Chapter 1:

Introduction of Carbon Nanotubes: Properties, Synthesis, Characterization and Applications

1.1. Background
1.2. Introduction of carbon and their allotropes
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1.1. Background

In present scenario, human life is surrounded with different electronic appliances and gadgets such as radio, television, computer, mobile, tab, etc. Although, early age discovery of few of these equipments especially television and computing systems were enabled with the invention of thermionic cathode and development of vacuum electronics, however, it disappeared completely from these devices after discovery of transistor in 1947 and later on integration of the basic circuit elements in integrated semiconductor microelectronic devices. Basic circuit elements of microelectronic devices are transistor, resistor and capacitor. These circuit elements are versatile, cheap and robust compared to vacuum electronics. Integration of circuit elements and invention of transistors enabled the miniaturization of electronic devices such as computing system from room size ENIAC (electronic numerical integrator and computer) in 1946 and EDVAC (electronic discrete variable automatic computer) in 1951 to desktop computer in second-last decade of 20th century and laptop, palmtop in 21st century. However, further scaling down of these devices is being studied to enable some other revolutionary applications for its mass uses and user friendly applications.

Great visionary Richard Feynman [1] lectured in a speech in 1959 that "there's plenty of room in the bottom". This introduced and guided the basic research work in atomic and molecular regime and given a platform to re-think about the nano dimension devices. Few years later in 1965, Intel co-founder Moore predicted that cramping and squeezing of more circuit components on single silicon chip will result in reduction of their unit cost and miniaturization of computing systems. Moore's prediction was the driving force for semiconductor industry and laid down the

foundation of new fabrication technology, process designing and their exciting technological applications. This resulted in advancement of processing or fabrication technology and miniaturization of electronic equipments. According to Moore’s law, the dimensions of individual devices in integrated microelectronic circuit decreases by a factor of approximately two after every two years. This scaling down of devices has driven the technological advancements in last few decades of 20th century and resulted in development of different microprocessors, chips and many more. Advancement in process technology and reduction of cost made computing devices more accessible to people worldwide, and making the innovations and computing more user friendly from the smallest handset to the largest cloud computing and server.

Further scaling down of these devices has faced serious limitations. These limitations are related to the fabrication technology, material parameters and device performances as device dimension shrink down to a critical dimension below 22 nm range. These limitations include lithography of substrate, short channel effects, electron tunneling through short channels and thin insulator films, leakage currents, passive power dissipation, variations in device structure, doping, etc. These limitations can be overcome to some extent by modifying the channel material and dielectric or insulating oxide of the conventional metal oxide semiconductor field effect transistor (MOSFET) with some other nano material and high K-dielectric film. Replacement of channel with single carbon nanotubes (CNTs) or an array of CNTs [2] and insulator film by a high dielectric constant material such as hafnium oxide, zirconium oxide, etc. are reported to facilitate/enable further scaling down of device dimensions.

Moreover, there are certain applications where these solid state microelectronic devices are impractical and the one and only one potential solution for these applications is again the same vacuum electronics that was abandoned earlier after invention of transistor. Although, thermionic cathodes possess certain major disadvantages, such as high power consumption, bulky size, small life, etc. however, other alternative of thermionic cathodes for these specialized applications is not yet known. Few of these specialized applications such as microwave tubes for high-power radio frequency transmission, certain military systems, X-ray machines, modern day...

electron microscopy, etc. are still running with the same vacuum tube principle. These systems use high speed of propagation of electron inside a high vacuum tube to achieve desired operations. Similar to modern integrated semiconductor systems, vacuum electronics based devices need to be integrated at micro-scale for its successful applications.

With growing demand of device miniaturization, same as in the case of integrated semiconductor technology, vacuum electronics also need to be miniaturized for robust and compatible application with silicon technology in cathode ray tube, field emission display, vacuum microelectronics, x-ray tube, etc. Nanomaterials, nano-science and nanotechnology have attracted considerable attention due to their comparable nanometer dimension and their great promise in device miniaturization. The development of nanotechnology and nano-science was guided by revolutionary lecture of Feynman and improvement of electron microscope resolution followed by invention of scanning tunneling microscope in 1981. Later on during second last decades of 20th century, nanotechnology research was further boosted with the discovery of fullerenes in 1985 [3] and CNTs in 1991 [4]. Nano comes from a Greek word ‘nanos’ which means dwarf. Nanotechnology is the study of functional and advanced nano-material at the atomic and molecular scale that deals with a size range between 1 to 100 nm or few nanometers to few micrometers.

Since the landmark paper by Iijima [4], CNTs have attracted remarkable attention for different technological application. CNT is the fourth allotropes of carbon and it has diameter in nanometers and length in micrometers. CNTs [5] are reported to have numerous technological applications [6, 7] such as electron source [8], field effect transistor (FET), sensor, composites [9], nano tips or probe etc. Tans et al [2, 10] proposed that CNTs can replace the channel of MOSFET [7] for CNT field effect transistor (CNTFET) application. The key advantages of CNTFET [6, 7] are due to its high mobility, ballistic transport, high trans-conductance, high current density, low threshold field, better control over channel formation, etc. However, CNTFET fabrication technology and process compatibility with silicon [7] limit the practical application of CNTFET. Major issues related to CNTFET [2] fabrication includes positioning of CNTs at desired location, electrical contact formation between CNTs and electrodes, mass production and repeatability in properties of CNTs. Other
promising application of CNTs may be as an electron emitter source [8, 11, 12] due to its whisker geometry owing to their one dimensional structure. Utsumi [13, 14] reported that whisker shape geometry exhibit highest field enhancement compared to other structure. Many research groups have developed and demonstrated field emission devices or electron field emitters using nano and micro-structured material such as CNTs, silicon Spindt emitter [15-18], zinc oxide nano rod [19-21], nano-belts [22], silicon carbide nano-wires [23, 24], aluminum nitride nano-needles [25, 26], silicon nano-wires [18], tin oxide nano-whiskers [27] and more recently graphene sheet [28, 29]. Among them, CNTs are considered to be relatively better electron emitter source [14, 30] because of their unique physical, electrical, chemical and mechanical properties [31].

CNT based field emitter arrays were reported to be developed using various experimental methods [32-35] such as the suspension-filtering [36], screen printing [37], electrophoresis, micro contact printing [38], spray [34], etc for different applications. These experimental methods are post growth cathode development approaches. In these methods, synthesized CNTs were mixed in different conducting paste and mixture was transferred on the desired substrate. The major disadvantages with these methods are poor adhesion [36] of CNTs with substrate, lack of vertical alignment [39, 40], and no control on patterning [11] of CNTs in desired structure. In addition to the above experimental methods, CNT field emitter arrays were also reported to be prepared using a simple approach of direct chemical vapor deposition (CVD) growth of CNTs on desired substrate. Direct CVD growth method resolves the above issues of poor adhesion, patterning [11, 41] and vertical alignment of CNTs on the substrate to some extent. However, CVD growth is carried out at elevated temperature of more than 600°C and thus limits its wide application on different substrate such as glass, indium tin oxide (ITO), etc. All these fabrication approaches have some advantages and disadvantages, however direct CVD growth method is preferred over the others and is used in my research work.

