Carbon Nanostructures

• Structures

• Physical Properties:
  Optical (band gap, density of states)
  Electrical (conductance and resistivity)
  Thermal (thermal conductivity)
  Mechanical

• Fabrication Methods

• Applications
One electron system

Consider the behavior of an electron in a hydrogen atom. The electron is attracted by a positive nucleus and the Coulomb potential function is given by,

\[ V(r) = \frac{-e^2}{4\pi\varepsilon_0 r} \]

\[ E_n = -\frac{me^4}{8\varepsilon_0^2 h^2 n^2} = -\frac{13.6 \text{ eV}}{n^2} \]
# State Function in 3-D

<table>
<thead>
<tr>
<th>Quantum numbers</th>
<th>Meaning</th>
<th>Corresponding variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n = 1, 2, 3, \ldots )</td>
<td>Principal quantum number. Shell</td>
<td>( R(r) )</td>
</tr>
<tr>
<td>( l = 0, 1, 2, \ldots (n-1) )</td>
<td>Orbital angular momentum Quantum number. Subshell</td>
<td>( \Theta(\theta) )</td>
</tr>
<tr>
<td>( m_l = \pm l, \pm (l - 1), \ldots, 0 )</td>
<td>Magnetic quantum number. Orientation of subshell</td>
<td>( \Phi(\phi) )</td>
</tr>
</tbody>
</table>

Spin Quantum Number; \( s = +/- \frac{1}{2} \)

\[
\psi_{nlms}(r, \theta, \phi, s) = R(r)\Theta(\theta)\Phi(\phi)S(s)
\]
Pauli exclusion principle: In any given system (an atom, molecule or crystal), no two electrons can occupy the same quantum state. This principle also states that the joining of atoms to form a system (crystal) does not alter the total number of quantum states. Using this principle, we can determine how many electrons are allowed per shell or subshell.

<table>
<thead>
<tr>
<th>$n$</th>
<th>$l$</th>
<th>$m_l$</th>
<th>$s$</th>
<th>Allowed states in subshell</th>
<th>Allowable states in complete shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>$\pm 1/2$</td>
<td>2 (1s-subshell)</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>$\pm 1/2$</td>
<td>2 (2s-subshell)</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-1</td>
<td>$\pm 1/2$</td>
<td>6 (2p-subshell)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>$\pm 1/2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>$\pm 1/2$</td>
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<td>$\pm 1/2$</td>
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<td></td>
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<td>1</td>
<td>$\pm 1/2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>-2</td>
<td>$\pm 1/2$</td>
<td>10 (3d-subshell)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>-1</td>
<td>$\pm 1/2$</td>
<td></td>
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<td></td>
<td>0</td>
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<td>$\pm 1/2$</td>
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<tr>
<td></td>
<td>2</td>
<td>2</td>
<td>$\pm 1/2$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Carbon Structures

- Its atomic number is 6 (has 6 electrons)
Carbon-based materials are unique in many ways. One distinction relates to the many possible configurations of the electronic states of a carbon atom, which is known as the hybridization of atomic orbitals.

- In the crystalline phase of carbon atoms the valence electrons give rise to 2s, 2px, 2py, 2pz orbitals which are important in forming covalent bonds in carbon materials. Since the energy difference between the upper 2p energy levels and the lower 2s level in carbon is small compared with the binding energy of the chemical bonds, the electronic wave functions for these four electrons can readily mix with each other, thereby changing the occupation of the 2s and three 2p atomic orbitals so as to enhance the binding energy of the C atom with its neighboring atoms. This can be addressed as the reason of the mechanical strength of the carbon materials.
- This mixing of 2s and 2p atomic orbitals is called hybridization.
Carbon Structure

• In carbon, three possible hybridizations occur: sp, sp2, and sp3
• Group of 4 elements such as Si, Ge exhibit primarily sp3 hybridization.
• Carbon differs from Si and Ge insofar as carbon does not have inner atomic orbitals except for the spherical 1s orbitals and the absence of nearby inner orbitals facilitate hybridization involving only valence s and p orbitals for carbon.
Carbon Structure

- Carbon has four electrons in its outer valence shell; the ground state configuration is $2s^2\ 2p^2$. In diamond, carbon atoms exhibit sp\(^3\) hybridization, in which four bonds are directed toward the corners of a regular tetrahedron. The resulting three-dimensional network is extremely rigid, which is one reason for its hardness. The bond length between sp\(^3\) carbons is 1.56Å. Diamond behaves as an insulator because all electrons are localized in the bonds within the sp\(^3\) network.
The splitting of the 3s and 3p states of silicon into the allowed and forbidden energy bands.
The unit cell of diamond lattice structure. The position of each lattice point is shown with respect to the 000 lattice point.
Carbon Structure

• In graphite, sp2 hybridization occurs, in which each atom is connected evenly to three carbons in the xy plane, and a weak bond is present in the z axis. The C-C sp2 bond length is 1.42Å. The sp2 set forms the hexagonal lattice.

