim et al (2011) had reported a novel growth method to control the size and atomic structure of the CNTs. This study has demonstrated the growth of both SWCNT and MWCNTs from iron-containing proteins.

1.4.3.1 Advantages of CVD

CVD is a simple and economic technique for synthesizing CNTs at low temperature and ambient pressure, when compared to arc-discharge and laser-ablation methods. In the case of yield and purity, CVD is much superior to the arc and laser methods. Also CVD is the best method to control the structure or CNT architecture. CVD is an adaptable technique in case of providing platform for the use of plenty of hydrocarbons (solid, liquid or gas), the use of various substrates and designing CNT growth in a different forms (eg: powder, thin or thick films, aligned or entangled, straight or coiled nanotubes). CVD also offers better control on the growth parameters.

1.4.4 CNT growth mechanism

The growth mechanism of CNTs is a subject of debate. There exist numerous reports on the possibilities which are often contradicting. The most widely-accepted general mechanism can be described as follows. The
interaction of hydrocarbon vapor with the “hot” metal nanoparticles decomposes the hydrocarbon into carbon and hydrogen molecules. The carbon gets dissolved into the metal and the hydrogen escapes away. The carbon solubility in metal nanoparticle upon reaching the saturation point precipitates out and crystallizes in the form of a cylindrical network. The tubules are considered energetically stable with no dangling bonds. This process involves mainly two processes: Hydrocarbon decomposition (exothermic process) and carbon crystallization (endothermic process). Thus a specific thermal gradient generated inside the metal particle drives the reaction continues further.

In general, two growth models are proposed for the growth of CNTs. They are “tip-growth” and “base-growth” models. Figure 1.10 (a) represents the mechanism behind the tip –growth model. When the catalyst–substrate contact is weak, hydrocarbon decomposes on the top surface of the metal. This pave path for the diffusion of carbon molecules into the metal. Upon reaching the saturation limit, CNT precipitates out across the metal bottom, pushing the whole metal particle off the substrate (step (i)). Further growth of CNT continues, if the metal’s top is exposed for hydrocarbon decomposition (step (ii)). The CNT growth is terminated when catalytic activity is ceased by excess coating of carbon over the metal (step (iii)). This is known as “tip-growth model” (Baker et al 1972).

Figure 1.10 (b) illustrates the mechanism involved in “base-growth model.” In the case of strong catalyst–substrate interaction, hydrocarbon decomposition is followed by carbon diffusion similar to the tip-growth case. Here, the CNT precipitation does not drive the metal particle up. Hence, the precipitation is constrained to emerge out from the top surface of metal. Initially, carbon crystallizes out as a hemispherical dome which then extends up in the form of graphitic cylinder. Later hydrocarbon deposition occurs on
the lower peripheral surface of the metal, and permit dissolved carbon diffuses upward. Consequently CNT grows up with the catalyst particle rooted on its base; for this reason, this is known as “base-growth model” (Baker et al 1975).

Figure 1.10 Growth mechanisms for CNTs: (a) tip-growth model, (b) base-growth model (Kumar & Ando 2010)

1.5 FACTORS INFLUENCING THE GROWTH OF CARBON NANOTUBES

1.5.1 Catalysts

For the typical synthesizing CNTs, nanometer-size metal particles are essential to permit hydrocarbon decomposition at a lower temperature than the spontaneous decomposition temperature of the hydrocarbon. In general, the commonly-used metals are Fe, Co, Ni, for the reason that of (i) high solubility of carbon in these metals at high temperatures; and (ii) high
carbon diffusion rate in these metals. In addition, high melting point and low equilibrium-vapor pressure of these metals provide a broad temperature window of CVD for a wide range of carbon precursors. It was reported that Fe, Co, and Ni have stronger adhesion with the growing CNTs and hence they are more capable in forming CNTs with low-diameter (Ding et al. 2008).

Solid organometallocenes (ferrocene, cobaltocene, nickelocene) also act as excellent catalyst for CNT growth. They contribute metal nanoparticles in-situ which catalyzes the hydrocarbon decomposition. The catalyst-particle size determines the tube diameter. Campbell and co-workers has reported the particle size dependence and a model for growth of CNTs (Morjan et al. 2004). The key feature to produce pure CNTs is attaining hydrocarbon decomposition on the surface of catalyst and elimination of aerial pyrolysis. In addition to the transition metals (Fe, Co, Ni), other metals of this group, such as Cu, Au, Ag, Pt, Pd were also reported as good catalyst for the CNT growth. (Moisala et al. 2003).

It is worth to reveal that transition metals are efficient catalysts not only in CVD but also in arc-discharge and laser-vaporization methods. Therefore this is an open area of research to correlate different CNT techniques with respect to the catalyst’s role in different temperature and pressure range.

1.5.2 Catalyst Supports

In general, a catalyst works in a different way on various support materials. Frequently used substrates in CVD are graphite (Baker et al. 1975), quartz (Kumar & Ando 2003), silicon (Kumar et al. 2004), silicon carbide (Ding et al. 2003), silica (Mattevi et al. 2008), alumina (Hongo et al. 2002), zeolite (Willems et al. 2000), CaCO₃ (Couteau et al. 2003), magnesium oxide
(Ward et al 2003) etc. The catalyst–substrate interaction is an important parameter to be examined with utmost attention for an efficient CNT growth. Metal–substrate reaction would prevent the catalytic behaviour of the metal. The yield and quality of CNTs mainly depend on the surface morphology and textural properties of the substrate material. Zeolite supports incorporated with catalysts in their nanopores have bestowed significantly high yields of CNTs with a narrow diameter distribution (Hernadi et al 1996).

Alumina materials are reported to be a superior catalyst support than silica due to strong metal–support interaction in alumina. This permit high metal dispersion and thus a high density of catalytic sites over alumina (Nagaraju et al 2002). Such interactions avoid aggregation of metal species and creating unnecessary large clusters that result in graphite particles or defective CNTs (Ago et al 2004). This was confirmed by in-situ XPS analysis of CNT growth from different precursors on iron catalyst supported on alumina and silica substrates (Mattevi et al 2008). There also reports on thin Alumina flakes loaded with iron nanoparticles, leading to high yield of aligned CNTs of high aspect ratio (Pint et al 2008). It was reported that the oxide substrate, mainly used as a physical support for the metal catalyst, involve in a few chemistry in the CNT growth (Noda et al 2007). Consequently, the chemical state and structure of the substrate play a very essential role than that of the metal.