Title of my research work is "Study of Carbon Nanotubes Based Field Emission Devices and their Characterization". During the research work, CNT based electron emitter sources were developed using direct CVD growth and their electron emission parameters were traded off using various techniques so that they
can exhibit enhanced emission properties. Entire work is organized in seven different chapters of my thesis. The elaborative descriptions of each chapter are presented below.

Chapter 1 is an introductory report on literature survey which gives brief description of carbon with different allotropic forms. Different structural forms of CNTs, their classification and their extraordinary properties have been reviewed and discussed in different sections. Further, a review article has been presented on different growth methods, growth mechanism, characterization techniques and applications of CNTs.

Chapter 2 describes different electron emission mechanisms such as photo electron emission, thermionic emission, secondary electron emission, field electron emission and its background theory has been presented. Thermionic emission along with the field-enhanced thermionic emission or Schottky emission is also elaborated. Elaborative description of field emission and its analysis has been presented which is essential to understand the experiment and its dependence on different parameters. This is an introductory as well as analytical chapter which provides basic information about the electron emission techniques and methods employed to derive and obtain the field emission parameters which will be used in computing and analyzing the field emission results in the later chapters. Field emission parameters include work function, field enhancement factor, screening effect and effective emitting area. Derivation of field emission parameters using quantum mechanical field emission tunneling or Fowler-Nordheim equation have also been considered at the end.

Chapter 3 gives a detailed description of the experimental methodology employed for the development of the CNTs based field emission devices. Experimental methodologies employed to realize the CNTs based field emission devices include CNT field emitter development, their characterization and FE measurement in diode configuration. This chapter elaborates the process steps used for development of CNTs based field emission devices i.e. CNTs based cathode or CNT emitter arrays, which includes substrate cleaning, photolithography, catalyst sputtering, lift off process and synthesis of CNTs using chemical vapor deposition or plasma enhanced chemical vapor deposition. Different characterization tools such as scanning electron microscope, transmission electron microscope, etc. employed to
study the morphology and the changes introduced after treatment has also been elaborated. Finally, field emission study of the developed CNT emitter arrays has been discussed at the end.

Field emission current density of the CNTs emitter arrays are reported to be governed by Fowler-Nordheim (F-N) equation. F-N equation predicted that emission current density is dependent on work function and enhanced electric field. The two main experimental approaches that can be used to enhance the emission current of existing cathode are reduction of effective work function and improvement of field enhancement factor. Work function of a material is highly sensitive to the surface properties, adsorbate and internal structure. Surface properties are reported to be altered using surface modification approach by decorating them with low work function materials. Conventional thermionic cathodes employ coating of low work function material such as lanthanum hexaboride (LaB$_6$), barium oxide etc. Similar modification on the CNTs emitter surface, by coating them with different low work function material, has been tried as an effective and simple approach to increase the emission current of existing CNT cathodes.

Chapter 4 illustrates the different surface modification techniques employed to alter the electron emission current of the existing CNT emitter arrays. In this chapter, CNTs surfaces were modified with a different low work function material such as lanthanum hexaboride (LaB$_6$) and cesium iodide (CsI) and effect of surface modification on their FE has been studied and analyzed. LaB$_6$ is a traditional low work function material and has well established industrial applications in filaments of thermionic cathodes. In conventional thermionic cathodes, thick film of LaB$_6$ is coated on the tungsten filaments and their properties are well reported by different authors. However in this chapter, LaB$_6$ nano particles (NPs) were successfully decorated on the patterned CNT emitter arrays and their effect was studied as comparative change in FE. Subsequently, FE-results were analyzed in light of effective change in work function due to LaB$_6$ NPs decoration. Work function of LaB$_6$ NPs decorated CNTs was also estimated using mathematical reverse engineering. Furthermore, cesium iodide nano particles decoration using thermal evaporation and its influence on the emission current density of the CNT emitter
arrays has also been described. The possible reasons of this has been compared and studied in light of Fowler Nordheim equation.

Chapter 5 reports effect of temperature treatment on FE of as-grown and low work function decorated patterned CNT emitter arrays. Broken bonds, internal structure stress and amorphous carbon deposited during growth of the CNTs have been reported to be changed using thermal treatment. CNT emitter arrays were temperature treated in different environment such as vacuum and air. To achieve the enhanced emission current, as-grown CNTs were temperature treated in vacuum and air at 1050°C and 400°C respectively. Furthermore, thermal treatment has been tailored with the low work function decoration. Cesium iodide nano particles decorated CNTs were vacuum annealed and oxidized CNTs were decorated with LaB₆ NPs.

Chapter 6 summarizes the effect of structural engineering on field emission current of CNT emitter arrays. Structural engineering of CNT cathode in diode structure involves the modification of CNT emitter arrays pattern. Owing to the high aspect ratio, CNTs inherently keep the merit of very high field enhancement factor. However, further trading in field enhancement factor is required for improved emission current. The combined effect of the high aspect-ratio of CNTs and a low work function material is expected to contribute towards the enhanced electric field which along with relatively lower work function and this may result into a very high current density. Different CNT emitter arrays were developed and its field emission measurements were carried out to examine their effect on emission current density. Present article intended to examine, analyze and illustrate the effect of edge length on field emission of those different CNT emitter arrays that have minor difference in edge length with major differences in graphitization and growth area.

Chapter 7 describes the conclusions and future plans of research work.

1.2. Introduction of carbon and their allotropes

Carbon has pre-historic discovery and is widely distributed in nature such as sun, stars, comets, and atmospheres of most of the planets in different compounds and various allotropic forms. In compound forms, carbon exists in different forms of
hydrocarbon, oxides, carbides, sulfides carbonates etc and their derivatives. Coal, petroleum, and natural gas are chiefly occurring hydrocarbons. Moreover, carbon also exists in some isotopic forms such as C\textsuperscript{12}, C\textsuperscript{14} etc. In 1961 the International Union of Pure and Applied chemistry adopted the C\textsuperscript{12}-isotope as the basis of atomic weights estimation and C\textsuperscript{14}-isotope, with a half-life of 5715 years, were used for life time or age estimation of materials such as wood, archaeological specimens, etc.

Carbon is sixth element of the periodic table. It is tetravalent in nature owing to the four valence electrons in their outer most shell. It is unique among the elements of periodic table because it has ability to form three different hybridization states such as sp, sp\textsuperscript{2} and sp\textsuperscript{3} and can form single, double and triple bonds with carbon atom itself and with other element too. Carbon forms a very large number of organic compounds with hydrogen, oxygen, nitrogen, and other elements. There are close to ten million known carbon compounds, many thousands of which are vital to organic and life processes. Without carbon, the basis of life on earth would be impossible.

**Hybridization of the carbon atom**

Figure 1.1 Illustration of sp\textsuperscript{3}, sp\textsuperscript{2} and sp hybridization of carbon atom and its bonding (source: http://mcat-review.org/bonding.php).