• The pz orbital is responsible for a weak bond, a van der Walls bond. The spacing between the carbon layers is 3.35Å. The free electrons in the pz orbital move within this cloud and are no longer local to a single carbon atom (delocalized). This is the reason why graphite can conduct electricity.
Graphene Structure
Carbon Structure

Graphite Sheet

*Hexagonal lattice of interacting p orbitals*

*Weak interactions between layers*
Carbon Structure

• Carbon materials are found in variety forms such as graphene, graphite, diamond, carbon fibers, fullerenes, and carbon nanotubes.

• Carbon is the only material in the periodic table that has isomers from 0 dimensions (0D) to 3 dimensions (3D), as is shown in table below.
# Carbon Hybridization

<table>
<thead>
<tr>
<th>Structure</th>
<th>0-D</th>
<th>1-D</th>
<th>2-D</th>
<th>3-D</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isomer</td>
<td>C60 fullerene</td>
<td>nanotube</td>
<td>Graphite fiber</td>
<td>diamond</td>
</tr>
<tr>
<td>Hybridization</td>
<td>sp2</td>
<td>sp2</td>
<td>sp2</td>
<td>sp3</td>
</tr>
<tr>
<td>Bond Length [Å]</td>
<td>1.40 (C=C)</td>
<td>1.44 (C=C)</td>
<td>1.42 (C=C)</td>
<td>1.54 (C-C)</td>
</tr>
<tr>
<td></td>
<td>1.46 (C-C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electronic Properties</td>
<td>Semiconductor Eg=1.9 eV</td>
<td>Metal or semiconductor</td>
<td>semimetal</td>
<td>Insulator Eg = 5.47eV</td>
</tr>
</tbody>
</table>
Carbon has been studied and used for centuries, and carbon science was long thought to be a mature field. Diamond (3D) and graphite (2D) are considered as two natural crystalline forms of pure carbon. So when a whole new class of carbon materials—the fullerenes, such as C60—appeared in the last few decades, many scientist were surprised. As the result, the concepts and understanding of long known carbon materials was changed.
Carbon Structures

Carbon Clusters:
Clusters have linear (for odd number of atoms) and closed nonplanar (for even number of atoms) geometries.

\[
\begin{align*}
C & \quad C \\
C & \quad C \quad C \\
\quad & \quad | \quad | \\
\quad & \quad C \quad C \\
\quad & \quad | \quad | \\
C & \quad C \quad - \quad C
\end{align*}
\]
C60 is the roundest and most symmetrical large molecule known to man. BuckminsterFULLERENE continues to astonish with one amazing property after another. Named after American architect R. Buckminster Fuller who designed a dome with the same fundamental symmetry, C60 is the third major form of pure carbon; graphite and diamond are the other two.
C60

It has 12 pentagonal and 20 hexagonal faces symmetrically arrays
C60
Molecules made up of 60 carbon atoms arranged in a series of interlocking hexagons and pentagons, forming a structure that looks similar to a soccer ball. C60 is actually a "truncated icosahedron", consisting of 12 pentagons and 20 hexagons. It was discovered in 1985 by Professor Sir Harry Kroto, and two Rice University professors, chemists Dr. Richard E. Smalley and Dr. Robert F. Curl Jr., [for which they were jointly awarded the 1996 Nobel Prize] and is a molecule composed of a single element to form a hollow spheroid [which gives the potential for filling it, and using it for novel drug-delivery systems.]
The buckyball, being the roundest of round molecules, is also quite resistant to high speed collisions. In fact, the buckyball can withstand slamming into a stainless steel plate at 15,000 mph, merely bouncing back, unharmed. When compressed to 70 percent of its original size, the buckyball becomes more than twice as hard as its cousin, diamond."
C60 Crystal Structure, FCC (26% empty)

- C60 is soluble in benzene, single crystals can grow by slow evaporation from benzene.

- Molecules are separated by 1 nm and are held by van der Waals forces.

- 26% of the volume of the unit cell is empty.
Alkali-Doped C60, e.g. at 400 C, K3 C60, are conductors (C60 are insulators) and they become superconductors at low temperatures (18 - 30 K)
• Buckyball Fullurene C$_{540}$
Carbon nanotubes are thin, *hollow cylinders* made entirely of carbon. Their walls are formed *from graphene*, a honey-comb lattice of carbon atoms. These are large macromolecules that are unique for their size, shape, and remarkable physical properties. Their electrical properties is very depended on their cylindrical shape and C-C bonding geometry. These properties changes due to any mechanical or magnetic strain applied on the material. The tubes are tough and when bent or squeezed, spring back to their original shape.
History of carbon Nanotubes

• A US patent was given to two British scientists in 1889 on the production of carbon nanotubes utilizing marsh gas, otherwise known as methane. The method employed is essentially the same as used today. The patent describes the production of “hair-like carbon filaments” for electrical lighting.

• In 1960’s a group at National Carbon Company in Parma, Ohio and later on in 1970’s at the University of Canterbury in Christchurch, New Zealand, helped to characterize the carbon nanotubes.
History of carbon Nanotubes

• Then in 1983, a company called Hyperion Catalysis perfected ways to produce nanotubes and began incorporating them into the fuel line for cars. The nanotube’s high conductivity would dissipate any electrical charge that could build up potentially and spark. Today, most cars on the road use Hyperion’s nanotube incorporated fuel lines.

