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Carbon Nanotube: A Review on Introduction, Fabrication Techniques and Optical Applications

Ekta Singh[1], Richa Srivastava[3,*], Utkarsh Kumar[2], Anamika. D. Katheria[1]

[1]M.Tech Nano-optoelectronics, Babasaheb Bhimrao Ambedkar University, Lucknow, India
[2]Department of Applied Physics, Babasaheb Bhimrao Ambedkar University, Lucknow, India
[3]University Institute of Engineering and Technology, Babasaheb Bhimrao Ambedkar University, Lucknow, India
*Corresponding author: richadolly@rediffmail.com

Abstract Present review articles deals with the detail introduction, classification, fabrication techniques and optical application of carbon nanotubes. Presently various techniques are used to manufacture MWNTs or SWNTs. The optical properties of CNTs are closely linked to their structure and optical absorption of CNTs is of saturable intensity dependent nature. The various optical properties and detail application as light emitting diode are discussed.

Keywords: *CNTs, mobility, CVD, LED*

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1. Introduction

In 1985 it was generally believed that solid elemental carbon occurs in two different crystalline phases: diamond and graphite. They have different physical structure and properties. Diamond is in thermodynamic equilibrium at very high temperatures [3] and pressures; it occurs, nevertheless, as a metastable phase under atmospheric pressure and at room temperatures. In Figure 1 each carbon atom is tetrahedrally surrounded by four sp^3 covalently bonded carbon atom. The structure of graphite consists of graphene layers in which the sp^2 bonded carbon atom form a planar hexagonal honeycomb arrangement. The bonding of carbon atoms in a graphene sheet is very strong (covalent bond), whereas the bonding between two graphene layers is weak (vanderwall bonds) [1]. In 1985, a group of researcher (Richard smiley and Robert curl) of Rice University made an interesting discovery. They vaporize the sample of graphite with an intense pulse of laser light and used a stream of He gas to carry the vaporized carbon into a mass spectrometer. The mass spectrum showed peak corresponding to cluster of carbon atoms particularly strong peak corresponding to molecule composed of 60 carbon atom C_{60}.C_{60} was named as the new allotrope of carbon. It was spherical in shape and formed a ball with 32 faces, where out of 32 faces 12 are pentagon and 20 was hexagon as shown in [Figure 1]. Carbon molecules, where named after an architect Buckminster fuller, who was responsible for the design of C_{60}. The soccer ball shaped C_{60} molecule was named Buckminster fullerene or buckyballs. The unique geometric property of new allotrope of carbon did not end with soccer shaped molecule. Carbon nanotube (CNTs) were discovered by S. Iijima, [3] who was looking for new carbon structures, in the deposit formed on graphite cathode surfaces during the electric-arc evaporation (or discharge) that is commonly employed to produce fullerene soot. The CNTs have been synthesized by various methods e.g. electric arc discharge, laser evaporation and chemical vapor deposition [4,5,6]. The CNTs can be inert and can have a high aspect ratio, high tensile strength, low mass density, high heat conductivity, large surface area and versatile electronic behavior including high electron conductivity [1]. CNTs are expected to behave as ideal one-dimensional 'Quantum Wires' with either semiconducting or metallic behavior, depending upon the diameter and the orientation of tube axis (parallel or perpendicular to the C-C bond) [7,8]. Carbon nanotubes are broken down into vectors that describe the spiral symmetry of the nanotube. Nanotube structures are represented by the following parameters v as shown in Table 1 [9].

Table 1. Parameters of carbon nanotubes

PARAMETERS	FORMULA
1. Chiral vector	**Ch**= na_1+ na_2= (n, m)
2. Translational vector	**T** = t_1a_1+ t_2a_2= (t_1, t_2)
3. Chiral angle	Cosθ= (2n +m)/(2*√(n² + m² + n*m))
4. Length of chiral vector	L = a√ (n²+ m²+ n*m)

2. Classification of Carbon Nanotubes

A carbon nanotube can be described as a graphene sheet rolled into a cylindrical shape so that the structure is one-dimensional with axial symmetry. Nanotubes have caps on each end of the graphene sheets, which contain six pentagons. The caps are placed perfectly to fit the long cylindrical section. Carbon nanotubes are approximately a nanometer wide and a few microns long [3]. The classifications of the different symmetries of nanotubes are dependent on the unit cell.