The property, due to which carbon atoms being linked to another carbon atom by single, double and triple bond, is known as catenation property. Owing to the catenation property, carbon atoms have an ability to form different allotropic forms. Prior to the discovery of fullerene, CNTs and graphene, only three well-defined allotropes of carbon were known which are diamond, graphite and amorphous carbon, as depicted in Figure 1.2.
Diamond is three-dimensional crystalline array of carbon atoms where carbon-carbon atoms are linked by sp3 hybridization. The chemical bonds that hold the carbon atoms in diamonds structure are three-dimensional (3D) network of lattice atoms. Diamonds are also known to have different structural form and this is known as hexagonal diamond or lonsdaleite which is presented in Figure 1.3. However, graphite is a stacked sheet of two-dimensional (2D) network formed by hexagonal arrays of carbon atoms where carbon-carbon atoms are linked together by sp2 hybridization. The atomic bonds formed in graphite lattice are covalently bonded carbon-carbon atom and van der Waals force between the adjacent sheets. The weak van der Waals force resulted to the easy sliding of the graphite sheets with respect to each other and over each other, making it soft enough and so it is used in pencils to form the streak marks and writing on the paper. Amorphous carbon is free and reactive carbon that does not have any crystalline structure and possesses both sp3 as well as sp2 hybridization states. This is also called diamond-like carbon. The physical properties of carbon vary drastically with their allotropic form. The details of physical properties changes in case of diamond and graphite due to change in allotropic form is given in Table 1.1.
Table 1.1 Difference in physical properties of diamond and graphite owing to the difference in structural forms and hybridization state

<table>
<thead>
<tr>
<th></th>
<th>Diamond</th>
<th>Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Cubic system</td>
<td>Hexagonal system</td>
</tr>
<tr>
<td>Clear and</td>
<td>Black and opaque</td>
<td></td>
</tr>
<tr>
<td>transparent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardest known</td>
<td>One of the softest material</td>
<td></td>
</tr>
<tr>
<td>abrasive</td>
<td>Soft and very good lubricant</td>
<td></td>
</tr>
<tr>
<td>Excellent</td>
<td>Very good conductor of electricity</td>
<td></td>
</tr>
<tr>
<td>electrical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>insulator</td>
<td></td>
<td></td>
</tr>
<tr>
<td>High thermal</td>
<td>Thermal insulator</td>
<td></td>
</tr>
<tr>
<td>conductivity</td>
<td></td>
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</tbody>
</table>

In 1985, Kroto, Curl, Smalley [3] and their group accidently synthesized third form of carbon allotropes using laser vaporization technique of graphite rods in an inert (helium) gas atmosphere. From the mass spectra of evaporated carbon samples/soot, they observed a cage like molecular structure composed of 60 carbon atoms joined together by single and double bonds to form a hollow spherical shape with 12 pentagonal and 20 hexagonal faces. This resembles a highly symmetrical $C_{60}$ sphere design of football, or soccer ball. The $C_{60}$ molecule was named buckminsterfullerene or, buckyball or fullerene after the American architect R. Buckminster Fuller, as a respect of token, because geodesic dome structural principle of Fuller were used for finding the structural stability of the 60 carbon atoms. In 1996, this pioneering discovery and the trio scientist, Kroto, Curl, and Smalley, were awarded with Nobel Prize. Same as diamond, fullerene also have different structural forms such as $C_{60}$, $C_{70}$, $C_{540}$ and these structural forms are given in Figure 1.3.

A fourth form of carbon allotrope was identified by Sumio Iijima of Japan in 1991 [4] and is known as CNTs. Therefore in 21st century, carbon has four different known allotropic forms and further experiments and structural models were tested to know the other possible forms of carbon. All of them have totally different physical properties and posses very unique electrical, mechanical and thermal properties. Similar to diamond and fullerene, CNTs are known to have different structural forms.
More recently, one atomic thick layer of graphite or the single two-dimensional hexagonal arrays of carbon atoms, known as graphene, are attracting remarkable attention due to their unique and extraordinary properties. Graphene is a mono layer of sp2 bonded carbon atoms tightly packed in a two dimensional honeycomb lattice. The carbon-carbon bond length in graphene is about 0.142 nm. Graphene layers stacked together forms graphite with an inter-planar spacing of 0.335 nm. Each carbon atom is bonded in-plane together with σ bonds, providing a solid
hexagonal network while the out-of-plane $\pi$ bonds accomplish the weak interaction between different graphene layers. Bilayer and few layer graphene consist of 2 and 3 to 10 layers of these 2D sheets, respectively. Four basic allotropic forms of carbon are presented in Figure 1.4.

![Figure 1.4](image)

**Figure 1.4** Typical illustrations of the four basic allotropes of carbon: Diamond, fullerene or buckminsterfullerene ($C_{60}$), graphite or bilayer graphene, and CNTs.

The discovery of fullerene [3], CNTs and graphene has laid down the foundation of a new branch of science known as nanotechnology nearly in the last decade of the 20th century. The discovery of fullerenes greatly expanded research to find out more number of different known allotropic forms of carbon, which until the last decade of 20th century were limited to graphite, diamond, and amorphous carbon such as soot and charcoal. Bucky-balls and bucky-tubes, also known as fullerene and CNT due to their spherical and tubular structure, have been the subject of intense research, both due to their unique chemistry and for their technological applications, especially in materials science, electronics, and nanotechnology. These materials are known as advanced material. The field of nanotechnology is divided into three major categories according to the structural forms of carbon allotropes, (i) zero-dimensional (0D) nanostructures such as quantum dots, fullerene (ii) one dimensional (1D)
nanostructures like nano-tubes, nano-wires, nano-rods and (iii) two-dimensional (2D) structures example graphene, boron nitride, molybdenum sulfide and tungsten sulfide nano sheets etc. Carbon emerges as one of the most remarkable elements found in a significant number of compounds. Nanostructures of carbon are the most studied of all other elements due to the ease in synthesizing these thermodynamically stable carbon structures.

1.3. **Carbon nanotubes (CNTs)**

CNTs are a unique hexagonal arrangement of carbon atom [4, 31] as one-dimensional (1D) tubule in cylindrical shape. It is theoretically envisioned to be a rolled up sheet of graphene with capping of hemi-spherical fullerene at both the ends. The rolling of graphene at different angles, orientation and curvatures determines their properties. CNTs are also interpreted to be an extended or elongated fullerenes or bucky-balls and are called bucky-tubes. CNTs are known to have extraordinary electrical [31] and thermal properties, excellent mechanical strength and chemically inert.

![Image of CNTs](image)

**Figure 1.5** Illustrations of (a) SWCNTs, (b) DWCNTs and (c) MWCNTs.

Same as diamond and fullerene, CNTs also known to have three different structural forms depending upon the number of graphene sheets rolled up, as depicted in Figure 1.5. These are single walled CNTs (SWCNTs), double walled CNTs (DWCNTs) and multi-walled CNTs (MWCNTs). A lot of controversies exist on the structural forms of MWCNTs, DWCNTs and SWCNTs. The well acknowledged structural form and its detail are presented below.
1.3.1. Single walled CNTs

Single walled CNTs (SWCNTs) structure was envisioned and conceptualized to be a wrapping of one atomic thick layer of graphite, known as graphene, into a seamless cylinder. Similar to the graphene sheet, SWCNTs are further classified [31] into three types such as chiral SWCNTs, zigzag SWCNTs and armchair SWCNTs according to different wrapping angle of the graphene sheet.