1.5.3 CNT Precursors

The most frequently used carbon precursors are methane, ethylene, acetylene, benzene, xylene and carbon monoxide. Using iron nanoparticle as a catalyst, Endo et al (1993) described the growth of CNT from pyrolysis of benzene, while JoseYacaman et al (1993) reported helical MWCNTs at 700°C from acetylene. Afterward, other precursors consisting of cyclohexane
Li et al. (2007) and fullerene (Morjan et al. 2004) were used for the growth of MWCNTs. Dai et al. (1996) first reported SWCNTs from disproportionation of carbon monoxide at 1200°C, in the presence of molybdenum nanoparticles. Soon after, SWCNTs were also reported using benzene, acetylene (Satishkumar et al. 1998), ethylene, (Hafner et al. 1998), methane, (Flahaut et al. 1999) cyclohexane (Gruneis et al. 2006), fullerene (Maruyama et al. 2003) etc. by using different catalysts. Maruyama et al. (2002) described the low-temperature synthesis of high-purity SWCNTs from alcohol on Fe–Co-impregnated zeolite support and ethanol turn out to be the most popular CNT precursor in the CVD method (Gruneis et al. 2006). The extraordinary feature of ethanol involves the amorphous carbon free growth of CNTs, due to the etching effect of OH radical (Murakami et al. 2003).

According to the general observation, low-temperature CVD (600–900°C) yields MWCNTs, while high-temperature (900–1200°C) reactions promote SWCNT growth. This represent that SWCNTs have a higher energy of formation. In general, MWCNTs can be easily grown (than SWCNTs) from majority of the hydrocarbons. Whereas SWCNTs can only be grown from chosen hydrocarbons (viz. carbon monoxide, methane, etc. which possess good thermal stability in the range of 900–1200°C). Normally the best known carbon precursors of MWCNTs (viz. acetylene, benzene, etc.) are unstable at higher temperature and result in deactivation of catalyst to produce large amounts of carbonaceous compounds than CNTs.

The molecular structure of the carbon precursor also has an adverse effect on the morphology of the CNTs. Linear hydrocarbons (viz. methane, ethylene, acetylene, etc) thermally decomposed into atomic carbons or linear dimers/trimers of carbon, normally result in the growth of straight hollow CNTs. In contrast, cyclic hydrocarbons (viz. benzene, xylene, cyclohexane, fullerene, etc) generate curved/arched CNTs inside (Morjan et al. 2004).
1.6 CLASSIFICATION OF POROUS MATERIALS

Extending the innovative idea of molecular templates to supramolecular aggregates, a new period was started in the design and synthesis of porous materials with tailored mesoporous structures (Kresge et al. 1992). Ordered mesoporous solids are built of inorganic/organic hybrid units of long range order with amorphous walls, tunable textural and structural properties with highly controllable pore geometry and narrow pore size distribution in the 2–50 nm range. Although zeolites are used on a technical scale in catalysis and separation, ordered mesoporous solids have recently come into the field of commercialization with applications in adsorption, catalysis, separation, energy storage and conversion to optoelectronics and nanotechnology (Ji & Zhang 2009).

Figure 1.11 Classification of porous materials
The porous materials are classified into three types such as microporous, mesoporous and macroporous. According to the IUPAC definition these materials can be microporous \((D < 2 \text{ nm})\), mesoporous \((D = 2–50 \text{ nm})\) or macroporous materials \((D > 50 \text{ nm})\) depending on the pore diameter \((D)\) (Sing et al. 1985). The classification of porous material is given in Figure 1.11. The microporous materials have limited pore size with low surface area and the constant channel size. Hence, due to lack of pore size flexibility, the microporous materials are not capable for the synthesis of CNTs. Even though macroporous materials possess some disadvantages like disordered structure, the CNTs growth occurs over the external surface of the support. The new family of mesoporous molecular sieves with remarkably large uniform pore structures is an ideal material for the synthesis of CNTs.

1.7 MESOPOROUS MATERIALS

The porous materials are solid forms of matter inbuilt with interconnected or non-interconnected pores (viz. channels, cavities or interstices). The internal structural design of the void space decides the physical and chemical properties; such as reactivity, thermal and electric conductivity, in addition to the kinetics of several transport processes. The characterization of porous materials, find application in numerous areas including catalysis, adsorption, purification, separation, etc. The advantageous aspects for such applications are pore accessibility, narrow Pore Size Distribution (PSD), relatively high specific surface area and easily tunable pore sizes. Ordered porous solids with regularly arranged pore system, architect the materials with various cylindrical, window-like, spherical or slit-like pore shapes and sizes. Synthetic zeolites and associated porous materials fit in to the group of ordered microporous solids and have been commercially utilized on a large scale (Endo et al. 2004).
The possible applications of mesoporous materials were highly constrained as they possessed high heterogeneity in pore size with irregular arrangements. In 1969, the first report on ordered mesoporous material was mentioned in a patent with the lack of sufficient characterization. The scientists at the Mobil Oil Corporation in the early 1990's and Japanese researchers (Inagaki et al 1993) were the first to discover the ordered mesoporous solids. Mesoporous siliceous materials (e.g.: MCM-41, MCM-48, MCM-50, SBA-1, SBA-15, SBA-16 and KIT-6) have been synthesized via self-assembly methods by means of long-chain ionic and anionic surfactants as templates (Kleitz et al 2003). The MCM-41 act as a potential catalyst and catalyst support due to their large pore volume (>1.0 cc/g), high surface area (>1000 m²/g), large pore diameter (>2 nm) and narrow pore size distribution. The MCM-41 materials put forward the opportunity to extend shape-selective catalysis ahead of the micropore (zeolite) materials, allowing the control over larger molecules. In addition, by introducing the metal ions, MCM-41 proves excellent catalytic activity in synthesizing various nanostructures.