• Began in 1991, when Sumino Limijima and his colleagues created some multiwalled nanotubes at the research laboratory of the electronics multinational NEC in Tsukulba, Japan.

• Around 1998 the first transistors utilizing carbon nanotubes began to emerge.
CNT Structure

- Among Nanostructures, CNT has demonstrated a vast relationship between physical properties (in particular the transport property) and its geometry.
- Electromechanical properties are very depend on chirality.
- The conductance of a metallic CNT is lowered by mechanical strain; can be used as an active element in MEMS/NEMS like strain gauges or pressure sensors.
- Axial strain predicted to alter the band gap (metallic-to-semiconductor or vice versa); changes the conductance by increasing or decreasing the band gap.
Carbon nanotubes are hexagonal sheets of graphene, which are single layers of graphite atoms, in the form of rolled up chicken wire.

Due to their hexagonal nature, they are part of a class of molecules called fullerenes, which are closed-caged molecules containing only hexagonal and pentagonal interatomic bonding networks.
Types of CNT

- There are two types of carbon nanotubes.
- One type is called Single-Wall-Nanotube, or SWNT. This type consists of only one cylinder, and represents the most promising type in the use of transistors. Their diameter is usually 0.33 to 5.0 nm and their lengths are 2 to 100 μm.
- So it is practically a 1-D structure.
Types of CNT

• The other type is Multi-Walled-Nanotubes, or MWNTs. They are a bunch of SWNT in a Russian doll type of configuration, with SWNTs placed inside larger SWNTs. A MWNT’s diameter ranges from 3 to 50 nm and their lengths are several microns.
Structure of Nanotubes
Graphene Structure
To understand nanotube we need to know few basic terms. Considering the unrolled nanotube in figure above, the two unit vector $\hat{a}_1$ and $\hat{a}_2$ are defined as shown in the figure. The chiral vector of the nanotube, $Ch$, is defined as the vector normal to the circumference vector in the direction in which it is being

i.e. $Ch = n\hat{a}_1 + m\hat{a}_2$
Structure of Nanotubes

- The chiral vector is used to determine the direction and magnitude of the circumference of a CNT

\[ \vec{C} = n \vec{a}_1 + m \vec{a}_2 \]
Structure of Nanotubes; another example

• Where \( \hat{a}_1 \) and \( \hat{a}_2 \) are unit vectors in the two-dimensional hexagonal lattice, and \( n \) and \( m \) are integers. The nanotubes are described by these numbers as \((n, m)\). Another important parameter is the chiral angle, which is the angle between \( \text{Ch} \) and \( \hat{a}_1 \).

• If \( (n - m) \) is divisible by 3 then the tube is metallic and if \( (n - m) \) is not divisible by 3 then the tube is a semiconductor. On the basis of Chirality nanotubes can be divided into three classes:
  • Zigzag if either \( n = 0 \) or \( m = 0 \)
  • Armchair if \( n = m \)
  • Chiral if \( n \neq m \)

• Armchair type is always metallic and the other two types can be either metallic or semiconductor depending on their Chiral condition.
structure
Hexagonal Lattice \((n,m)\)

- \(n - m = 3q\) (\(q\): integer): metallic
- \(n - m \neq 3q\) (\(q\): integer): semiconductor
Zigzag nanotubes correspond to \((n, 0)\) or \((0, m)\) and have a chiral angle of \(0^\circ\), armchair nanotubes have \((n, n)\) and a chiral angle of \(30^\circ\), while chiral nanotubes have general \((n, m)\) values and a chiral angle of between \(0^\circ\) and \(30^\circ\). Nanotubes can have either be metallic or semiconducting properties.
Structure of Nanotubes

Different types nanotubes:  a. Zigzag,  b. Armchair,  c. Chiral
Structure of Nanotubes
• The zigzag is characterized by its Zigzag shape in symmetry axis
• The armchair by its armchair shape in symmetry axis
• The chiral has been known by its twisted shape as highlighted. By combining and the condition for type of conductor, armchair will always be metallic, while the others can be metallic or semiconductor.
Buckytube C60

Drawings of the two nanotubes which can be capped by one half of a $\text{C}_{60}$ molecule. (a) Zig-zag $(9,0)$ structure, (b) armchair $(5,5)$ structure.
Chiral vector is defined as $C_h = n\mathbf{a}_1 + m\mathbf{a}_2$ using the vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ for the hexagonal lattice. Note that for the hexagonal lattice a unit cell is made of 2 atoms. Note also depending on textbook, $\mathbf{a}_1$ and $\mathbf{a}_2$ are defined as 2 vectors with 120 deg. openings.
With this definition in the figure $a_1$ and $a_2$ can be expressed using the Cartesian coordinate $(x, y)$.

$$a_1 = \left(\frac{3}{2}a_{cc}, \frac{\sqrt{3}}{2}a_{cc}\right)$$

$$a_2 = \left(\frac{3}{2}a_{cc}, -\frac{\sqrt{3}}{2}a_{cc}\right)$$

Here, $a_{cc}$ is the bond length of carbon atoms. For graphite $a_{cc} = 1.421$ Å. This same value is often used for nanotubes. But, probably, $a_{cc} = 1.44$ Å is a better approximation for nanotubes. It should really depend on the curvature of the tube. A slightly larger value for more curvature is known.