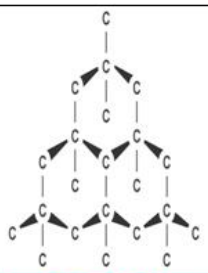
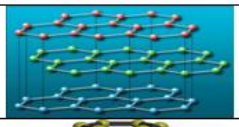
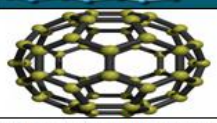
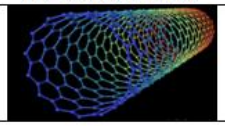
Diamond		Cubic (F.C.C) a= 3.566A Hexagonal a=2.463A c= 6.714A
Graphite		Hexagonal a =2.463A c= 6.714A
Fullerene		Cubic (F.C.C) a= 14.17 A
Carbon nanofoams	Carbon clusters with an average diameter 6-9nm	
Carbon nanotubes (CNTs)		Single-walled CNT Multi-walled CNT

Figure 1. Allotrope Forms of Carbon

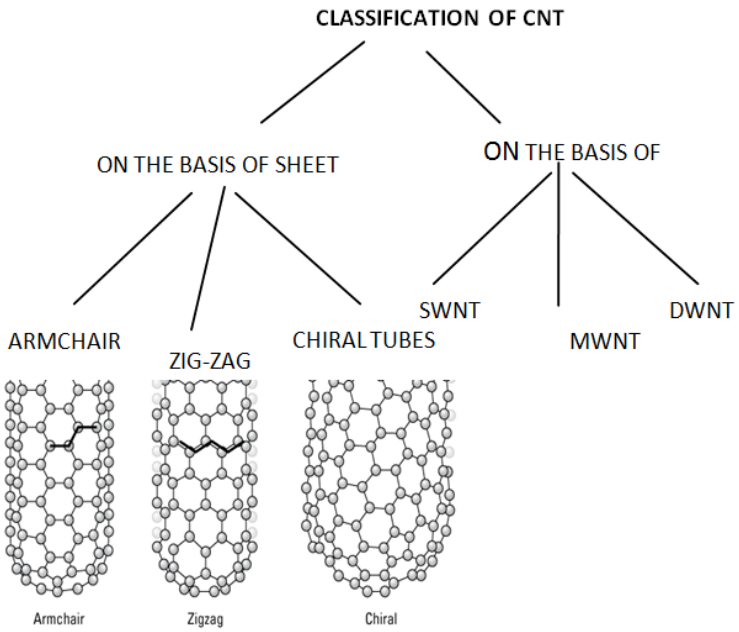


Figure 2. Classification of carbon nanotubes

3. Synthesis Techniques

There are many techniques used to produce MWNTs or SWNTs. Method such as electric arc discharge, laser vaporization and chemical vapor deposition techniques are well established to produce a wide variety of CNTs [1]. These methods are described in following sections.

3.1. Arc-Discharge

The arc discharge method is one of the method by which CNTs were produced by Iijimia [3]. CNTs can be synthesized in the arc-discharge as shown in figure. DC provides higher yields of CNTs, which are deposited on the cathode. One important condition of stabilization of arc-discharge is maintaining a constant distance between the graphite electrodes of around 1 mm [10].

Synthesis of MWNTs by arc discharge has been achieved in He gas [11,12]. When a graphite rod containing a metal catalyst (Fe, Co, etc.) is used as the anode with pure graphite cathode, single wall carbon nanotubes (SWNTs) are generated in the form of soot [13,14]. It was found that presence of hydrogen gas in the growth region gives the optimum synthesis of MWNTs with high crystallinity (having regular graphene sheets at an interlayer spacing of 0.34nm) and few coexisting carbon nanoparticles [15-21]. In contrast, fullerenes could not be produced in gas atmosphere, which include hydrogen atoms, that is the essential difference between CNT and fullerene production [22].