1.7.1 Mesostructure Formation Mechanisms of MCM-41

To date, numerous models have been proposed to explain the formation of mesoporous materials. Alike zeolite synthesis, the surfactants act as templates forming ordered organic-inorganic composite materials (Lind et al 2002). Later the surfactant is expelled out from the porous silicate network by calcination process. But, in contrast to zeolites, the templates are liquid crystalline self-assembled surfactant molecules. The development of the inorganic-organic composites is derived from electrostatic interactions between the positively charged surfactants and the negatively charged silicate species. Numerous studies that explored the building mechanism of MCM-41 appeared to be at first inconsistent. The “Liquid-Crystal Templating” (LCT) mechanism proposed by the Mobil researchers was based on the similarity
between liquid crystalline surfactant assemblies (i.e. lyotropic phases) and M41S materials (Beck et al 1992 and Kresge et al 1992). The general behavior were the dependence of mesostructure on the hydrocarbon chain length of the surfactant tail group (Beck et al 1994), the consequence of variation of the surfactant concentrations and the influence of organic swelling agents. The two pathway mechanism postulated by the Mobil researchers, using MCM-41 (which has hexagonally packed cylindrical mesopores) as the representative M41S material, (Figure 1.12).

i. The aluminosilicate precursor species filled the space between a pre-existing hexagonal lyotropic liquid-crystal (LC) phases and deposited on the micellar rods of the LC phase.

ii. The inorganic mediated the ordering of the surfactants into the hexagonal arrangement.

![Figure 1.12 Two possible pathways for the LCT mechanism](image)

In both cases, the inorganic components (negatively charged at the high pH values) organized with the positively charged ammonium head groups of the surfactants and condensed into a solid continuous framework. The formed organic-inorganic mesostructure could be observed as a hexagonal array of surfactant micellar rods embedded in a silica matrix.
Finally, mesoporous MCM-41 framework was obtained by the removal of the surfactants. Noteworthy, the pathway (i) did not occurred because the surfactant concentrations used were far below the CMC necessary for hexagonal LC formation (Vartuli et al 1994). In the case of the second mechanistic pathway (ii) LCT was unclearly postulated as a cooperative self-assembly of the ammonium surfactant and the silicate precursor species below the CMC.

1.7.2 Heteroatom Substituted MCM-41

The neutral framework possessed by the pure siliceous mesoporous molecular sieves almost confines their applications. To facilitate the molecular sieves with potential catalytic applications, it is feasible to modify the nature of the framework by introduction of heteroatom by hydrothermal methods (similar to zeolites). In addition, various other elements can also be incorporated on the surface of the materials by grafting or impregnation methods. There are more than a few synthesis methods proposed and productively used to synthesize mesoporous MCM-41 molecular sieves (Schmidt et al 1994 and Zhao & Goldfarb 1995). The first report on mesoporous silicates and aluminosilicates synthesized in alkaline condition was done by Kresge et al (1992), while Huo et al (1994) described the first synthesis of porous silicates in acidic condition. Yanagisawa et al (1990) reported pillared layered silica using surfactant cations and after calcination obtained a mesoporous silica.

Substitution of $\text{Si}^{4+}$ ions by other heteroatoms in the MCM-41 structure can be used to impart catalytic activity to the chemically inert mesoporous silicate framework. During the substitution of trivalent cations (like $\text{Al}^{3+}$, $\text{B}^{3+}$, $\text{Ga}^{3+}$ and $\text{Fe}^{3+}$) for silicon in the walls of the mesoporous silica, the framework have negative charges that can be balanced by protons,
supply acid sites (Tuel & Gontier 1996). There are reports on the incorporation of Fe to MCM-41 materials by various methods, describing Fe states in various MCM-41 matrices and its catalytic behavior (Decyk et al 2003).

1.7.3 Synthesis of CNTs using MCM-41

The advantages of MCM-41 comprises of high surface area, distinct regular pore shape, narrow pore size distribution, large pore volume and tunable pore size. In addition, high thermal, hydrothermal, chemical and mechanical stability of MCM-41 is extremely favorable for a number of significant applications such as adsorption and separation, ion-exchange, catalysis and molecular hosts. The mesoporous molecular sieves are an excellent transporter of catalyst, to synthesis nanotubes, nanorods, nanoparticles, etc. These nanomaterials are prepared inside or outside the mesopores (Huang et al 2004).

Metal substituted mesoporous molecular sieves are explored as catalysts for oxidation reactions, acid catalysed reactions, hydroxylation reaction, polymerisation reactions and in the field of nanotechnology. The mesoporosity and the well defined pore structure in addition with high surface area create MCM-41 materials a promising catalyst for the synthesis of SWCNTs and MWCNTs. It was reported by Somanathan & Pandurangan (2009) that MWCNTs can be synthesized over Pt impregnated Al-MCM-41 catalyst by decomposition of acetylene. Using mesoporous Mn-MCM-41 molecular sieves as catalyst, Subashini & Pandurangan (2009) have reported the synthesis of MWCNTs. There are also various reports on the synthesis of multi-walled carbon nanotubes SWCNTs over bimetallic mesoporous materials (Atchudan et al 2009) and Co grafted Mo-MCM-41 catalyst (Lee et al 2011).
The potential of non crystalline inorganic solids, such as hydroxides, hydrated phosphates, silicates and oxides, subjected to scientific investigation is often neglected due to the disadvantages linked to structural characterization coupled to low reproducibility based on the preparation. Even though they lack structural order, the prepared non-crystalline materials possess reproducible properties. Certain features can varied depending on the synthetic procedure and data of the resulting structure.

The mechanism of precipitate formation is depended on the chemical dynamic equilibrium state involving the precipitate and solute ions. The precipitation occurs, if the ionic product of the salt exceeds its solubility product constant \( K_{sp} \). The “precipitates” exhibit different forms and stoichiometries during the formation and ageing (Kolthoff 1982).

For example, the formation of aluminum phosphates by neutralization of an acidic solution of \( \text{Al}^{3+} \) and hydrogen phosphate ions depends on various factors such as: precursor ions variability and concentration, stoichiometry, temperature during reaction process and the precipitation pH. The features of the precipitates are:

(i) They are complex structure (amorphous hydrated structures or complex co-precipitated mixtures) with various phosphate and aluminum species, originating from multiple equilibria reactions. For example, in aqueous solutions with a pH < 3, aluminum present as \([\text{Al(H}_2\text{O)}_6]^{3+}\), abbreviated as \( \text{Al}^{3+} \). In a less acidic solution, \([\text{Al(H}_2\text{O)}_6]^{3+}\) undergoes deprotonation, resulting \([\text{Al(H}_2\text{O)}_5(\text{OH})^{2+}] \) and hydrocomplex salts. Minimum solubility take place at pH ~ 7 with the
precipitation of hydrous Al(OH)$_3$. In the case of more basic solution this solid redissolves, because of the formation of tetrahedral aluminate ion [Al (OH)$_4$]. The aluminum (III) is detected as Al$_2$O$_{10}$ dimers in acid condition (Moolenaar et al 1970). Ion protonation/ deprotonation can result in the formation of multiple phosphate species. Finally in aluminum polyphosphate, this leads to a large number of complex species (Lima et al 1995).