Since the length of $a_1$, $a_2$ are both $|a_1| = |a_2| = \sqrt{3}a_{cc} \equiv a$, this $a$ is the unit length. Hence,

$$a_1 = \left(\frac{\sqrt{3}}{2}, \frac{1}{2}\right)a$$

$$a_2 = \left(\frac{\sqrt{3}}{2}, -\frac{1}{2}\right)a$$
Length of the Chiral vector $C_h$ is the peripheral length of the nanotube:

$$C_h = \sqrt{3}a_{c-e}\sqrt{n^2 + nm + m^2}$$

For Armchair nanotube ($m = n$): $C_h = 3na_{c-e}$

Further examples, for (5,5): $C_h = 15a_{c-e}$, for (10,10): $C_h = 30a_{c-e}$

For zigzag nanotubes ($m = 0$): $C_h = \sqrt{3}na_{c-e}$

Further examples, for (10,0): $C_h = 10\sqrt{3}na_{c-e}$, for (16,0): $C_h = 16\sqrt{3}a_{c-e}$

Hence, the diameter of nanotube $d_t$ is

$$d_t = \frac{C_h}{\pi} = \frac{\sqrt{3}a_{c-e}}{\pi} \sqrt{n^2 + nm + m^2}$$

For armchair ($n = m$):

$$d_t = \frac{3n}{\pi}a_{c-e}$$

For zigzag ($m = 0$):

$$d_t = \frac{\sqrt{3}n}{\pi}a_{c-e}$$
The unit lattice vector (translational vector) $\mathbf{T}$, perpendicular to the chiral vector is expressed as

$$\mathbf{T} = \left[(2m + n)\mathbf{a}_1 - (2n + m)\mathbf{a}_2 \right]/d_R$$

The length $T$ is the unit lattice length along the tube axis direction.

$$T = \sqrt{3}C_h / d_R = 3a_{c-c} \sqrt{n^2 + nm + m^2} / d_R$$

Here,

$$d_R = \begin{cases} d & \text{if } n-m \text{ is not a multiple of } 3d \\ 3d & \text{if } n-m \text{ is a multiple of } 3d \end{cases}$$

and $d$ is the highest common divisor of $(n,m)$.

For armchair $(m=n)$: $d = n$, $d_R = 3d = 3n$, $T = \sqrt{3}C_h / (3n)$

Then, $T = \sqrt{3}(3na_{c-c}) / (3n) = \sqrt{3}a_{c-c}$

For zigzag $(m=0)$: $d = n$, $d_R = d = n$, $T = \sqrt{3}C_h / n = \sqrt{3}(\sqrt{3}na_{c-c}) / n = 3a_{c-c}$
The Chiral angle $\theta$ (angle between the chiral vector and the zigzag direction) is defined as
\[
\theta = \tan^{-1}\left[ \frac{\sqrt{3}m}{m + 2n} \right]
\]

Armchair $m = n$: $\theta = \tan^{-1}\left[ \frac{1}{\sqrt{3}} \right] = 30^\circ$

Zigzag $m = 0$: $\theta = \tan^{-1}[0] = 0^\circ$

For chiral tubes: $0 < \theta < 30^\circ$

Number of hexagons in a unit cell $N$ is
\[
N = \frac{2(m^2 + n^2 + nm)}{d_R}
\]

Armchair $m = n$:
\[
N = \frac{2(m^2 + n^2 + nm)}{d_R} = \frac{6n^2}{3n} = 2n
\]

Zigzag $m = 0$:
\[
N = \frac{2(m^2 + n^2 + nm)}{d_R} = \frac{2n^2}{n} = 2n
\]
ASSUMPTIONS AND LIMITATIONS OF BAND STRUCTURE THEORY

To simplify the understanding of the band structure of a material, the following assumptions are considered.

- **Homogenous system**: the material for which the band structure is calculated is assumed to be homogenous.
- **Infinite-size system**: a large piece of material must be considered for the bands to be continuous.
- **Non-interactivity**: it is assumed that the electrons have a static potential and doesn’t interact with lattice vibrations, other electrons and photons.
- **Small systems**: for small systems like a small molecule or a quantum dot, the band structure isn’t continuous.
There are various methods to calculate band structures of a material.

- **Tight-binding approximation**: uses atomic orbitals as basis wave functions.
- **Form the name “tight binding”,** it suggests that the electrons in an atom should be tightly bound to the atom to which they belong and should have limited interactions with the surrounding atoms of the solid.
CNT Band structure

\[ a_1 = \left( \frac{3}{2}a_{cc}, \frac{\sqrt{3}}{2}a_{cc} \right) \]

\[ a_2 = \left( \frac{3}{2}a_{cc}, -\frac{\sqrt{3}}{2}a_{cc} \right) \]

\[ |a_1| = |a_2| = \sqrt{3}a_{cc} \equiv a, \]

\[ a_1 = \left( \frac{\sqrt{3}}{2}, \frac{1}{2} \right)a \]

\[ a_2 = \left( \frac{\sqrt{3}}{2}, -\frac{1}{2} \right)a \]
Now the reciprocal lattice vectors are defined as the figure below:

The conversions of base vectors are simply calculated as follows:
CNT Band structure

\[ \mathbf{b}_1 = \frac{2\pi}{a_1}, \mathbf{b}_2 = \frac{2\pi}{a_2} \]
\[ \mathbf{a}_1 \cdot \mathbf{b}_1 = 2\pi, \mathbf{a}_2 \cdot \mathbf{b}_2 = 2\pi \]
\[ \mathbf{b}_1 = \left( \frac{1}{\sqrt{3}}, 1 \right) \frac{2\pi}{a} = \left( \frac{1}{2}, \frac{\sqrt{3}}{2} \right) \frac{4\pi}{\sqrt{3}a} \]
\[ \mathbf{b}_2 = \left( \frac{1}{\sqrt{3}}, -1 \right) \frac{2\pi}{a} = \left( \frac{1}{2}, -\frac{\sqrt{3}}{2} \right) \frac{4\pi}{\sqrt{3}a} \]

Chiral \( C_h \) and Lattice \( T \) vectors are transformed to \( K_1 \) and \( K_2 \) vectors as follows:

\[ C_h = n\mathbf{a}_1 + m\mathbf{a}_2, \quad C_h = \sqrt{3}a_{c-c} \sqrt{n^2 + nm + m^2} \]
\[ T = \left[(2m+n)\mathbf{a}_1 - (2n+m)\mathbf{a}_2\right]/d_R, \quad T = \sqrt{3}C_h/d_R = 3a_{c-c} \sqrt{n^2 + nm + m^2}/d_R \]

Discrete unit vector along the circumferential direction:
\[ K_1 = \left[(2m+n)\mathbf{b}_1 + (2n+m)\mathbf{b}_2\right]/Nd_R \]

Reciprocal lattice vector along the nanotube axis:
\[ K_2 = (m\mathbf{b}_1 - n\mathbf{b}_2)/N \]
Let’s check the following:

\[ |\mathbf{K}_1| = \frac{2\pi}{a} \frac{2\sqrt{n^2 + mn + m^2}}{Nd_R} \]

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

\[ = \frac{2\pi}{a} \frac{1}{\sqrt{n^2 + mn + m^2}} \]

\[ = \frac{2\pi}{C_h} \]

\[ |\mathbf{K}_2| = \frac{2\pi}{a} \frac{2}{\sqrt{3}} \frac{d_R \sqrt{n^2 + mn + m^2}}{N} \]

\[ = \frac{2\pi}{a} \frac{2}{\sqrt{3}} \frac{d_R \sqrt{n^2 + mn + m^2}}{2(n^2 + mn + m^2)} \]

\[ = \frac{2\pi}{a} \frac{1}{\sqrt{3}} \frac{d_R}{\sqrt{n^2 + mn + m^2}} \]

\[ = \frac{2\pi}{C_h} \frac{1}{\sqrt{3}} \frac{d_R}{T} = \frac{2\pi}{T} \]
BAND STRUCTURE OF GRAPHENE

- To depict the electronic conditions of a carbon nanotube, we should first understand the electronic structure of graphene.
- From tight binding approximation calculations, the energy dispersion relation for graphene is given as
  \[ E = \pm \gamma \sqrt{1 + 4 \cos \left( \frac{3}{2} k_x a \right) \cos \left( \frac{k_y a}{2} \right) + 4 \cos^2 \left( \frac{k_y a}{2} \right)} \]
- Where \( \gamma \) is carbon – carbon interaction energy \( \gamma = 2.9 \text{eV} \), and \( a \) is the unit length vector in the hexagonal lattice, given as \( a = \sqrt{3} a_{cc} \).
- Where, \( a_{cc} \) is the bond length of the carbon atom, whose value for graphite is \( a_{cc} = 1.421 \text{Å} \).
- In the case of a carbon nanotube, \( a_{cc} = 1.44 \text{Å} \) is a better approximation.
Energy Band Structure of Graphene

- The above equation is plotted in the MATLAB software by calculating $E$ at various points of $k_x$ and $k_y$. Where $k_x$ and $k_y$ could be defined as components of the wave vector $\vec{k}$,
- Where, $\vec{k} = k_x \hat{i} + k_y \hat{j}$
- The value of energy $E$ is calculated along $k_x$ and $k_y$ at a sampling rate of 0.05 per step.
- This value could be further reduced so that the line space vectors could be further divided into smaller segments and consequently better results could be obtained.
• The conduction and valence bands are meeting at only two points in k-space called K points.
• Since the conduction and valence bands meet at two points, and at the rest of the points there is a presence of band gap, Graphene is a semi metal.
BAND STRUCTURES OF CARBON NANOTUBE

- From the band structure of graphene, the band structure of carbon nanotube could be obtained by quantizing the wave vector in circumferential direction.