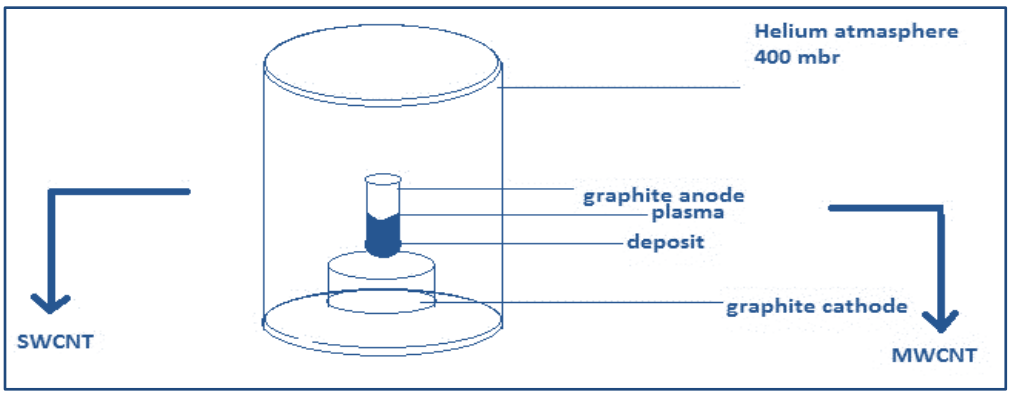


Figure 3. Electric arc discharge

3.2. Laser Ablation

An efficient route for the synthesis of bundles of SWNTs with a narrow distribution is the laser evaporation technique. In this method, a piece ofgraphite target is vaporized by laser irradiation under high temperature in an inert atmosphere. MWNTs were found when a pure graphite target was used. The quality and yield of these products have been found to depend on the reaction temperature. The best quality is obtained at 1200℃ reaction temperature. At lower temperature, the structure quality decreases and the CNTs start presenting many defects. The yield of SWNTs strongly depends on the type of metal catalyst used and is seen to increase with furnace temperature, among other factors [5]. In 1996, dual pulsed laservaporization was used to optimize the laser oven method further to produce SWNTs yields of 70% [23]. Sample were prepared by laser vaporization of graphite rods with 1.2 at ratio of a 50:50 mixture of Co and Ni powder at 1200℃ in following argon at 500 torr, followed by heat treatment in vacuum at 1000℃ to stimulate the $C_{60}$and other smaller fullerenes. In this method, the amount of carbon deposited as soot is minimized by the use of two successive laser pulses: the first to ablate the carbon-metal mixture and the second to break up the larger ablated particles and feed them into the growing nanotube structures. These SWNTs were nearly uniform in diameter and self- assemble into ropes (bundles) which consisting of 100 to 500 tubes in a two-dimensional triangular lattice. It is also possible to produce SWNTs using a CO_2- laser focused on a graphite metal target in the absence of an oven [24]. In this context, Ar and N_2 were determined to be the best atmosphere to generate SWNTs bundles, whereas they produced only small amount of CNTs. Similarly, the diameter of tube depend upon the laser power. Other laser experiment revealed that porous targets of graphite-Co-Ni (nitrate) yield twice as much SWNTs material from the standard metal carbon target [23,24,25]. Recently, Eklund et al. reported ultrafast (subpicosecond)laser pulses are able to produce large amount of SWNTs [26].

The laser vaporization method was developed for fullerene and CNT production by Smalley's group [27]. First used for fullerene synthesis [1] and further applied to produce CNTs [28] in 1996, especially SWNTs. The synthesis system consists of a furnaces, quartz reactor tube and laser beam source (Figure 4). It can also consist of a reactor chamber and a laser source. A laser beam of YAG is focused onto the graphite rod target located inside the reactor tube. The target is vaporized in high-temperature argon buffer gas and carried to the copper collector vaporized in high-temperature argon buffer gas and carried to the copper collector cooled down with coater. This method has several advantages, such as high-quality SWNT production, diameter control, investigation of growth dynamics, and the production of new materials. High-quality SWNTs with minimal defects and contaminants, such as amorphous carbon and catalytic metals, can be synthesized using laser-furnace method followed by suitable purification processes [28,29,30].