(ii) The precipitates include net charges and variable stoichiometry. The ratios of phosphate groups to hydroxyl or aluminum atoms can differ extensively (Cheung et al 1986).

(iii) Ions within the precipitate show various solvation degrees around the cores, with condensed oxo bridges that enhance the formation of polynuclear complexes in monomeric or polymeric blocks (Galembeck et al 1996). Phosphate ion condensation/polymerization leads to the formation of condensed phosphates. On drying at higher temperatures these form linear, cyclic and/or cross-linked/branched phosphates (Oliver et al 1998). In general, inorganic phosphate solids are considered as polymers having chain-like structures similar to organic polymers (Otaigbe & Beall 1997). In the case of amorphous inorganic phosphate solids, their structure are stabilized by electrostatic and hydration bonds, along with a strong participation of hydroxyl and hydrogen bridges.

Recently, wide range of research has been focused on these compounds structural peculiarity to explore innovative technologies. The applications are fundamentally focused toward the method of synthesis of
these amorphous compounds. The parameters include the addition method of raw materials, P/Al ratios and calcination temperature.

1.8.1 Aluminum Phosphate as Catalyst

There are many reports on the synthesis of aluminum phosphate as a catalyst support including sol-gel synthesis techniques with materials that comprise of simple salts of aluminum and a variety of phosphate sources (Hill et al 1981 and Climent et al 2002). Hill et al (1981) had reported the preparation of aluminum phosphates precipitate by neutralization in a batch stirred reactor of a solution having aluminum and phosphate ions. This technique is carried out for synthesizing amorphous Al-rich AlPO$_4$ and yields homogeneous amorphous aluminum phosphate (with Al/P ratio between 5:1 to 1:1). The surface area was reported in the range of 100 to 300 m$^2$/g, with pore-diameter below 1 μm and pore volume beyond 0.1 cm$^3$/g. This is accompanied with 0.1 to 4% of chromium, yielding a catalyst for ethylene polymerization (Kehl 1978). It was also reported that amorphous AlPO$_4$ obtained by the sol–gel method, have superior textural and acid-base properties (Kumar et al 2006, Bautista et al 1999, Parida & Mishra 1996). Amorphous Al-rich AlPO$_4$ have better thermal stability than Al-poor compositions that crystallize at very lower temperatures. Aluminum ions present in these mixed phosphates, play a vital role in preventing the sintering of solids, which is generally responsible for lowering surface areas. In addition, upon increasing the amount of aluminum ions in amorphous solid generate higher number of acid-base sites for improving the catalytic performance (Bautista et al 2003).
1.8.2 Mechanisms of AlPO₄ formation

There are much steps undertaken in understanding the mechanism of formation of novel structured, micro and mesoporous aluminophosphates (Afeworki et al 2006). The formation of these structured compounds is explained on the basis of chemical information and well-documented aluminosilicates similarities (Auerbach et al 2005). But the initial stages of amorphous phosphates formation are vague.

According to the literature, particle formation is considered as the outcome of a phase separation driven towards solid-liquid phase equilibrium. On the other hand, the formation of the amorphous aluminum phosphates is reported as result of a liquid-liquid phase separation, where the particle consists of concentrated and highly viscous liquid phase touching a dilute phase. A clear proof on phosphate liquid-liquid phase separation is reported in Cr³⁺-polyphosphate-H₂O system (De Azevedo et al 2002). In this case a dark green aqueous phase is formed contacting a clear phase.

Generally two basic mechanisms are postulated for the formation of particles out of a supersaturated solution: Nucleation and growth or spinoidal phase separation. Since the particles do not grow upon aging under many storage conditions, the nucleation and growth are considered less importance. But, mainly follow Ostwald ripening (Ratke & Voorhees 2002).

The models for aluminophosphate formation emphasis on the structures of one-dimensional chains (building blocks), two-dimensional porous layer and three-dimensional open-framework. The complex structures can be built from raw metastable linear chains as follows: (a) dynamic hydrolysis of Al-O and P-O bonds; (b) formation of terminal Al-OH and P-OH groups; and (c) intra/inter chains condensation, with loss of water,
Figure 1.13 (Babu et al 1994). The cross-linking occurred due to chain condensation result in a structured material.

![Chemical structure diagram]

**Figure 1.13** Dehydration process in aluminum phosphate chain through Al-OH and P-OH terminal bonds condensation

At some stage in the particle growth, the condensation to build new structures can be prepared with different types of chain as well as among chains and aluminum and/or phosphate solutes that exist in the system. These aluminum and phosphate ions that depend on the reaction pH can be incorporated between the chains. Hence correspond to a novel variable to obtain special functionalities. This is normally called “chain encapsulation” (Oliver et al 1998).

The chemical concepts used to study the formation of structured aluminophosphates may be extrapolated to amorphous phosphates formation, because it was reported that the rapid precipitation of primary chains produce non-crystalline structure, with weakly arranged layers (Oliver et al 1998).

### 1.8.3 Synthesis of CNTs using AlPO₄

Tang et al (1998) reported the template technique to fabricate ultra-small SWCNTs in the channels of AlPO₄-5 single crystals. The final
products have perfectly aligned, nearly mono-sized SWCNTs with a diameter as small as 0.4 nm. They described three possible structures for the 0.4 nm SWCNTs: the zigzag (5, 0), the armchair (3, 3), and the chiral (4, 2). Wang et al (2000) also reported the synthesis of 0.4-nm-sized SWNTs by means of pyrolyzing hydrocarbon molecules in 1-nm-sized channels of AlPO -5 (AFI) single crystals.

Lee et al (2006) reported the use of AlPO₄-5 crystallites loaded with various concentrations of Fe-catalyst nano-clusters for the growth of CNTs with a variable amount of areal density, to obtain optimum field emission conditions. Martin et al (2008) attained growth of SWCNTs in the pores of AlPO₄-5 and L type zeolites using a Rapid Thermal (RT) CVD set up. Various carbon structures were reported by optimizing vacuum pre-treatment and a H₂ pre-treatment for catalyst activation. The L type zeolites promoted the growth of carbon structures perpendicular to the zeolites surface. To date, there are no reports on the synthesis of CNT using amorphous AlPO₄ as catalyst. Hence, the present work focuses on the growth of CNT using amorphous AlPO₄.