- the value $k_y$ remains the same for a carbon nanotube as well as for graphene in energy dispersion relation. The only change is now the vector $k_x$ resembles a circle, which is the circumference of the carbon nanotube.

\[
E = \pm \gamma \sqrt{1 + 4 \cos \left( \frac{3}{2} k_x a \right) \cos \left( \frac{k_y a}{2} \right) + 4 \cos^2 \left( \frac{k_y a}{2} \right)}
\]

Dispersion relation of graphene
• $k_\perp$, the electron wave number, is quantized and because the diameter is small (~1nm), the spacing between quantized values is large.

• $k_\parallel$ is continues and electrons are free to move along this wavevector.

• The continuum of $k_\parallel$ states in each $k_\perp$ mode are called 1-D subbands.
Tight-binding approximation shows that the conduction and valence bands meet only at two points in k-space, called: K points
BAND STRUCTURES OF CARBON NANOTUBE at m = n

\[ E = \pm \gamma \sqrt{1 + 4 \cos \left( \frac{q \pi}{n} \right) \cos \left( \frac{k_y a}{2} \right) + 4 \cos^2 \left( \frac{k_y a}{2} \right)} \]

- The line space k vectors are divided into multiple steps at a period of 0.005 for a smoother curve.
• it could be seen that the valence and conduction bands meet at 6 points.

• This could be clearly seen in the 2-dimensional plot that there isn’t any band gap. Hence, the carbon nanotube at chirality $m = n$ has metallic characteristics.
BAND STRUCTURES OF CARBON NANOTUBE: general form

- For general condition of CNT, the wave vector quantified in circumferential direction as \( k \cdot C = k_x c_x + k_y c_y = 2\pi p \), where \( p \) is an integer.
- Each line \( k_x \) and \( k_y \) gives one dimensional energy bands.
- Hence CNT with different values of \( c_x \) and \( c_y \) have different electronic properties.
- The terms \( c_x \) and \( c_y \) are determined by the chiral integers \( m, n \) where, \( c_x = a(\sqrt{3}n + \left(\frac{3}{2}\right)m) \) and \( c_y = a\left(\frac{3}{2}\right)m \).

\[
E = \pm \gamma \sqrt{1 + 4 \cos \left(\frac{3c_x k_x a}{2C} - \frac{3\pi pa c_y}{C^2}\right) \cos \left(\frac{\sqrt{3}c_y k_y a}{2C} + \frac{\sqrt{3}\pi pa c_x}{C^2}\right) + 4 \cos^2 \left(\frac{\sqrt{3}c_y k_y a}{2C} + \frac{\sqrt{3}\pi pa c_x}{C^2}\right)}
\]

- Here, the values of \( c_x \) and \( c_y \) are calculated from the supplied values of \( m, n \).
Energy Band of Carbon Nanotube

- (a) Shows the E-k relation of Zigzag CNT(7,0),
- (b) Shows the E-k relation of Armchair CNT(7,7),
- (c) Shows the E-k relation of Zigzag CNT(12,0)
Energy Band of Carbon Nanotube

(a) Shows the Band structure relation of Zigzag CNT(7,0), (b) Shows the Band structure of Armchair CNT(7,7), (c) Shows the Band structure of Zigzag CNT(12,0).
Effects of Strain on Band Structure
Effects of Strain on Band Structure
Due to the thermal activation of electrons over the energy gap results in empty valence states and occupied conduction states.

The off-state conductance of semiconductor CNT is non-zero, and it is depend on the temperature and the band gap.
Tuning of Band gap in CNT

\[ I = \left| t \right|^2 \frac{2e}{h} \cdot \frac{2}{E_F + E_{\text{gap}}} \int_{E_F}^{\infty} (f_R(E) - f_L(E)) dE , \]

\[ = \left| t \right|^2 \frac{2e^2}{h} \frac{2}{1 + \exp\left(\frac{E_{\text{gap}}}{k_b T}\right)} V \]
pnp device

\[ V_{\text{tip}} = 0 \]

\[ E_{\text{gap}} \]

\[ E_F \]

\[ x_{\text{tube axis}} \]

\[ V_{\text{tip}} \approx 1 \text{V} \]

\[ \zeta \]

\[ V_{\text{tip}} > 1 \text{V} \]

\[ \varepsilon \] is steepness of the barrier

\[ I/(4e^2V/h) \]

\[ kT = 25 \text{ meV} \]

\[ \varepsilon = 5 \text{ meV/nm} \]

\[ \varepsilon = 2.5 \text{ meV/nm} \]
Effect of magnetic field on the CNT band structure

• $qv_F D/4$ is the magnetic moment of an electron traveling in a loop of diameter $D$ with velocity of $v_F$. Changes in the energy of electron states can be described by the interaction of this orbital magnetic moment with an axial magnetic field.
Effect of magnetic field on the CNT band structure
Other Physical Properties

• Carbon Nanotubes are able to conduct heat so well that they are more efficient than a diamond, which is one of the best heat conductors.

• Carbon Nanotube hexagonal structure gives it great strength. In fact, they are stronger than steel and yet are only a quarter as dense.