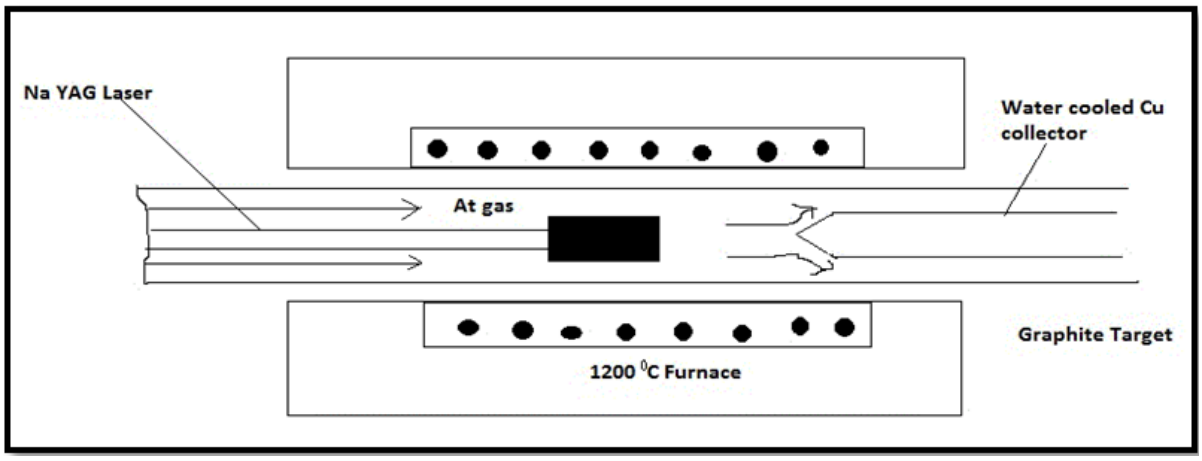


Figure 4. Block diagram of laser ablation

3.3. Chemical Vapor Deposition

Chemical vapor deposition is a process used to produce high purity, high-performance solid materials. This process is often used in the semiconductor industry to produce thin films. It is a technique for synthesizing materials in which chemical component in vapor phase react to form a solid film at some surfaces (substrate) [35]. Ability to control the components and physical conditions of the gas phase, the solid surface and the envelope that surrounds them determine the capability to control the properties of the use CVD to deposit materials in various forms including: monocrystalline, polycrystalline, amorphous, and epitaxial.

3.4. Mechanism

CVD is a sequential process which starts from the initial vapor phase, progresses through a series of quasi-steady sub-processes, and culminates in the formation of a solid thin film of its final micro or nanostructure [8].

In general, the CVD process can be divided into two broad steps, one is transport of gas phase material to the reaction zone withthe reaction of material and other is the deposition of the film on the substrate. The transport process involves the gas supply, convection of gas-phase materials due to pressure gradient or buoyancy of hot gases and diffusion of gaseous reactant to the substrate surface. The deposition process involves the adsorption of the reactant species on to the substrate surfaces sites by surface migration followed by surface chemical reaction between the reactant species, usually catalyzed by the surface, then the desorption of the reaction by-products take place followed by diffusion of the by-products away from the surface and finally incorporation of the condensed solid products into the macro/nano-structure of the growing film. [3]

In a CVD chamber, the flow of gaseous fluid as it moves through the reactor after being injected from the gas supply. Two types of convection generally take place inside the chamber, one is forced convection due to pressure gradient across the chamber and the other is the free convection due to buoyancy of hot gases. Another important process involved is the viscous friction experienced by the gas molecules, when they come very close to the substrate surface. Due to this the flow velocity slows down and the remaining transport of reactant to the surface occurs only by the diffusion through the relatively stationary boundary layer of fluid as shown in Figure 5. Once the transitions from convection to the diffusion take place, the source gas molecules are adsorbed to the surface followed by the surface reaction to produce the required material. The important factors that influence the homogeneous reaction are the gas residence time near the surface and gas heating, both of which are functions of the gas flow rate and flow pattern. Depending on these factors, the reaction often begins in the gas phase rather than occurring entirely at the substrate surface. Generally, the gas phase reactions are homogeneous and produce powdery material and surface reaction are heterogeneous and produce thin films. In general, the reactants are selected in such a way that the driven reactions always produce gaseous by-products (rather than solid materials) so that they can be removed easily by desorption and diffusion processes.