1.9 PROPERTIES OF CNT

The exceptional properties of CNT as an ideal material for various applications are as follows: High electrical conductivity, Highly flexible that can be bent considerably without damage, High thermal conductivity, Good field emission of electrons, High mechanical properties, High aspect ratio (length = ~1000 x diameter). The physical properties of carbon nanotubes are listed in Table 1.1.
Table 1.1 The Physical Properties of Carbon Nanotubes (Adams & Thomas, 2000)

<table>
<thead>
<tr>
<th>Equilibrium Structure</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Diameter of SWCNT’s</td>
<td>1.2 - 1.4 nm</td>
</tr>
<tr>
<td>Distance from opposite Carbon Atoms</td>
<td>2.83 Å</td>
</tr>
<tr>
<td>Analogous Carbon Atom Separation</td>
<td>2.456 Å</td>
</tr>
<tr>
<td>Parallel Carbon Bond Separation</td>
<td>2.45 Å</td>
</tr>
<tr>
<td>Carbon Bond Length</td>
<td>1.42 Å</td>
</tr>
<tr>
<td>C - C Tight Bonding Overlap Energy</td>
<td>~2.5 eV</td>
</tr>
<tr>
<td>Group Symmetry (10, 10)</td>
<td>C5V</td>
</tr>
<tr>
<td>Lattice: Bundles of Ropes of Nanotubes</td>
<td>Triangular Lattice (2D)</td>
</tr>
<tr>
<td>Lattice Constant</td>
<td>17 Å</td>
</tr>
<tr>
<td>Lattice Parameter:</td>
<td></td>
</tr>
<tr>
<td>(10, 10) Armchair</td>
<td>16.78 Å</td>
</tr>
<tr>
<td>(17, 0) Zigzag</td>
<td>16.52 Å</td>
</tr>
<tr>
<td>(12, 6) Chiral</td>
<td>16.52 Å</td>
</tr>
<tr>
<td>Density:</td>
<td></td>
</tr>
<tr>
<td>(10, 10) Armchair</td>
<td>1.33 g/cm³</td>
</tr>
<tr>
<td>(17, 0) Zigzag</td>
<td>1.34 g/cm³</td>
</tr>
<tr>
<td>(12, 6) Chiral</td>
<td>1.40 g/cm³</td>
</tr>
<tr>
<td>Interlayer Spacing:</td>
<td></td>
</tr>
<tr>
<td>(n, n) Armchair</td>
<td>3.38 Å</td>
</tr>
<tr>
<td>(n, 0) Zigzag</td>
<td>3.41 Å</td>
</tr>
<tr>
<td>(2n, n) Chiral</td>
<td>3.39 Å</td>
</tr>
</tbody>
</table>
Table 1.1 (Continued)

<table>
<thead>
<tr>
<th>Optical Properties</th>
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</thead>
<tbody>
<tr>
<td><strong>Fundamental Gap:</strong></td>
</tr>
<tr>
<td>For ((n, m); n-m \text{ divisible by 3} ) [Metallic]</td>
</tr>
<tr>
<td>For ((n, m); n-m \text{ not divisible by 3} ) [Semi-Conducting]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Electrical Transport</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Conductance Quantization</strong></td>
</tr>
<tr>
<td><strong>Resistivity</strong></td>
</tr>
<tr>
<td><strong>Maximum Current Density</strong></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thermal Transport</th>
</tr>
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<tbody>
<tr>
<td><strong>Thermal Conductivity</strong></td>
</tr>
<tr>
<td><strong>Phonon Mean Free Path</strong></td>
</tr>
<tr>
<td><strong>Relaxation Time</strong></td>
</tr>
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<table>
<thead>
<tr>
<th>Elastic Behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Young's Modulus (SWCNT)</strong></td>
</tr>
<tr>
<td><strong>Young's Modulus (MWCNT)</strong></td>
</tr>
<tr>
<td><strong>Maximum Tensile Strength</strong></td>
</tr>
</tbody>
</table>

1.9.1 Electrical and Electronic Properties

Bachtold and coworkers (2000) have validated that, the low metal-tube contact resistances have permitted the investigation of the intrinsic electronic properties of SWCNTs, resulting in ballistic transport. The ballistic transport represents minimal electron scattering within SWCNTs, which
potentially occur from the reduced dimensionality for phonon scattering in 1D systems and the bonding characteristics of CNTs. The high carrier mobilities \( \sim 10,000 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \) in SWCNT-based field-effect-transistors (FETs) happens due to this weak electron-acoustic phonon coupling in semiconducting SWCNTs (Durkop et al 2004). The maximum current carrying capability in an individual metallic or semiconducting CNTs take place due to the backscattering of electrons from the high-energy optical phonons at higher bias voltages; this saturation typically happen at \( \sim 25 \mu\text{A} \) for SWCNTs (Yao et al 2000). This provides the CNTs to have the ability to carry the largest current densities of 109 A/cm\(^2\) known of any metal, which is 1000 times larger than that of Cu, generally used in the IC industry for interconnect applications.

The ballistic transport and large carrier mobilities of CNTs propose them to a best candidate for field-effect-transistor (FET) applications. Also, the large current carrying capability of the nanotubes is a key inspiration for considering them as feasible candidates for interconnects in the CMOS IC industry. In addition, the large current carrying capability of CNTs is also exploited in field-emission applications. In field emission, electric-field development at the end of a sharp metallic tip results in the emission of electrons. The field emission from CNTs has possible applications as electron sources for next generation scanning-electron-microscopes (SEMs) and transmission-electron-microscopes (TEMs).

1.9.2 Mechanical properties

In nature, carbon–carbon bond present in a graphene layer is considered the strongest chemical bond. CNTs built of rolled-up graphene layers, have exceptional mechanical properties and have become a topic of great interest in the field of nanotechnology. Among various applications of
CNTs, composite reinforcement or lubrication, are related somehow or other to their mechanical properties. Hence, numerous experimental and theoretical studies have been focused towards their characterizations.

The mechanical properties of a material in the linear system are usually represented by the definition of a series of moduli (elastic constants, Young’s modulus, Poisson ratio, etc.). It was theoretically predicted that the value of Young’s modulus was in the range of 1–5 TPa. It can withstand very large mechanical strains before failure with a tensile strength hundred times larger than that of steel. These extraordinary mechanical properties arise from the unique sp² bonding in CNTs, similar to graphene.