![Typical illustration of graphene sheet](image)

**Figure 1.6** Typical illustration of graphene sheet [31]. This describes the chiral vector, chiral angle, unit vectors and chiral index. Classification of graphene sheet: armchair, zigzag and chiral according to different symmetry, chiral angle and chiral vectors.

The wrapping of graphene sheet at different angle and orientations is represented by a pair of indices \((n, m)\), called chiral index and the angle with respect to the chiral vector is known as chiral angle as depicted in Figure 1.6 and Table 1.2. The integers \(n\) and \(m\) denote the number of unit vectors along two directions in the honeycomb crystal lattice of carbon in the graphene sheet. If \(m = 0\), the nanotubes are called zigzag nanotubes, and if \(n = m\), the nanotubes are called armchair nanotubes. Otherwise, they are called chiral as shown in Figure 1.7 and Table 1.2. Chiral vector of SWCNTs is represented through equation (1.1) and schematic of vector addition is presented in Figure 1.6.
\[ \vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \] (1.1)

Where \( n \) \& \( m \) are chiral indices and \( \vec{a}_1 \) \& \( \vec{a}_2 \) are real space unit vectors. The rolling of graphene sheet at different angle and orientations with respect to the axial direction of the cylinder, known as chiral axis determines its properties particularly electrical and optical properties. Details of the electrical and optical properties are discussed in section 1.4. Chiral angle of the zigzag SWCNTs, armchair SWCNTs and chiral SWCNTs are mentioned in Table 1.2. The diameter of CNTs can be calculated from its chiral indices \((n, m)\) through the relation as follows.

\[ d = \frac{\alpha}{\pi} \sqrt{m^2 + n^2 + mn} \] (1.2)

For analysis of their electrical properties, the chiral vector of unrolled honeycomb lattice of SWCNTs is defined theoretically along the twisting angle, which is perpendicular to the axial direction of cylinder and is known as translational vector.

**Figure 1.7** Classification of SWCNTs according to chiral vector: Zigzag, chiral and armchair CNTs [31].
Table 1.2 Classification of SWCNTs according to chiral index

<table>
<thead>
<tr>
<th>CNT classification</th>
<th>Chiral angle “θ” [31]</th>
<th>Chiral indices ((n, m)) [31]</th>
</tr>
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<tbody>
<tr>
<td>Armchair SWCNTs</td>
<td>30°</td>
<td>((n, m))</td>
</tr>
<tr>
<td>Zigzag SWCNTs</td>
<td>0°</td>
<td>((n, 0))</td>
</tr>
<tr>
<td>Chiral SWCNTs</td>
<td>0° &lt;θ&lt;30°</td>
<td>((n, m))</td>
</tr>
</tbody>
</table>

1.3.2. Double walled CNTs

In case of double-walled CNTs (DWCNTs) and multi-walled CNTs (MWCNTs), more than one graphene sheets are rolled up into the concentric cylindrical manner such that they have axial symmetry. Same as SWCNTs, DWCNT are envisioned to have concentric wrapping of two hexagonal sheets of graphene into seamless cylinder as shown in Figure 1.5(b).

1.3.3. Multi walled CNTs

Multi-walled CNTs (MWCNTs) are multiple concentric SWCNTs precisely nested within one another. In other words, MWCNTs consist of multiple rolled up layers of graphene in concentric tubules and its illustration is shown in Figure 1.5(c). Different models were proposed to describe the structures of multi-walled nanotubes. In general, sheets of graphite are envisioned to be arranged up in concentric cylinders i.e. smaller SWCNTs lies within the larger SWCNTs. The interlayer distance in multi-walled CNTs is close to the distance between graphene layers in graphite, approximately 3.4 Å. Its individual shells can be described as SWCNTs, which can be either metallic or semiconducting. Because of statistical probability and restrictions on the relative diameters of the individual tubes, one of the shells and thus whole MWCNTs usually behaves as a zero-gap metal.

1.4. Properties

Extensive experiments have been carried out to probe the electrical, mechanical, chemical and thermal properties of CNTs. These studies suggested that CNTs are reported to have extraordinary electrical properties, high mechanical
strength, excellent thermal conductivity and chemically inert nature. CNTs are reported to have one dimensional structure as its length is in micrometer range and diameter is of few nano meters. Same as fullerene is a zero dimensional material, CNTs are known to be a one dimension material. The detail of each property will be discussed in different subsections.

1.4.1. Electrical properties

From tight binding analysis [31], it had been seen that CNTs have both metallic and semiconducting properties that depends upon their chiral index. The electronic properties of CNTs are known to be extraordinary as it possess both metallic as well as semiconducting behavior. Especially notable facts of the CNTs are that they can be either metallic or semiconducting depending on their structure. Thus, some nanotubes have conductivities higher than that of copper, while others behave more like silicon. There is great interest in the possibility of constructing nano scale electronic devices from CNTs, and some progress is already made in this area. However, in order to construct a useful device, one requires to arrange many thousands of CNTs in a defined pattern and needs full control, and we do not yet have the degree of control necessary to achieve this. There are several areas of technology where CNTs are already being used. These include flat-panel displays, scanning probe microscopes and sensing devices. The unique properties of CNTs will undoubtedly lead to many more applications.

Because of the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. For a given \((n, m)\) CNTs, if \(n = m\), the nanotube is metallic; if \(n - m\) is a multiple of 3, then the nanotube is semiconducting with a very small band gap, otherwise the nanotube is a moderate semiconductor. Thus all armchair \((n = m)\) nanotubes are metallic, and \((6, 4), (9, 1)\) CNTs, etc. are semiconducting. Condition for metallic nanotube is that \((2n + m)\) or equivalently \((n - m)\) is divisible by 3, otherwise the CNT shows semiconducting behavior. However, this rule has exceptions, because curvature effects in small diameter CNTs have strong influence on electrical properties. Thus, a \((5, 0)\) SWCNTs that should be semiconducting in fact is metallic according to the calculations.
Similarly, zigzag and chiral SWCNTs with small diameters that should be metallic have finite gap and armchair nanotubes remain metallic always. In theory, metallic nanotubes can carry an electric current density of $4 \times 10^9$ A/cm$^2$, which is more than 1,000 times greater than those of metals such as copper.

Figure 1.8 Metallic and semi-conducting CNTs [31] depending upon the chiral indices (n, m).

Because of their quasi 1D structure or nanoscale cross-section, electrons propagate only along the tube-axis and electron transport involves quantum effects. As a result of this, CNTs are frequently referred to as one-dimensional conductors. The maximum electrical conductance of a SWCNTs is $2G_0$, where $G_0 = 2e^2/h$ is the conductance of a single ballistic quantum channel.