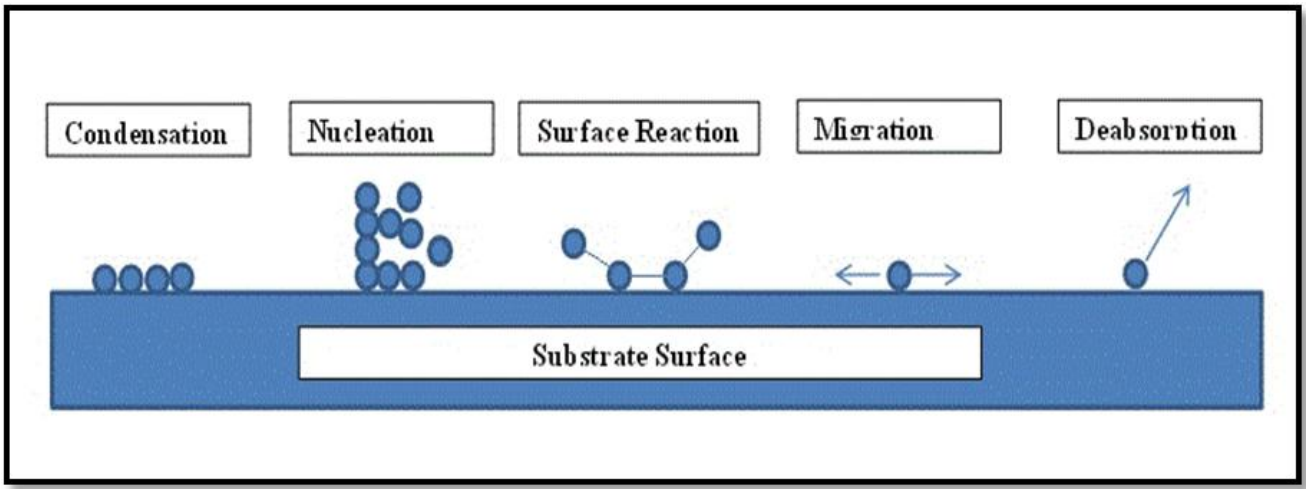


Figure 5. Schematic diagram of various processes involved in CVD

4. Optical Properties of CNT

The optical properties of CNTs are linked closely to their structural and electronic properties and are fully governed by one parameter, its chiral vector, which describes how the carbon-atom honeycomb is organized with respect to the CNT axis [37]. Depending solely on this parameter, CNTs may behave as a direct band-gap semiconductor or as a metal.

Its chiral vector determines the electronic properties of a CNT. This vector describes how the graphene sheet is rolled when forming the nanotube. The chiral vector, $C_h$is expressed by two real space unit vectors a_1 and a_2 and two integers n and m as shown in equation 1:

$$C_h = na_1 + ma_2. \quad (1)$$

Graphene is a semimetal, when the single-layer graphene is rolled to form a tube an extra level of confinement into quasi-1D structure is added. CNTs behave as metals if the subtraction of the integer values n and m is an integer multiple of 3(n-m=3k) otherwise it is a semiconductor (n-m not equal to 3). Hence, statistically

we can conclude that 2/3 of CNTs will be semiconductor; while 1/3 will be metallic. Saturable absorption is a result of excitonic absorption in semiconductor nanotubes [36]. The density of states of a state semiconducting CNT can be numerically calculated. The electronic density of states of CNT, originates from the "slicing of graphene density of states due to the quasi-1D Confinement of the electrons, which leads to the presence of the characteristic Van Hove singularities observed in their electronic densities of state (DOS) of two CNT. CNTs absorb photons in the same way an ordinary direct bandgap semiconductor would do when the energy of the photon is equal to the bandgap of the CNT.The CNTs bandgap is inversely proportional to the diameter of the tube. It is particularly fortunate that the diameter ofCNT typically ranges from 1nm to 2nm, which leads to an optical absorption that overlaps the 1550nm window commonly used for fiber optic technologies.

4.1. Saturable Absorption

The optical absorption of CNTs is of saturable, intensity-dependent nature; it is therefore, a suitable material to employ for passively mode-locked laser operation. Passive mode locking is achieved by incorporating an intensity-dependent component into the optical give threshold intensity, after which it saturates and becomes transparent. Such saturable absorbers discriminate in favor of pulse formation over continuous wave lasing [33].

4.2. Third Order Nonlinearity

The first theoretical studies on the third order nonlinearity of CNTs appeared in 1998 nonlinear refractive index coefficient, $n_2$as high as $2*10^{-8}$ (m^2/W) [37]. To put this theoretical value into context, $n_2$for the silica glass is $3*10^{-20}$ (m^2/W) and chalcogenide glass, which is recently receiving much attention as a suitable material for the fabrication of highly nonlinear fibers has a $n_2$value of $2*10^{-18}$ m^2/W.Thedifficulty is that for most third order nonlinear optical materials, the third order susceptibility was too low for practical applications; the extremely high n_2 of CNT opened a new potential application for CNT.Optical nonlinearity is due to optical intensity dependent nonlinear response of dielectric materials. When the optical intensity of propagating light in a dielectric medium is low, stimulated polarization is linearly proportional to the optical intensity. However, at high optical intensities, the stimulated polarization, P, exhibit a nonlinear response to the optical electric field, E as described by equation 2.

$$P = \epsilon\left(X^1.E + X^2.EE + X^3.EEE + \ldots\ldots\right) \qquad (2)$$

X^1, X^2, X^3correspond to linear, second and third order susceptibility.