The electrical conductivity of SWCNTs changes slightly for small bending angles, but decreases by an order of magnitude for larger bending angles (~45°). This effect is due to sp³ bonding states that arise locally in the vicinity of the bend (Nardelli & Bernholc 1999). Hence result in electron localization which reduces electrical conductance in the CNTs. The excellent mechanical properties and low weight of NTs and nanofibers (NFs) make them ideal filling materials in polymer composites. The NTs and NFs can enhance the strength and stiffness of a polymer, along with multifunctionality (such as electrical conductivity) to polymer based composite systems.

1.10 APPLICATIONS OF CARBON NANOTUBES

Since 1991, the discovery of CNTs has suggested numerous potential applications. The use of CNTs includes electron field emitters for vacuum microelectronic devices, as nanoprobe by attaching individual CNTs to the end of an Atomic Force Microscope (AFM) tip, as excellent supports in heterogeneous catalysis, as microelectrodes in electrochemical reactions and
SWCNTs as efficient media for lithium and hydrogen storage. In future, some of these could become right marketable applications, but others require further modification and optimization. The applications in the field of mechanical reinforcing and electronic device applications are predicted or tested to be extremely promising. Development of functional devices/structures based on nanotubes will certainly have a significant influence on future technology requirements.

1.10.1 Nanocomposites

The mechanical behavior of carbon nanotubes has attracted widespread attention since nanotubes are described as the “ultimate” carbon fiber ever made. The traditional carbon fibers (Dresselhaus et al. 1988) is reported about fifty times the specific strength (strength/density) of steel and are exceptional load-bearing reinforcements in composites. CNTs are thus considered to be a perfect candidate for structural applications. Carbon fibers are mainly used as reinforcements in high strength, light weight, high performance composites. One can naturally come across these in a range of products varying from expensive tennis rackets to spacecraft and aircraft body parts. Recently, NASA has invested huge amounts of money in developing carbon nanotube-based composites for applications such as the pioneering Mars mission.

The main application of nanotubes depending on their mechanical properties will be as reinforcements in composite materials. Even though nanotube-filled polymer composites are a noticeable materials application area, there are only few successful experiments, which demonstrate the advantage of using nanotubes as fillers over traditional carbon fibers. The main disadvantage is in creating a good interface between nanotubes and the polymer matrix and achieving good load transfer from the matrix to the
nanotubes, in loading. The explanation for this is basically two-fold. First, nanotubes are atomically soft and have almost the similar diameters and aspect ratios (length/diameter) as polymer chains. Second, CNTs are always ordered into aggregates which act differently in response to a load, as compared to single nanotubes.

There exits various debates on the interface strength in nanotube-polymer composites (Ajayan et al 1994 and Calvert 1999). The measured strength is reported to vary depending on the polymer used and processing conditions. In few cases, fragmentation of the tubes has been observed, which confirms a strong interface bonding. Also, the effect of sliding of layers of MWCNTs and easy pull-out are observed, signifying poor interface bonding. Micro-Raman spectroscopy has authenticated the latter, signifying that sliding of individual layers in MWCNTs and shearing of individual tubes in SWCNT ropes can be limiting factors for good load transfer, which is important for building high strength composites.

To exploit the benefit of nanotubes as reinforcing structures in high strength composites, the aggregates should be broken up and dispersed or cross-linked to avoid slippage. Besides, the surfaces of nanotubes have to be chemically modified (functionalized) to attain strong interfaces between the surrounding polymer chains. The advantages in using CNTs for structural polymer (e.g., epoxy) composites are as follows. The toughness of the composites can be enhanced by nanotube reinforcements by absorbing energy during their highly flexible elastic behavior. This is particularly essential for nanotube-based ceramic matrix composites. An increase in fracture toughness on the order of 25% has been observed in nano-crystalline alumina nanotube composites, with no negotiation on hardness.
Other fascinating applications of nanotube-filled polymer films will be in adhesives where a decoration of CNTs on the exterior of the polymer films would modify the characteristics of the polymer chains due to interactions among the nanotubes and the polymer chains. The high surface area of the CNT structures and their dimensions same as that of the linear dimensions of the polymer chains give novel surface properties to such nanocomposites. The low density of the CNTs is also an advantage for nanotube-based polymer composites, in contrast to short carbon fiber reinforced composites. CNTs also offer multifunctionality, such as improved electrical conduction. In contrast to traditional carbon fibers, CNTs have better performance during compressive loading due to their flexibility and low tendency to fracture under compressive loads.

1.10.2 Memory Devices

For past few decades semiconductor device technology has been advancing extremely fast. The size of semiconductor devices has reduced, while their density has increased. Also, their operating power has decreased and their cost of fabrication has come down. Now, the main part of our daily life depends on semiconductor technology and devices. Since 40 years, Moore's law is considered one of the most trustworthy prediction laws in this field (Moore 1998). Initially only several components were integrated, currently billions of semiconductor device components can be positioned into a chip size of a thumbnail. Advanced semiconductor fabrication technology allows the mass production of semiconductor devices with a significant dimension as small as 20 nm. There are various types of semiconductor devices, including logic devices, memory devices and displays (Kim & Lee 2007). In this type of device, the requirement for memory devices with high-density, high-speed and low power consumption is mainly high. Among these, non-volatility comprises one of the most significant properties, portable
Electronic devices (such as mobile phones, digital cameras, portable media players, e-books and laptop computers) need high-performance and high-density non-volatile memory devices.

The term “Non-volatility” means the information stored in the device can be retained even when the power is switched off. Hence, various attempts have been made to build up high-density, low-cost, and non-volatile solid-state storage devices (Kim & Lee 2007, Dearaujo et al 1995, Hamann et al 2006). Among different types of non-volatile memory, flash memory devices with a floating gate as the charge storage layer is considered very valuable, because of their massive memory capacity, which is essential for many applications (Bez et al 2003 and Cappelletti et al 1999).