1.4.2. Optical properties

Optical properties of CNTs [31] were observed due to electronic transitions within one-dimensional density of states (DOS). A typical feature of one-dimensional crystals is that their DOS is not a continuous function of energy, but it descends gradually and then increases in a discontinuous spike [31]. In contrast, three-dimensional materials have continuous DOS. The sharp peaks found in one-
dimensional materials are called Van Hove singularities as given in Figure 1.9. Optical properties of CNTs refer to the Raman spectroscopy, emission and absorption spectra with recent discovery in photoluminescence behavior. Optically active nature of CNTs offers their quick and non destructive characterization.

![Figure 1.9 Density of states (DOS) of (a) metallic SWCNTs and (b) semiconducting SWCNTs (source: English Wikipedia, the free encyclopedia, 2013).](image)

### 1.4.3. Mechanical properties

The high strength of sp2 bonded carbon-carbon atoms gives CNTs amazing mechanical properties. The stiffness of a material is measured in terms of its Young's modulus, the rate of change of stress with respect to applied strain. The Young's modulus of the best nanotubes can be as high as 1000GPa [42, 43] which is approximately 5 times higher than steel. The tensile strength of nanotubes can be up to 63GPa, around 50 times higher than steel. CNTs are the reported [44] to be one of the strongest and stiffest materials yet discovered in terms of tensile strength and elastic modulus respectively. This strength results from the covalent sp2 bonds formed between the individual carbon atoms. MWCNTs were reported to have tensile...
strength of 63 GPa [42, 45]. Studies suggested that individual CNTs shells have elastic strengths of 100 GPa [43]. Owing to the low density [46] and high strength, the specific strength of CNT fibers [47] are much higher than the than the commercially available fibers.

Although, it is well acknowledged [44] that the elastic strength of individual CNT shells is extremely high, however, few reports [43] also suggested that weak shear interactions between adjacent shells and tubes lead to the significant reductions in the effective strength of MWCNTs and CNT bundles down to only a few GPa [43]. This has been recently addressed to improve the strength by applying high-energy electron irradiation [43] in cross-linked hierarchical CNT bundles. They suggested that cross linking of inner shells and tubes effectively attributed to increases the strength of these materials to approximately 60GPa for MWCNT and 17GPa for DWCNT bundles. Moreover, few papers also reported [44] that CNTs are not strong enough to withstand high pressure under compressive load and buckling, kinking were observed by them. They suggested that owing to their hollow structure and high aspect ratio, CNTs tend to undergo buckling when placed under compressive load, torsional strain and bending stress. SWCNTs can withstand a pressure up to 24GPa without deformation. Furthermore, Popov et al [48] reported that bulk modulus of super hard phase of SWCNTs is 462 to 546 GPa, which is higher than diamond (single diamond crystal have 420 GPa).

1.4.4. Thermal properties

CNTs are reported [49] to have high thermal conductivity. It is a very good thermal conductor along the tube axis and good insulators lateral to the tube axis. This property is known as ballistic conduction. Pop et al [49] show that a SWCNTs has a room temperature thermal conductivity of 3500 W·m$^{-1}$·K$^{-1}$ [49] along the tube axis. This is much higher than the thermal conductivity of copper (385 W·m$^{-1}$·K$^{-1}$) which is well known for its good thermal conductivity. They also reported that with increase in room temperature, thermal conductivity decrease sharply and suggested that this decrease is attributed to the phonon scattering. However, Sinha et al [50] reported that
SWCNTs film exhibit off-axis thermal conductivity of 1.64 W·m⁻¹·K⁻¹ at room temperature.

1.4.5. Chemical properties

CNTs are reported to exhibit novel properties of chemical inertness. For some specific application such as sensor and to make it selective to particular agent, CNTs need to be functionalized with chemically selective species. Functionalization of CNTs is well reported tough process and requires rigorous and aggressive acid treatment at high temperature. Environmental particulates and gases generally adsorbed on the walls of CNTs but it cannot react readily with this.

1.5. Synthesis of CNTs

The discovery of CNTs and their unique properties has led to an entirely new understanding of the behavior of carbon materials, and it has opened a new chapter of nano-science and nanotechnology as quoted in section 1.2 and the new chemistry of complex systems at the atomic scale that exhibit advanced materials behavior. Nanotubes in particular exhibit a wide range of novel mechanical and electronic properties as discussed earlier in section 1.4. They are excellent conductors of heat and electricity, and they possess an astonishing tensile strength. Such properties boost the promise and exciting applications of CNTs in electronics, structural materials, and medicine although few research suggest the toxic nature of CNTs. Practical applications, however, will only be realized when accurate structural control has been achieved over the synthesis of these new materials and to characterize them for a particular application.

1.5.1. Catalyst deposition

Although there have been some studies reporting growth of CNTs without catalyst in arc discharge process [4], it is widely acknowledged that transition metal catalyst [51, 52] are needed for SWCNTs and MWCNTs growth. It is also believed that the catalyst on the substrate must be in the form of particles instead of smooth, continuous film. The metals which act as catalysts are basically transition [53] metals.
like iron, nickel, cobalt and molybdenum. These metal catalysts can be applied on the substrate from solutions containing them or they can be directly deposited using some physical technique. The type of CNT required or their end use decides the choice of approach. For example if we use solution form of catalyst, the powder form of CNTs will be obtained while if we use the solid film of catalyst over the substrate, the CNTs over the substrate can be obtained which is required for applications like field emission display and electronic application. The powdered CNTs will be useful for studying the purification and functionalization of CNTs.

Physical technique such as electron beam evaporation, thermal evaporation, pulsed laser deposition, radio frequency (RF) sputtering, and magnetron sputtering have been successfully used in catalyst preparation. These techniques are easy and amenable to produce small patterns. Usually a thin catalyst film (less then 20nm) is deposited by these techniques. The eventual particle size and the resultant nanotube diameter seem to correlate to film thickness. Generally thinner film leads to smaller particles and tube diameters but some optimization is always required, as only after a particular thickness of the catalyst film the growth will take place. Although a small grain size is not guaranteed in as prepared films. This depends on the growth technique and the different pre treatment parameters used for breaking the films into desired particle size. The catalyst film breaks into small islands due to surface tension, as well as the compressive stress due to mismatch of the thermal expansion coefficient of substrate and the catalyst film. In case of CVD, a pretreatment of ammonia has been used where a catalyst film is simultaneously etched into small particles.

1.5.2. Growth mechanism

Growth mechanism is the way in which CNTs are presumed to be formed layer by layer. The growth mechanism of CNTs is not exactly known yet. It is still a subject of controversy, and more than one growth mechanism has been proposed that might be operative during the formation of CNTs. There are several theories on the exact growth mechanism for nanotubes. One theory postulates that metal catalyst particles are supported on the substrate as shown in Figure 1.10(a)-(b).
It presumes that the catalyst particles are spherical or pear-shaped. In this case the deposition of nascent or reactive carbon will take place on only one half of the surface and this is the lower curvature side for the pear shaped particles. The carbon diffuses along the concentration gradient and precipitates on the opposite half, around and below the bisecting diameter. However, it does not precipitate from the apex of the hemisphere, which accounts for the hollow core that is characteristic of these filaments. For supported metals, filaments can form either by extrusion of CNTs upward and is also known as base growth, presented in Figure 1.10(a). CNTs grow upwards from the metal particles and metal catalyst remains attached to the substrate, or the particles detach and move at the head of the growing nanotube, labeled as tip-growth. Depending on the size of the catalyst particles, SWCNTs or MWCNTs are grown. In arc discharge, if no catalyst is present in the graphite, MWCNTs will be grown on the C particles that are formed in the plasma.
1.5.3. Different growth techniques

Several growth techniques have been identified worldwide for synthesis of CNT. Out of all these, here I am going to discuss mainly those three growth techniques, which are in common uses.