• No matter how much they are squeezed, the Nanotube will just bend or buckle, but not break. They will always pop back into original shape.
Other Physical properties

- **Young’s modulus**: 10 times that of steel
- **Tensile strength**: 45 billion Pascals (steel 2 billion Pascals)
- **Metallic conductivity**: billion Amperes per square centimeter (copper fails at one million Amperes per square centimeter)
- **Heat conductivity**: 2 times as that of diamond.
Other Physical properties

- Ballistic transport
- Conductance quantization
- Wrapping modes of quantized electron wavefunctions encircling the CNT, each mode contains a wavefunction along the tube, described by $k_\parallel$, associate with a 1-D channel.
Other physical Properties

• Studies showed that nanotubes of type n-m=3x, where x is zero or any positive integer, were metallic and therefore conducting. The fundamental gap would therefore be 0.0 eV. All other nanotubes behave as a semiconductor. The fundamental gap is a function of diameter, where the gap was in the order of about 0.5 eV. It is shown that the energy gap follows a function as:

\[ E_{\text{gap}} = 2 \frac{y a}{d} \]

• Where y is the C-C tight bonding overlap energy (2.7 ± 0.1 eV), a is the nearest neighbor C-C distance (0.142 nm), and d is the diameter. This shows that the fundamental gap ranged from around 0.4 eV - 0.7 eV, which it is in good agreement with the values obtained from one-dimensional dispersion relations.
Electrical property

- The density of electronic states as a function of energy has been calculated for a variety of nanotubes. As an example, consider the density of states for metallic (8, 8), (9, 9), (10, 10) and (11, 11) armchair nanotubes. While conventional metals have a smooth density of states, these nanotubes are characterized by a number of singularities, where each peak corresponds to a single quantum subband.
Physical Properties

Density of States in Metallic Nanotubes

Density of States in Semiconducting Nanotube
DOS for various zigzag tubes

Energy (eV)

Density of States (states/1C–atom/eV)

(10,0)

(20,0)

(30,0)

(40,0)
Electrical property

- **Electrons in nanotubes**

  The unique electronic properties of carbon nanotubes are due to the quantum confinement of electrons normal to the nanotube axis. In the radial direction, electrons are confined by the monolayer thickness of the graphene sheet. Around the circumference of the nanotube, periodic boundary conditions come into play. For example, if a zigzag or an armchair nanotube has 10 hexagons around its circumference, the 11th hexagonal will coincide with the first.
Because of this quantum confinement, electrons can only propagate along the nanotube axis, and so their wavevectors point in this direction. The resulting number of one-dimensional conduction and valence bands effectively depends on the standing waves that are set up around the circumference of the nanotube. These simple ideas can be used to calculate the dispersion relations of the one-dimensional bands, which link wavevector to energy, from the well known dispersion relation in a graphene sheet.
Electrical property

- It is shown that about one-third of small-diameter nanotubes are metallic, while the rest are semiconducting, depending on their diameter and chiral angle.
- In general, an \((n, m)\) carbon nanotube will be metallic when \(n - m = 3x\), where \(x\) is an integer. All armchair nanotubes are metallic, as are one-third of all possible zigzag nanotubes.
Electrical property

- Although the choice of $n$ and $m$ determines whether the nanotube is metallic or semiconducting, the chemical bonding between the carbon atoms is exactly the same in both cases. This surprising result is due to the very special electronic structure of a two-dimensional graphene sheet, which is a semiconductor with a zero band gap. In this case, the top of the valence band has the same energy as the bottom of the conduction band, and this energy equals the Fermi energy for one special wavevector, the so-called K-point of the two-dimensional Brillouin zone (i.e. the corner point of the hexagonal unit cell in reciprocal space). Theory shows that a nanotube becomes metallic when one of the few allowed wavevectors in the circumferential direction passes through this K-point.
Electrical property

• As the nanotube diameter increases, more wavevectors are allowed in the circumferential direction. Since the band gap in semiconducting nanotubes is inversely proportional to the tube diameter, the band gap approaches zero at large diameters, just as for a graphene sheet. A nanotube with diameter of about 3 nm, the band gap becomes comparable to thermal energies at room temperature (kT).
Electrical property

- It is shown that concentric pairs of metal-semiconductor and semiconductor-metal nanotubes are stable. Nanometre-scale devices could therefore be based on two concentric nanotubes or the junction between nanotubes. For example, a metallic inner tube surrounded by a larger semiconducting (or insulating) nanotube would form a shielded cable at the nanometre scale. One might then envisage nanoscale electronic devices made completely from carbon that would combine the properties of metals and semiconductors, without the need for doping
Carbon Nanotubes Production Processes

• Production processes for carbon nanotubes, vary from blasting carbon with an electrical arc or a laser to growing them from a vapor. These processes vary considerably with respect to the type of nanotube produced, quality, purity and scalability. Carbon nanotubes are usually created with the aid of a metal catalyst and this ends up as a contaminant with respect to many potential applications, especially in electronics. IBM has very recently, however, grown nanotubes on silicon structures without a metal catalyst.
**CARBON ARC METHOD:**
Nanotubes can be synthesized using a carbon arc. A potential of 20-25V is applied across carbon electrodes of 5-20 um diameter and separated by 1mm at 500 Torr pressure of flowing helium. Carbon atoms are ejected from the positive electrode and form nanotubes on the negative electrode. As the tubes form, the length of the positive electrode decreases, and a carbon deposit forms on the negative electrode. Iron is incorporated as a catalyst in the central region of the positive electrode. If no catalysts are used, the tubes are nested or multi-walled types (MWNT), which are nanotubes within nanotubes. The carbon arc method can produce single walled nanotubes of diameters 1-5 nm with a length of 1 um.
Arc Discharge
Arc discharge is the earliest method used to create nanotubes. It involves vaporizing carbon to create the nanotube.
Fabrication