Flash memory possesses a simple device structure, that makes device scaling much easier compared to other types of memory devices. Currently the flash memory comprises highest density among other memory devices and involves advanced technology for fabricating flash memory devices. Flash memory employs the threshold voltage shifts with respect to the memory states (programmed/erased states). An additional essential device structure is the resistive switching memory device. A resistive switching memory device works on the difference in resistance of the memory states (low and high resistance states). They have a simple device structure (metal/insulator/metal (MIM) structure) adapted for high-density memory devices with a low fabrication cost (Waser & Aono 2007 and Waser et al 2009) Therefore, these memory device find use in reconfigurable fabrication of logic circuit and novel devices.
1.10.2.1 Resistor-based memory devices

Resistive switching random access memory (ReRAM) devices make use of the stable resistance changes formed in response to the applied bias voltages. These memory devices have substantial interest due to their simple memory structures, low power consumption and high-speed operations (Guan et al 2008 and Son & Shin 2008). There are various types of resistive switching memory devices whose device operation changes according to the type of memory device. Most of the semiconductor companies are actively developing resistive switching memory devices using inorganic materials. A typical device structure in metal-insulator-metal (MIM) consists of two metal layers as the top and bottom electrodes and insulator materials as the switching elements. Hence the fabrication of a high density memory device using cross-bar structures was achieved. Figure 1.14 represents a schematic diagram of typical cross-bar type device structure. The line width of the top and bottom electrodes determines the memory density of this device. The metal lines are normally fabricated using lithography techniques (such as optical lithography, e-beam lithography).

There are various reports on resistive switching behavior in various materials systems including chalcogenide, perovskite oxides, binary transition metal oxides (TMO), etc. (Guan et al 2008 and Son & Shin 2008). Researchers have broadly investigated TMO materials such as NiO, TiO$_2$, Al$_2$O$_3$, Nb$_2$O$_5$, as suitable materials for ReRAM. Earlier reports propose that the resistive switching behavior originate from the formation of a conducting filament inside the oxide material and the switching behavior can be described by the controlled formation and rupture of this conducting filament (Son & Shin 2008 and Rossel et al 2001).
Figure 1.14 Schematic diagrams of device structures for resistor-based memory devices and their typical device operation schemes. (LRS, HRS, and NDR in represent low-resistance state, high-resistance state, and negative differential resistance, respectively. $V_{\text{reset}}$ and $V_{\text{set}}$ are reset and set voltages, respectively) (Lee 2011).

Figure 1.14 demonstrates a schematic representation of the typical resistive switching behavior in ReRAM. The set voltage ($V_{\text{set}}$) is defined as the critical voltage at which the memory device is changed from the HRS to the LRS, and the reset voltage ($V_{\text{reset}}$) is defined as the critical voltage at which the reverse process occurs (LRS / HRS). The increase of applied voltage from 0V to the threshold voltage is referred to as the forming voltage ($V_{\text{forming}}$). After the forming process, the device retains LRS. Starting from this state, the applied voltage raise from 0 V to a critical point ($V_{\text{reset}}$), the current level quickly drop off from the LRS to the HRS, related to the reset process (exhibiting a negative differential resistance; NDR). After the reset process, when the applied voltage raise again from 0 V, the current level suddenly increases at some critical point ($V_{\text{set}}$), till the compliance level, represents the set process. The set and reset processes are repeatedly
performed by sweeping the gate voltage, and the LRS and HRS are denoted as the binary states for nonvolatile memory device applications.

In the recent years, conductance and resistive switching characteristics of polymer memory devices with CNT have attracted much interest (Liu et al 2009, Vasu et al 2011 and Pradhan et al 2006). Noteworthy, the amount of charges stored in a cell are encoded “0” and “1”, but a polymer or organic memory stores data based on the high and low conductivity response to an applied electric field. Pradhan et al (2006) have observed electrical bistability and large conductance switching in functionalized carbon nanotube (CNT)-conjugated polymer composites at room temperature. The concentration of the CNTs in the polymer matrix controlled the degree of bistability.

In practice, many different materials can be utilized for resistive switching memory devices and different mechanisms have been reported to explain the resistive switching behaviors. In addition, the memory density is less compared to flash memory devices and long-term reliability is not confirmed. Thus extensive research should be performed for enhanced understanding of resistive switching behavior and to determine the reliability problem.

1.10.2.2 Nano-floating gate memory devices

Tiwari et al (1996) reported the first formation of nanocrystal-based charge trap flash memory devices. They demonstrated n-channel metal-oxide-semiconductor field-effect transistor (MOSFET) embedding Si nanocrystals in the gate oxide as the charge storage elements. This memory device resulted in low voltage operations (program/erase voltages < 3 V) and high endurance properties (endurance cycle ~10⁹). After then, lot of development has been
made towards the fabrication of nanocrystal-based flash memory devices (King et al 2001, De Blauwe 2002, Talapin et al 2010). In major of these reports, the devices are fabricated on p-type Si substrates having a thin tunnelling oxide layer. Above the tunnelling oxide layer Semiconducting/metallic nanoparticles are developed and, subsequently, a blocking oxide and gate electrode are deposited and patterned to fabricate MOS-capacitor structure memory devices. The memory operations are determined from the capacitance-voltage response.

The most essential component in this type of memory device is the nanoparticles used as the charge trapping elements. Different types of metallic nanoparticles have been used to nanoparticle-based memory devices (Talapin et al 2010). The metallic nanoparticles are dispersed over the tunnelling oxide coated silicon substrates. Mostly the charge trapping layer is formed by the self-assembly process. The thin metallic layers coated over the tunnelling oxide-covered silicon substrates are converted into metallic nanoparticles through Ostwald ripening, by performing a post-annealing process. Here, the thin metallic layer can be converted to metallic nanoparticles because of the minimization of the surface energy (Liu et al 2002). Even though, this is a simple method reported to have good performance related to program/erase characteristics, but have a disadvantage of metallic contamination in the gate oxide layer and/or diffusion of metallic components to the interfaces of the memory devices while synthesizing metallic nanoparticles (Lee et al 2005).

There are reports on high dielectric constant (high-k) materials to act as gate dielectric layers (Chan et al 2008). HfAlO was used as the tunnelling/blocking oxide layers for studying the programmable memory characteristics of gold nanoparticle-based memory devices. A dielectric layer composed of Al$_2$O$_3$/HfO$_2$/SiO$_2$ was used as band engineered tunnelling oxide layer for gold nanoparticle based memory devices (Lee et al 2008). The
Dielectric materials having various band gaps were placed in stacks as the tunnelling oxide layer, enhance the charge injection efficiencies and improves the data retention properties. Also, Polymeric insulator materials have been used as tunnelling/blocking dielectric layers. Kim et al. reported polyimide (PI) as both the tunnelling and blocking dielectric layers in gold nanoparticle related non-volatile memory devices (Kim et al 2007). This work resulted in a memory window of 3.4 V at an applied bias of 15 V.