1.5.3.1. Arc discharge method

Nearly two decades ago, Iijima at NEC fundamental research laboratory in Tsukuba, Japan, first observed CNTs in the soot of carbon prepared by the carbon arc discharge evaporation method [4] that was intended for the synthesis of \( \text{C}_{60} \) fullerene. The schematic of arc discharge method is shown in Figure 1.11. Here cathode works as the deposit electrode, which collects soot and the anode is a movable carbon rod, which is consumed in the arc. The apparatus is attached to a vacuum pump and an inert gas supply, usually helium (He) and argon (Ar). The carbon arc discharge method used for synthesis of CNTs is simple and easy to operate however, to obtain CNTs with high yields and purities; a careful control over the experimental conditions is needed.

![Figure 1.11 Schematic of arc discharge method.](image-url)
1.5.3.2. **Laser ablation method**

In 1995, T. Guo et al. [51] at Rice University first reported the laser ablation technique for synthesis of single-walled nanotubes.

![Schematic of laser ablation method.](image)

In this method, a pulsed or continuous laser beam is applied to a carbon target in order to vaporize the mixture of graphite and metal catalyst (Co, Ni). The main difference between continuous and pulsed laser used is that the pulsed laser needs a much higher light intensity i.e. 1000 kW/cm$^2$ compared to 12 kW/cm$^2$. The carbon target is contained within a horizontal tube with the flow of inert gas, usually helium and argon (Ar) at a pressure of 500 Torr. The whole assembly is kept inside an oven at a temperature of 1200°C as shown in Figure 1.12. The CNTs are collected on a water cooled copper (Cu) collector outside the furnace from evaporated graphite.

1.5.3.3. **Chemical vapor deposition**

Although the two methods mentioned above are the primary methods used for the production of CNTs but they have few major disadvantages. First, both arc discharge and laser ablation technique lack control on CNTs growth. Second, these methods are relatively cost ineffective because growth temperature in arc discharge and laser ablation methods are too high and therefore they consume huge amount of energy. Third, CNTs grown through these methods have unwanted carbon and metal impurities. However in chemical vapor deposition (CVD) synthesis method, excellent
alignment as well as position control at nanometer scale with control over the diameter and deposition rate can be achieved at relatively low temperature.

For CVD growth technique, a thin patterned or continuous layer of metal catalyst (Fe, Co, Ni or their alloy) is deposited on Si substrates, using thin film deposition techniques like sputtering, e-beam and thermal evaporation. Energy supply to the carbon containing source gases, which is injected inside the reactor through gas line with MFC control, is done by resistively heated coil or ionized plasma. These energy sources are used for cracking of gas molecule into reactive atomic carbon, which precipitates at catalyst nano islands leading to the formation of CNTs. Commonly used carbon feedstock gases include different hydrocarbons (CH$_4$, C$_2$H$_2$, C$_2$H$_4$, C$_2$H$_6$), carbon monoxide etc. CVD growth technique is further classified into thermal CVD, plasma enhanced CVD, low pressure CVD, etc.

1.5.3.3.1. *Thermal chemical vapor deposition*

In thermal CVD method, catalyst deposited substrate were positioned on to the sample holder. Sample holder then kept within the quartz tube of CVD reactor. Now, sample is heated up to desired temperature using resistively heating coil. Pretreatment was carried out at optimized temperature of 850°C or more for formation of catalytic nano-island in the presence of ammonia (NH$_3$) and hydrogen (H$_2$) at atmospheric pressure. Here, catalyst nano-island act as a nucleating seeds for growth of CNTs. CNT growth was finally carried out at an elevated temperature range of 650°C-1200°C using carbon feedstock gases in presence of NH$_3$. Growth temperature depends up on the choice of carbon feedstock gases used.

1.5.3.3.2. *Plasma enhanced chemical vapor deposition*

In the plasma-enhanced CVD, after positioning the sample on the grounded electrode, a glow discharge of plasma is created using high frequency power supply at a pressure of 10$^{-1}$ mbar, inside the chamber that assists in pyrolytic dissociation of carbon feedback gases into the nascent atomic carbon. In this process, plasma enhances the process of dissociating the hydrocarbon into atomic carbon species and therefore growth of CNTs in PECVD occurs at relatively lower temperature [39] than
thermal CVD. However, individual CNTs, which are grown by PECVD, contain more defects in their sidewalls and are of poor quality because of the low growth temperature.

1.6. CNTs characterization

CNTs are gaining remarkable attention on account of their potential and diverse applications, which are attributed by virtue of their physical, electrical, mechanical and thermal properties. For analysis of these properties, physical morphology assessment and materialization of the proposed application, different characterization techniques are employed. These characterization techniques include electron microscope, atomic force microscope, Raman spectroscopy, thermo gravimetric analysis, ultraviolet visible near infrared spectroscopy, scanning tunneling microscope, Fourier transform infrared spectroscopy, etc. Diameter of CNTs is in few nanometers and length is in micrometer, optical microscopes are inefficient tools for morphological analysis of CNTs because its resolution seizes in this regime. Electron microscope such as scanning electron microscopy (SEM) and tunneling electron microscopy (TEM) [55] are two powerful instruments used for physical characterization of nano-scale materials and CNTs. Detail of each characterization techniques and their methodology employed to probe the properties has been elaborated. Summary of different CNTs characterization techniques will be presented in Table 1.3 with properties analysis.

1.6.1. Scanning electron microscope

Scanning electron microscope (SEM) is one of the most common tools used to probe the morphological changes and quality of the synthesized CNTs. A SEM instruments consisted of an electron gun, condenser lenses for electron beam focusing, and vacuum system. SEM uses a beam of focused electrons in raster scan aimed to analyze the specimen target. Focused electron beam moves in raster scan and imaging is produced. SEM is mainly used to study the surface or near surface structure of bulk specimens. The spatial resolution of SEM is approximately 15nm, and therefore, not as good as TEM, which can have spatial resolutions in the sub-
nanometer range; however, SEM images are generally much easier to image and interpret compared to TEM. Also SEM has the ability to image a comparatively large area of the specimen; the ability to image bulk materials, thin films etc., and the variety of analytical modes available for measuring the composition and nature of the specimen.