- **LASER EVAPORATION METHOD:**
- The quartz tube containing argon gas and a graphite target are heated to 1200°C. Contained in the tube, but somewhere outside the furnace, there is a water-cooled copper collector. The graphite target contains small amounts of cobalt and nickel that act as catalytic nucleation sites for the formation of the tubes. An intense pulsed laser beam is incident on the target, evaporating carbon from the graphite. The argon then sweeps the carbon atoms from the high temperature zone to the colder copper collector on which they condense into nanotubes. Tubes 10-20 nm in diameter and 100um long can be made by this method.
• In order for VLS growth to occur, the oven temperature must be chosen such that the catalyst carbon mixture will be in a liquid alloy state and the pure carbon can remain solid to precipitate out.

• Laser ablation will only grow SWNTs and not MWNTs. The SWNT produced is a high purity nanotube.

• Minimal cleaning is required, but they still end up tangled up, making them difficult to use. In addition, laser ablation is very expansive.
Nanotube growth

Pulsed Laser

Ar gas Flow controller

Graphite (contain small amount of Co and Ni) in Quartz Tube

Cold Finger

Lens

Tube Furnace
Phase diagram, temperature chosen so the catalyst and carbon mixture is liquid and the pure carbon is solid.
Fabrication

- CHEMICAL VAPOR DEPOSITION METHOD:
- The chemical vapor deposition method involves decomposing a hydrocarbon gas such as methane (CH4) at 1100 C. As the gas decomposes, carbon atoms are produced and then condense on a cooler substrate that may contain various catalysts such as iron. This method produced tubes with open ends, which does not occur when other methods are used. This procedure allows continuous fabrication, and may be the most favorable method for scale up and production.
CHEMICAL VAPOUR DEPOSITION

CVD Nanotube Production Apparatus
One solution to the placement problem is to directly fabricate the nanotubes utilizing chemical-vapor deposition (CVD). By controlling the placement of the catalyst, the positions of the nanotube can be controlled. The catalyst can be placed as a thin layer that is patterned either using photolithography or by heating the thin film or microcapsules to produce catalyst nanoparticles. Alternatively, the catalyst could be placed using an ink jet printing system. However, in either case the nanotube growth direction is random.

Control the direction of growth is with a magnetic field of about 1.5 Teslas. The nanotubes grow in the direction of the applied magnetic field.

Another alternative uses scratches in a substrate to control both the placement and direction of the growth, all in one-step. A silicon(100) substrate is used with a 100nm thick silicon dioxide cap.
Nanotube can grow in two ways. Both ways are the same except for whether the tube grows underneath the catalyst or above it. The process is similar but slower to VLS growth. The carbon in the form of gas is absorbed into the catalyst and the Nanotubes are then precipitated out.
CVD seams to be the best option for creating nanotubes to be used in transistors, since they are grown in place, and the process is only slightly expansive and is similar to lithography techniques used in IC manufacturing.

<table>
<thead>
<tr>
<th>Fabrication</th>
<th>Typical Yield</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc Discharge</td>
<td>up to 30% by weight</td>
<td>Cheap, Fast, Both SWNT and MWNT</td>
<td>Very dirty, length less than 50 microns, tangled</td>
</tr>
<tr>
<td>Laser Ablation</td>
<td>up to 70 %</td>
<td>Fast, high purity, very long nanotubes</td>
<td>still needs cleaning, expansive, tangled</td>
</tr>
<tr>
<td>CVD</td>
<td>20 - 100 %</td>
<td>no cleaning, direct on substrate, easiest to scale up</td>
<td>slightly expansive</td>
</tr>
</tbody>
</table>
Applications

• Nanotubes have a very broad range of electronic, thermal, and structural properties that change depending on the different kinds of nanotube (defined by its diameter, length, and chirality, or twist). They can transfer heat very efficiently and more useful in the circuit as they can be cooled faster. They can be made to perform as a metal or a semiconductor depending on the way they are rolled.

• Nanotubes can have single cylindrical wall (SWNTs) or multiple walls (MWNTs) i.e. cylinders inside the other cylinders.
Applications

• **Field Emission Properties**: used to make flat panel display, vacuum tube lamp, sensors..

• **High electrical conductivity = poor transmitters of electromagnetic energy**: used to shield computers, communication systems, or any other electronic facilities from electromagnetic radiations.
Applications of nanotubes

• **Devices:**
  • The nano-devices are based upon various nano-technologies. The devices are classified into three broad categories based on the operating principles and fabrication techniques.
  • **Carbon nanotube transistors**
  • Solid state quantum effect devices
  • Molecular electronic devices
  • Integration of those nanostructures together with MEMS technology is very promising for future photonic devices.
T-tube transistor (tube FET)
application

• Batteries
• Fuel Cells
• Composite materials
• Chemical and gas Sensors