Extensive research in the field of nanoparticle-based memory devices using colloidal metallic nanoparticles was also carried out (Talapin et al 2010). Here, the synthesis of metallic nanoparticles can be done in solution, and post-deposition annealing process to form metallic nanoparticles is ignored (Park et al 2006). Thus the size of the metallic nanoparticles can be controlled very easily. The advantage of solution processed metallic nanoparticles as the charge trapping layers involves very low temperatures synthesis, even at room temperature.

Recently, there exist various reports on the fabrication of nonvolatile memory devices using 1D nanostructure as the memory switching elements (Lu & Lieber 2007). The 1D nanostructure are synthesized using various techniques, such as vapour-liquid-solid (VLS) growth, chemical-vapour deposition, and atomic-layer deposition. The materials synthesized in the form of 1D nanostructures includes, semiconductors, insulators, polymers, and metals (Lu & Lieber 2006, Wu et al 2002, Han et al 2009). These 1D nanostructures are used in the fabrication of memory devices, particularly nanowires and nanotubes as the switching elements.

CNTs have many exceptional advantages for the application in memory devices such as tunable band gap, high thermal stability and chemical inertness, perfect sidewall structure and nearly zero surface states
Various reports with CNT as the floating gate memory involves various dielectric materials like Hafnium aluminium oxide and poly-4-vinyl phenol as insulating layer (Lu & Dai 2006 and Kim et al 2009). A flat-band voltage of 400mV and 1.3 V was observed using CNTs embedded in hafnium aluminium oxide and Poly-4-vinyl-phenol dielectric layers respectively. Cui et al (2002) reported the fabrication of molecular memory devices with semiconducting single-walled carbon nanotubes constituting a channel of 150 nm in length. Data storage is achieved by sweeping gate voltages in the range of 3 V, associated with a storage stability of more than 12 days at room temperature. A high-speed (100 ns) operation of charge trap SWCNT-FET memory elements having ALD grown HfO$_2$ as a gate dielectric was also report. The endurance of these memory elements is shown to exceed $10^4$ cycles.

1.11 SCOPE AND OBJECTIVES OF THE PRESENT RESEARCH WORK

Since the discovery of fullerenes and CNTs, various research fields in the area of carbon experienced a massive boom. To date the synthesis methodology of CNTs are limited to small quantities with complicated methods. In order to synthesis CNT with better purity and large scale production, CVD method is selected as one of the most appropriate method. CVD is the most suitable method for the low cost mass production method of CNTs. Hence the present work deals with the growth of CNTs by CVD.

Amorphous AlPO$_4$ built of tetrahedral units of AlO$_4$ and PO$_4$ is structurally similar to silica (Bautista et al 1998). This type of structure provides a feature of large surface area and high thermal stability, thus improve the catalytic properties. Furthermore the structural defects create OH
groups on the surface similar to the Si-OH groups of zeolites. Thus suitable introduction of heteroelements improve the catalytic performance of the AlPO$_4$ supported catalysts, owing to their proper dispersion and specific interactions with the support. Hence these features of amorphous AlPO$_4$ are exploited for the synthesis of MWCNTs, Y-CNTs and SWCNTs respectively.

Among various mesoporous materials, MCM-41 has salient features such as hexagonal arrangement with uniform channel structure. In addition, the tunable pore size (2–10 nm), large surface area ($\geq 1000 \text{ m}^2\text{g}^{-1}$) and moderate acidity are characteristics of MCM-41 silicates. The catalytic site for CNTs synthesis is offered by framework substitution with metals. Hence the features such as mesoporosity, the well-defined pore structure and high surface area make MCM-41 materials as suitable catalyst for the synthesis of CNTs.

It has been proved that electrophoretic deposition technique (EPD) is a perfect method for thin film metal catalyst preparation with functional materials on different substrates (Sugimoto et al 2006, Zhitomirsky 1998 and Koura et al 1995). EPD mainly involves three processes such as particle charging, particle transport under the applied electric field and deposition of particles with neutralization (Kanamura et al 2000). The attraction of this method lies in its simplicity, short time, low cost, and suitability for mass production. This work presents an extremely simple and inexpensive way of catalyst preparation for CNT synthesis.

In this thesis, the catalyst for the CNT deposition, carbon precursor, synthesis temperature and reaction time are discussed as the important parameters affecting the quality and quantity of the produced CNTs. Purification of the CNTs and the synthesis cost are considered as the important industrial parameters. The main objective of the work deals with
the synthesis of SWCNTs, MWCNTs, Y-CNT, Coiled CNTs using various porous catalysts and their application in memory devices and nanocomposites.

The scope of the present work are as follows:

- Amorphous aluminum phosphate (AlPO₄) was synthesized by co-precipitation method and chosen as a novel catalyst support for the present study. Various transition metals like cobalt, iron and nickel were loaded over AIPO₄ by wet impregnation method.

- Electrophoretic deposition technique was carried out to prepare metal catalyst over stainless steel plate. Various transition metal films like iron, nickel and cobalt were coated over SS by EPD.

- Mesoporous molecular sieves such as Fe-MCM-41, Sn-MCM-41 were synthesized by hydrothermal method. Bimetallic mesoporous molecular sieves Sn/Fe-MCM-41 were synthesized by wet impregnation method.

- The above synthesized catalytic materials were characterized by various physico-chemical techniques such as X-Ray Diffraction (XRD), Nitrogen Sorption Isotherms, Thermogravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FT-IR), Diffuse Reflectance Ultraviolet Visible Spectroscopy (DRS-UV), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).
The activity of the above synthesized materials for the formation of CNTs by CVD method was examined. The reaction parameters such as metal concentration over the catalytic template, flow rate of carbon precursors, growth time and temperature were optimized for the production of well-graphitized CNTs through acetylene decomposition over AlPO_4, SS and MCM-41.

The deposited carbon materials were purified and characterized by various physico-chemical techniques such as XRD, TGA, SEM, TEM and Raman spectroscopy.

The purified CNTs were used as an active layer for the fabrication of non-volatile memory devices. CNTs were embedded in hafnium gadolinium oxide (HGO) and polyvinyl alcohol (PVA) which acts as insulators to fabricate Metal-Insulator-Semiconductor (MIS) and PVA for Metal-Insulator-Metal type memory device (MIM).

The MWCNTs, amorphous aluminum phosphate coated MWCNTs and amorphous silica coated MWCNTs were used as a filler material for the fabrication of nanocomposites and their thermo-mechanical properties was also studied.