Field emission SEM (FESEM) uses a field emission cathode as an electron gun of a scanning electron microscope and provides narrow and fine probing beams both at low and high electron energy; this results in both improved spatial resolution and minimized sample charging and damage. FESEM produces clearer, less electrostatically distorted images with spatial resolution down to 1.5nm or better i.e. several times better than the conventional SEM. High quality, low voltage images are obtained with negligible electrical charging of samples. Accelerating voltages of SEM ranges from 0.5 to 30 kV.

Employing the SEM, surface morphology of as-grown CNTs as well as their quality can be analyzed. From the SEM micrograph shown in chapter 3, one can clearly see the vertical alignment and patterning of CNT bundles over the silicon substrate. From high resolution SEM (HRSEM) images, amorphous carbon contamination produced in the sample at the time of growth can also be analyzed. Energy dispersive x-ray spectroscopy (EDX or EDS) can be used to study the presence of metal catalyst or the grade of its removal achieved after the purification. Chemical composition of the sample is analyzed using EDS. EDX analysis of CNTs sample gives information about the quality of impurity.

1.6.2. Transmission electron microscope

Transmission electron microscopy (TEM) is one of the most common techniques used to visualize and determine the morphology of the nano materials, CNTs [56, 57] and nano-particles [57]. It is a very powerful electron microscope, used for analysis of nano materials down to the angstrom level. Same as SEM, TEM instruments have similar features such as an electron gun, condenser lenses, and a vacuum system. However, TEM images production and magnification principle is different from the SEM and thus TEM provides morphological information of the
nano-particles at higher magnification. In this technique, the specimen is illuminated by a beam of monochromatic electrons; some of the electron beam are transmitted through the objective lens and then projected onto a viewing screen. The viewing screen composed of a layer of the electron fluorescent material to produce an image.

Figure 1.13 TEM micrograph of (a) MWCNTs, 6.7nm diameter and five concentric graphene sheet, (b) DWCNTs, 5.5nm diameter and (c) MWCNTs, 6.5nm diameter and seven tubular graphitic sheet [4].

In TEM micrograph one can see particles as small as a few angstroms $10^{-10}$ m, which is near atomic levels. TEM is used to study the physical structure of CNTs i.e. SWCNTs, DWCNTs [4] and MWCNTs and their dislocations. High-resolution transmission electron microscopy (HRTEM) gives information about the number of
walls in MWCNT. HRTEM micrographs shown in Figure 1.13(a) and Figure 1.13(c) shows MWCNTs with 6.7nm diameter having five concentric graphene sheet and 6.5nm diameter having seven tubular graphitic sheet whereas Figure 1.13(b) present DWCNTs with 5.5nm diameter and two tubular concentric graphitic sheets.

1.6.3. **Atomic force microscopy**

Same as SEM and TEM, atomic force microscope (AFM) can also be used for the analysis of surface morphology. SEM and TEM give 2D image, whereas AFM images are three-dimensional. AFM is based on the raster scan of surface morphology of sample using sharp tip of a cantilever probe. Imaging in AFM is done with the help of monochromatic laser beam reflected from the back of cantilever. A typical AFM image of CNTs is shown in Figure 1.14.

![AFM Image of CNTs](image)

**Figure 1.14** AFM image of CNTs.

1.6.4. **Raman spectroscopy**

Raman spectroscopy is based on the Raman effect. Raman spectra of CNT are rich in information about their structure and properties [31]. The spectrum also tells us about the quality of the material, the structure of the tube, phonon and electron quantum confinement. Raman spectroscopy is commonly used for characterizing SWCNT bundles. Raman experiment can be done at room temperature and under ambient pressure, so it is quick, non-destructive and does not require any sample
preparation experimentation. This technique has the sensitivity to probe differences in the properties of CNTs prepared by different methods and under different conditions. It also analyzes purity [58-60], the degree of amorphous carbon contained, and impurities in the sample. Characterization of CNTs by Raman spectroscopy involves following three dominant Raman bands that are the radial breathing mode (RBM) at low frequencies, the tangential G band at higher frequencies and disorder-induced D-band as shown in Figure 1.15.

The radial breathing mode (RBM) Raman frequencies corresponds to the coherent vibration of the C atoms in the radial direction. These features are unique in CNTs and occur with RBM frequencies between 120 cm$^{-1}$ and 350 cm$^{-1}$ for SWCNTs with diameter range of 0.7 nm < d < 2 nm. These RBM frequencies are therefore very useful for identifying whether a given carbon material contains SWCNTs, through the presence of RBM mode and for characterizing the nanotube diameter distribution in the sample.

![Raman spectra of SWCNTs](image)

**Figure 1.15** Raman spectra of SWCNTs exhibit RBM peaks, defect peak, [60] silicon peak and graphitic peak.

The G-band of CNT is related to the strain i.e. carbon-carbon stretching in graphene plane. In SWCNT, G-band is composed of several peaks due to the phonon wave vector confinement along the SWCNT circumferential direction and due to symmetry-breaking effects associated with SWCNT curvature. The tangential G-band appears in the range of 1500 cm$^{-1}$ and 1605 cm$^{-1}$. The D-band of CNTs is associated
with the disorder lying in the nanotube. The disorder-induced D-band that appears in the range of 1300cm\(^{-1}\) and 1500cm\(^{-1}\) holds significant information about the crystalline quality of the CNTs. The D-band comes into existence in the Raman-spectrum only when sp\(^2\) hybridized carbon is lying adjacent to hetero-atoms, vacancy defects, grain boundaries, or other defects that reduce the crystalline symmetry of CNTs. Moreover, second overtone of defect peak, known as G’-band also appears near 2700cm\(^{-1}\).

1.6.5. Thermo gravimetric analysis

Thermo-Gravimetric Analysis (TGA) is based on the thermal oxidation of the CNT at elevated temperature treatment. Since, as grown CNTs have different impurities like amorphous carbon and metal impurities viz. iron, cobalt, nickel or their alloy. TGA is used to study the percentage of metal impurities lying in CNTs powder. By thermal treatment of the CNT sample at high temperature, amorphous carbon present in the sample burns at low temperature and CNT starts oxidizing. The remaining ash of CNT powder, obtained after temperature treatment, is analyzed, which gives information about the percentage of purity and thermal stability of CNT.

1.6.6. Ultraviolet visible near infrared

Ultraviolet visible near infrared (UV-Vis NIR) spectroscopy is a prominent tool for analysis of local density of states (DOS) and conductivity of those compounds which show electronic conjugation. CNTs show electronic conjugation due to the delocalized \(\pi\)-electrons lying in hexagonal ring structure of their unit cell. Also, due to the Quasi-1D structure of CNTs, electrons have one-dimensional confinement along their axial direction. This gives rise to discredited DOS, which is known as van Hove singularity. After exposure of CNTs sample in UV-Vis NIR radiation, electrons lying in the valence band of the CNTs go into the excited un-occupied conduction band. The emitted photons, when electron comes in to the valence band after de-excitation, give \(S_{11}\) & \(S_{22}\) peaks for semi-conducting CNTs and \(M_{11}\) & \(M_{22}\) peaks for metallic CNTs in the UV-Vis NIR spectra. Using these peaks, one can estimate electrical properties of CNTs i.e. metallic or semiconducting CNTs.
1.6.7. Scanning tunneling microscope

Scanning tunneling microscope (STM) works on the principle of quantum tunneling of electron from the sample toward the nano-scale prober of the microscope, after application of potential across the sample and probe tip. Since quantum tunneling of electrons is directly related to the density of electronic states of a system. Therefore through this instrument, one can study about the atomic structure and electronic properties of CNT.