5. Applications as Thin Film Led

A light-emitting CNT p-i-n junction was demonstrated with a single CNT. Such a device is a basic photonic building block and paves the way for application of CNTs in nano-optics and photonics [39]. The possibility of using single CNT device as a quantum light source has also been explored [41].The high quantum efficiency of our devices made it possible to produce narrow emission lines that in turn enabled us to analyze individual emission peak in detail. While the single-tube LED has such advantages when studying the underlying physics of electrical emission, the likelihood of a device failure is understandably high. Moreover, light output is limited by the maximum current a single CNT can carry. Small-diameter CNTs(d=1nm), when aligned at mid-gap with the Fermi level of the metal, have a typical device resistance in order of 1 to 10 M ohm, which sets the current level at a few hundred nanoamperes at normal operating voltages [43].

Consequently, the light emission properties of CNT films and networks [42] have been attracting recent interest beyond single CNT application. CNT films can be readily assembled from the solution and allow for the possibility of scaling up both the current and the amount of light. In addition, CNT films achieve more consistent and stable output among devices by "averaging-out" the heterogeneities of individual CNTs. In this review, we study on the realization of a light emitting p-i-n diode from highlyaligned film of semiconductor carbon nanotube that emits light in the near-infraredspectral range. A split gate design similar to the single-tube CNT diode allows fortuning both the rectifying electrical behavior of the diode and its light generationefficiency. The CNT film diode produces light that is polarized along the device channel, a direct consequence of the high degree of CNT alignment in the film thatreflects the polarization property of 1D natural of individual tubes.

5.1. Physical Characteristics of CNT Films and Top Gated Devices

If we deposited CNT thin film on Si/SiO_2 substrate from a suspension of 99% Semiconducting carbon nanotubes with diameter ranging from 1.3 to 1.7 nm, separatedby density-gradient ultra centrifugation. With this deposition technique, CNTsalign in parallel at contact line between the solution and a vertically immersed planarsubstrate. The slip-stick motion of the contact line during evaporation producesperiodic arrays of regular CNT thin film stripes that cover a large area of substrate.

5.2. Transport Characteristics of the CNT Film Doide

In the case of single-tube CNT diode, good transport behavior is critical for efficient light emission. This is not surprising since the radiative recombination rate of excitons in CNTs is much smaller than the non-radiative recombination rate [44]. Here, we discuss electronic transport of CNT film devices with top-spilt gate to confirm that they do indeed behave as diodes.

5.3. Electroluminescence Characteristics of the Cnt Film Doide

In general, the radioactive decay of excitons is responsible for light emission in CNTs.Excitions can be electrically generated in CNTs via

- Simultaneous injection of electrons and holes that form excitons and radiatively recombine (giving rise to threshold-lessambipolarelectroluminescene)
- Accelerating electrons or holes to energies sufficient to create excitons i.e., the so-called impact excitation (giving rise to unipolar electroluminescence with threshold characteristics) [42]. By using a p-i-n design, we aim to improve the control of simultaneous injection of electrons and holes in order to increase the efficiency of the threshold-less ambipolar electroluminescence, making the CNT film a more efficient light emitter.

The polarized light-emitting diodes are highly aligned and they are separated by semiconducting carbon nanotube films which show tunable light generation efficiencies and threshold-less light emission characteristics. Additional improvement in device performance can be expected by superior enrichment of the solution-processed CNT. Reduction of metallic tubes in the raw material will enable shorter device channels for better transport, or even eliminate percolation altogether, which means one can create devices equivalent to single-tube CNT LEDs in parallel. The bock diagram of CNT based LEDs is shown in Figure 6.

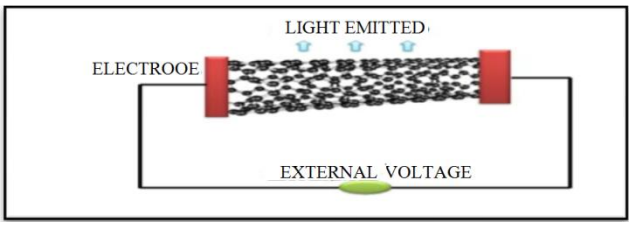


Figure 6. Bock diagram of CNT based LEDs

6. Conclusion

The study of present review is very helpful for fabrication of carbon nanotubes of different structures. Every synthesis techniques have its own advantages and application in different fields. From the applications point of view, the CNT film diode is perhaps the most promising type of device. The averaging effects that arise from using many tubes lead to reliable, robust and consistent performance. The benefits of the single-tube and film diodes create efficient nano-scale light sources with high output in the near-infrared that would prove useful in many technological applications. This plays an important part in advancing the science and technology of fascinating material.

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