**Table 1.3 Summary of CNTs characterization techniques**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Characterization tools</th>
<th>Properties Analyzed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Scanning electron microscope (SEM)</td>
<td>Surface and physical morphology, elemental analysis using EDX</td>
</tr>
<tr>
<td>2.</td>
<td>Transmission electron microscope (TEM)</td>
<td>Defects, open cap, metal particle encapsulation and 2D surface morphology etc.</td>
</tr>
<tr>
<td>3.</td>
<td>Atomic Force Microscopy (AFM)</td>
<td>3-D surface morphology</td>
</tr>
<tr>
<td>4.</td>
<td>Raman analysis</td>
<td>Radius, defect, graphitization and chiral index analysis etc.</td>
</tr>
<tr>
<td>5.</td>
<td>Thermo Gravimetric analysis (TGA)</td>
<td>% ash and metal impurities content</td>
</tr>
<tr>
<td>6.</td>
<td>Ultraviolet visible near infrared spectroscopy (UV-Vis NIR)</td>
<td>Electrical properties analysis i.e. metallic or semiconducting CNTs</td>
</tr>
<tr>
<td>7.</td>
<td>Scanning tunneling microscope (STM)</td>
<td>Atomic level imaging, chirality, electrical properties</td>
</tr>
<tr>
<td>8.</td>
<td>Fourier transform infra red spectroscopy (FTIR)</td>
<td>Chemical analysis such as functional group attachment etc.</td>
</tr>
</tbody>
</table>

1.6.8. Fourier transform infra red spectroscopy

This technique is based on the vibration spectra of CNTs. Fourier transform-infrared (FTIR) spectroscopy is used to identify the chemical changes introduced due
to functional groups attachment with the CNTs samples. The FTIR sample is prepared by grinding functionalized CNTs with KBr, and grinded CNT-KBr powder is made into the form of pellets. These pellets are used for qualitative analysis of functionalized CNTs. The FTIR peaks appear in the range of 1000 cm\(^{-1}\) and 3500 cm\(^{-1}\) for different functionalized group.

1.7. Applications of CNTs

Since the landmark report of CNTs by Iijima in 1991 [4], CNTs and their properties have been extensively studied and reported by various research groups. These studies conclude that CNTs exhibited extraordinary electrical properties [31], high mechanical strength, good thermal properties, high aspect ratio, and chemically inert behavior. Owing to their unique properties of high aspect ratio, good mechanical strength, chemical stability and semiconducting to metallic electrical behavior [61], CNTs have been regarded as one of the most promising material for plethora of applications ranging from biological [62], pharmaceutical, mechanical [63] to electronics [6]. One of their major electronic applications is development of a CNT based cathode for high and low current density devices such as vacuum microelectronics, field emission (FE) displays, etc. For vacuum microelectronics application, it is required to develop a CNT cathode possessing high electron emission current because cathode is the basis and centre of a FE device.

CNTs have unique electrical properties such as the ability to withstand high current density (10\(^9\) A/cm\(^2\)) low turn on electric field for cold electron emission and show ballistic transport because of their quasi one-dimensional configuration. Due to their unique properties, different research groups intensively study CNT’s behaviors for device application. Apart from these, CNT have extraordinary mechanical and chemical properties that make them potentially useful in many diverse applications viz field emitter [64], sensor, energy storage, nano-composites etc. CNT can also be used as nano interconnects due to their high current carrying capacity and ballistic conductance, which arises due to their quasi-1D quantum confinement.

One of the most promising and interesting applications of CNT is in the field of nano composites [9]. Nano composites are material matrix of more than one compound that is in nano-meter scale such that they possess properties better than
each individual component. Due to the exceptionally high surface area to volume ratio (typically in the range of $10^9$ m$^{-1}$) and high aspect ratio, high mechanical strength, superior thermal conductivity, and unique electrical & optical properties, CNT can be a very attractive reinforcing material and filler in material matrix of nano composite. CNT can also be an excellent material for manufacturing of light weight armor and aircraft. Another application of CNTs has been demonstrated as hydrogen storage. Due to their high surface area, appreciable amount of hydrogen can be stored, per unit weight of CNT. Apart for these applications, CNTs have also been identified as an excellent candidate for many other applications such as memory, nano tweezers, nano probe, solar applications, nano-genetic probe, nano electronics, AFM tip, etc. Excellent mechanical strength coupled with the light weight of CNTs give its great potential for aerospace, armoire applications. It has also been suggested that nanotubes could be used in the space elevator, an Earth-to-space cable.

1.7.1. Field emission and vacuum tube applications

The most promising application of CNTs are those involving electron field emission [14, 30] devices and nano-electronics such as field effect transistors,
interconnects and sensors. Since, diameter of CNT are in few nanometers and length is in microns, therefore it has high aspect ratio (Height/Radius), which makes them excellent material for field induced electron emission at room temperature, also known as cold cathode. CNT based cold cathode will be a very attractive electron sources in a variety of applications, including field emission displays [65, 66], X-ray tubes [67, 68], electron microscopy and vacuum microelectronics [69]. Numerous efforts have been made for realization of CNT based vacuum devices, in which vertically aligned, patterned CNTs are grown on substrate, which act as cathode. These cathodes are tested in diode and triode configurations. A typical current density-electric field (J-E) plot and F-N curves, obtained from current-voltage characteristics has been presented in Figure 1.17. This confirms the field emission behavior in diode structure and their suitability or applicability for vacuum electronics.

![Figure 1.17(a) J-E curves and (b) F-N Plots of CNT cathodes in diode configuration at different anode to cathode spacing.](image)

**1.7.2. Sensors**

CNTs have shown their potential candidature for sensor application due to their high specific surface area and novel chemical inertness behavior. Due to some major advantages in their physical, chemical and electrical behavior compared to other material sensors, CNT based sensor will be relatively more sensitive and
efficient. Firstly, each atom of SWCNT is a surface atom, so, the sensitivity of CNT based sensor is very high i.e. in ppt range. Second advantage is their ability to give sufficient electrical response with change in environmental condition at room temperature. This feature is very interesting for detection and realization of chemical and gas sensors. Thirdly, foreign species are only physisorbed on the walls of CNT, so re-utilization of CNT sensors will be possible after desorption of that foreign body. Also CNTs can be made highly sensitive and selective to a particular species by attaching its walls with a sensitive functional group, which works as receptors for that species.

For realization of CNT based sensors many device approaches can be used such as CNT resistor, capacitor, resonator, FET etc. Figure 1.18 shows a bottom gated CNTFET for sensor application, where conductivity change in the channel of CNTFET is analyzed for sensing of chemical and gas agents.

Figure 1.18 Bottom gated CNTFET for sensor application.

1.8. References


